ABUNDANCE AND BEHAVIOUR OF HEAVY METALS IN THE KHETRI COPPER MINE ENVIRONMENT, RAJASTHAN

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The thesis entitled **"Abundance and Behaviour of Heavy Metals in the Khetri Copper Mine Environment, Rajasthan"** embodies the original work carried out at School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India. This work has not been submitted in full or partial form for any other degree or diploma to any other university or institute.

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Dedicated to

My Parents and Sister

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Introduction and Literature Review

> "Civilization exists by geologic consent, subject to change without notice"
>
> **William James Durant (1885-1981)**

1.1 Introduction

Mining is important for economy of any country, but adversely affects the environment (air, soil, water, vegetation and human beings). Mining is a process for extraction of valuable minerals from ore. The selection of mining sites depends upon the economic feasibility of the extraction of mineral from ore.

Mines are of two types i.e. underground and surface/open cast, on the bases of excavation of ore from the earth. In underground mines, the ore is present below the surface of the earth and extracted by construction of tunnels or shafts below the surface. In surface mines, the ore is present at superficial layer of the earth and can easily be extracted by removing the upper surface of the earth. Based on the type of minerals, mines are classified into two broad categories such as metallic [Copper (Cu), Zinc (Zn), lead (Pb), Chromium (Cr) etc] and non-metallic (coal, marble, limestone etc). Among these two, the environmental impacts of metallic mines are more serious compared to non-metallic mines due to presence of sulphides.

Several large ore deposits found across the world are being mined since industrialization. The Cu deposits are found in different countries such as China (Daye, Jiurui, Hubei Chengmenshan, Jiangxi Province), Namibia (Ogonja), Australia (Broken Hill), England (Cornwall) and Kazakhstan among others. According to the United States Geological Survey (USGS) 2014, the total production of copper in the world is 18 million metric tons per year (Mt/yr). Currently, the demand is rapidly accelerating and increasing every year by 575,000 tons (Leonard, 2006).

India is a mineral rich country and mining activities are going on in many parts of the country namely Jharkhand, Odisha, Gujarat, Madhya Pradesh, Andhra Pradesh, Rajasthan, Maharashtra, Karnataka, Tamil Nadu, Chhattisgarh and West Bengal (Fig. 1.1). Rajasthan ranks the first in abundance of Cu resources with a sharing of 49.86 % (777.17 million tons) of total resources followed by Madhya Pradesh with 24.2 % (377.19 million tons) and Jharkhand with 18.48 % (18.48 million tons). Rest, 7.46% of total Cu resources in India are accounted by Andhra Pradesh, Haryana, Gujarat, Maharashtra, Karnataka, Nagaland, Meghalaya, Sikkim, Odisha, Tamil Nadu, West Bengal and Uttarakhand (Indian Bureau of Mines, 2013).

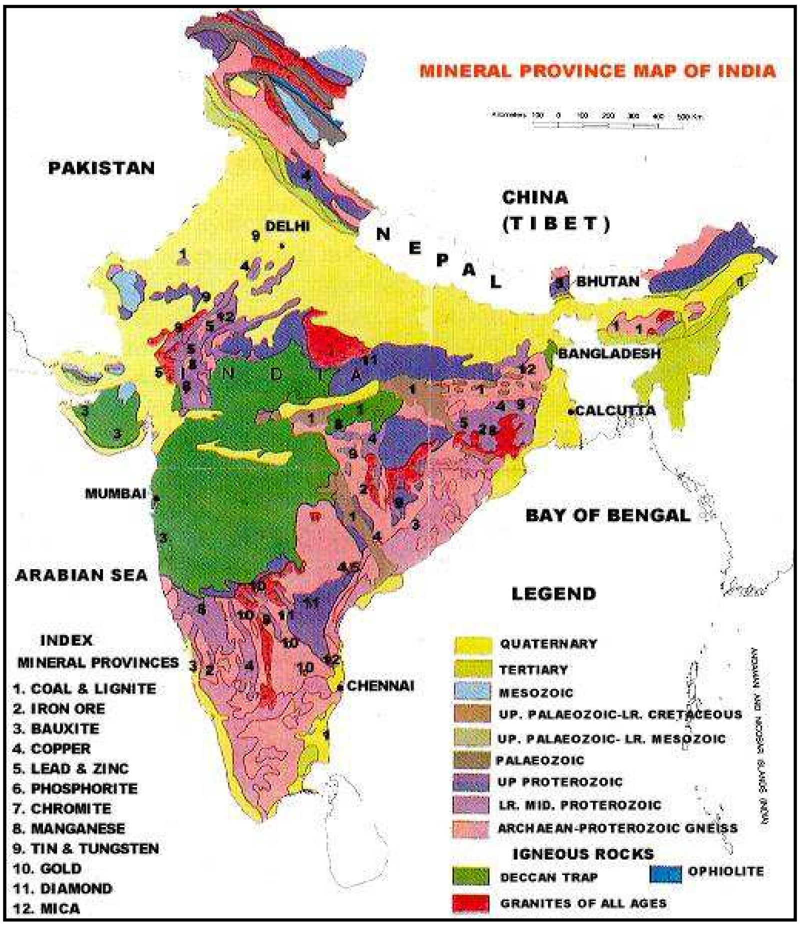


Fig.1.1 Map showing the locations of different ore deposits in India. (Source: Geological survey of India (GSI), Government of India)

Table 1.1 Number of mines in India during the years 2013-2014 and 2014-2015

Sector of minerals	2015-2016	2014-2015
All Minerals (atomic minerals, petroleum (crude), natural gas and minor minerals)	2100	2117
Public sector	660	670
Private sector	1440	1447
Fuel minerals	558	558
Metallic minerals	667	693
Copper ore	5	5
Non metallic minerals	875	866

Source: Indian Mineral Industry and National Economy (MSMP), March-2016

The Table-1.1 shows that the number of mines run by the private sector is more compared to the mines run by the public sector. The number of metallic mines decreases during the year 2014-2015 with respect to the year 2013-2014 while the number of non metallic mines increases. According to MSMP March-2016, the production of Cu ore in the year 2015-16 increased by 11% (3908000 tons) as compared to that in the previous year. A total of 5 Cu ore mines were reported (all in public sector) during the year 2015-16.

In India, the total production of Cu was 689,312 tons during 2012 and it is expected to double in the year 2020 (Madhya Pradesh Pollution Board (MPPCB), 2011). Therefore, intense mining along with its beneficiation is expected for Cu. India ranks 10th position in Cu production and contributes ~ 2.4% of the total world production.

Table 1.2 Copper production by three major contributors in India during the years 2011-2012 and 2012-2013

State	**2011-2012**			**2012-2013**		
	Ore Produced	% of Cu	Cu content	Ore Produced	% of Cu	Cu content
India	**3479189**	**0.97**	**33716**	**3638751**	**0.89**	**32505**
Rajasthan	1000485	0.87	8752	982926	0.84	8242
Madhya Pradesh	2082959	1.02	21204	2257288	0.91	20568
Jharkhand	395745	0.95	3760	398537	0.93	3695

Source: IBM, 2013

Hindustan Copper Limited is the leading producer of Cu in India. It has copper complexes in different states namely Khetri Copper Complex (KCC) in Rajasthan, Indian Copper Complex (ICC) in Jharkhand, Malanjkhand Copper Project (MCP) in Madhya Pradesh and Taloja Copper Project (TCP) in Maharashtra as shown in Fig.1.2. The Cu production by leading producer states (Rajasthan, Madhya Pradesh and Jharkhand) is shown Table 1.2.

The three main classes of Cu bearing ores i.e. carbonate, oxide and the sulfide are found in nature. The carbonate ores include malachite ($Cu_2CO_3(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$). The oxide ores are cuprite (Cu_2O) and tenorite (CuO). Cu ore commonly found in sulfides namely chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), covellite (CuS) and bornite (Cu_5FeS_4). Fresh copper sulphides are found in deeper parts of the earth, which are not exposed to weathering, and on coming near the surface these get oxidized and altered to form oxides and carbonates.

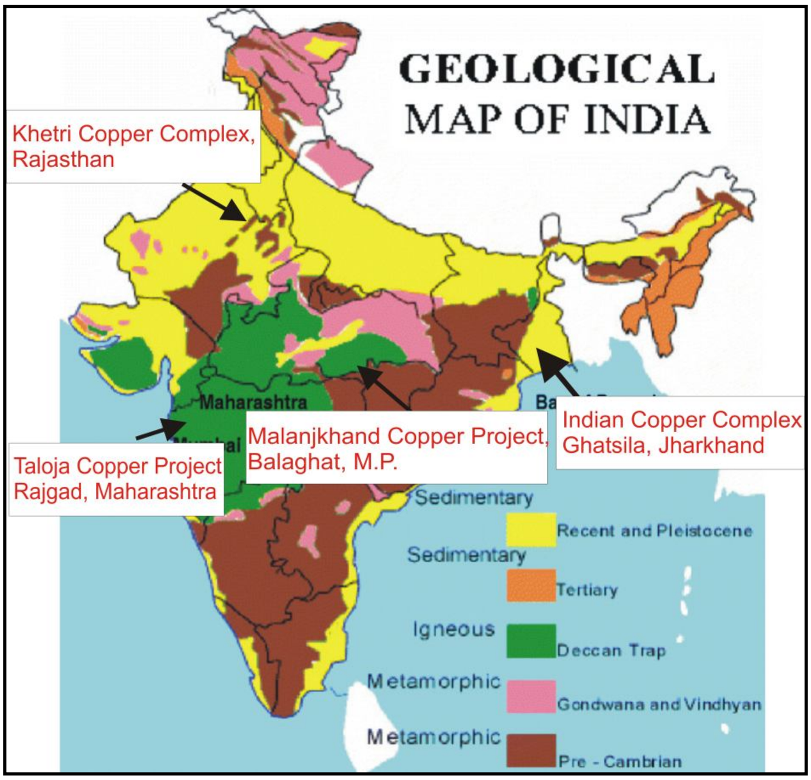


Fig.1.2 Map showing the locations of Cu ore deposits in India (Source: GSI, Government of India)

Urbanization and industrialization generates more demand for the base metals such as Cu, Zn and Pb. The production of Cu is increasing rapidly as its demand is also increasing in the industrial sector. It is used in the production of ceramics and pesticides. Cu is widely used in industries for electrical wire, electrical appliances, roofing and plumbing, and industrial machinery. Hence, due to its widespread applications, there is a huge demand for Cu, therefore extensive mining and thus more environmental contamination.

As mentioned above, though mining play's a key role in the country's economy but their adverse environmental impact can't be neglected. Apart from the adverse impacts in the local region, the waste generated during mining activities pollutes the surrounding environment during and after the mining activities. Mining generates major two types of wastes i.e. overburden materials and tailings. The overburden materials are the rocks that contain good amount of metals but their extraction is not feasible economically. Hence, they are mainly dumped near the mining sites. While, tailings are waste remains after the extraction of valuable fraction from the ore. Tailings also contain huge amount of metals or minerals. In the highly efficient units the tailings contain heavy metals in lesser quantity. Mainly overburden materials and tailings are dumped near to the mining location to save the transportation charges and/or time.

The ore has to be a fine grained to extract the valuable minerals. Hence, tailings the waste remains after the mineral extraction is also a very fine in nature. In case of metallic mining, air, soil and water are big environmental threats due to production of large quantities of sulfide-rich tailings and overburden materials containing high concentrations of heavy metals.

Mining activities damage the environment during and after the mine lifetime. During the life time of mines, the harmful gases and wastewater from smelter containing high concentration of heavy metals contaminate the surrounding environment. Transportation of mining waste through heavy vehicle is also one of the main sources for air pollutants. Along with this, excessive extraction of water resources during mining leads to decline in water table of the area. Mining deteriorates the water quality in both ways by exploiting the fresh water resources and by contaminating the fresh water resources.

Compared to groundwater, surface water gets easily contaminated. The contamination of surface water follows two paths the first by the atmospheric deposition of pollutants and the second by leaching of contaminants by runoff to the water bodies. While in groundwater only one path i.e. leaching of contaminants to the groundwater is seen. Therefore, the groundwater resources are supposed to be less contaminated compared to the surface water.

The area where groundwater resources are shallow the chances of contamination is high compared to the highly deep groundwater resources. The rocks which are impermeable or comparatively non reactive (silicates) in nature are acts as obstacle in the leaching of contaminants into groundwater. While, easily permeable rocks such as carbonates, shale or sulfides are highly permeable and water can easily percolate into the groundwater.

A large quantity of waste in the form of overburden materials, mine waste and tailings remains untreated in the environment after the life time of mines. Hence, even after the closure of mines, the management of waste is a big problem. It is also found that after the closure of mining, the mines are left abandoned without proper reclamation or restoration are the major threat for the ecosystem.

Heavy metals are mainly found in the form of sulfides in the nature such as chalcopyrite ($CuFeS_2$) for copper, pyrite (FeS_2) for iron, sphalerite (ZnS) for zinc, galena (PbS) for lead among others. These sulfides lead to the formation of Acid Mine Drainage (AMD) by the action of precipitation and oxygen present in the atmosphere. The formed sulphuric acid leads to the decrease in the pH of the water and soil. At low pH, the heavy metals become available in the atmosphere.

In a semi arid or arid region, the tailings are more prone to move away to distant places by winds. While in wet regions, the tailings are more prone to contaminate the groundwater resources due to leaching of heavy metals from tailings because of precipitation. The formation of AMD is also a common phenomenon in the wet region due to higher availability of water needed for AMD formation.

The heavy metals are non degradable in nature. Once they become available in environment they remain in the environment for longer duration. The plants accumulate the heavy metals from environment through soil, water and air. The pollutants dispersed in the environment are adsorbed by leaves and gets accumulated in the plants and vegetables. These contaminated vegetables become a main source of HM in human beings. The overview of environmental impacts of mines is shown in Fig. 1.3

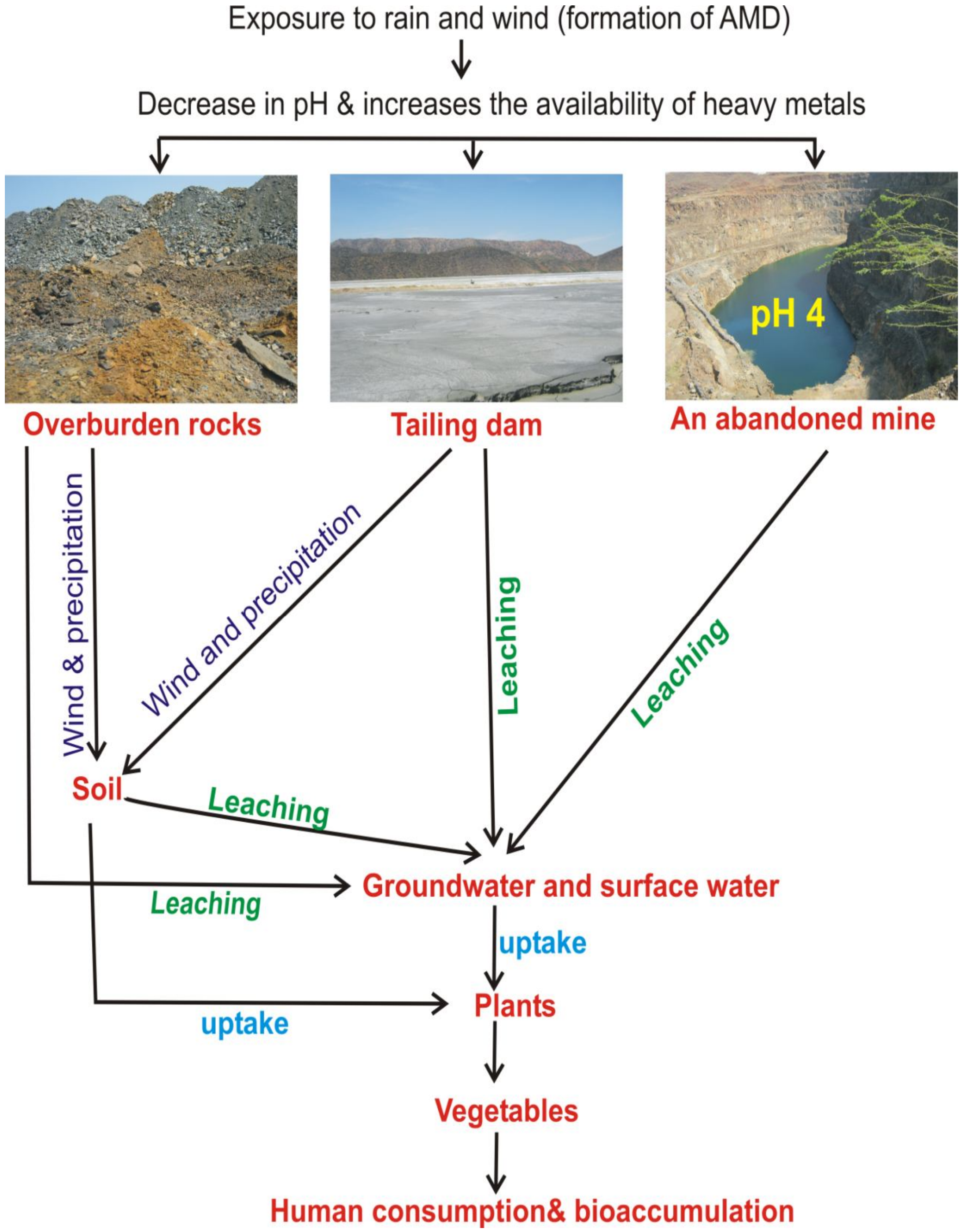


Fig. 1.3 An overview of environmental impacts of mines

1.2 Literature Review

Mining is the main contributor to environmental pollution by polluting the surrounding soil and groundwater. The leaching of heavy metals from waste dumps (overburden materials) and tailings to other play a crucial role. Therefore, presence of heavy metals in high concentration is observed in and around the mining area in different parts of the world.

1.2.1 Mining and environmental impacts

Heavy metal contamination is a major concern of the 21st century due to its persistence in the environment and human health risks. Industrialization, urbanization and mining activities along with agricultural activities lead to heavy metal contamination of soils. Among these, the effect of mining activities is the most dangerous (Krishna *et al*., 2013). Among heavy metals Fe, Cu, Ni, Mn and Zn are essential for organism's growth, while Cd, Pb, Ag and Hg are non essential but cause adverse health impacts.

Waste generated from mining activities which is rich in metals is one of the most important causes for deterioration of environmental quality (Larsen *et al*., 2001; Domenech *et al*., 2002). Both abandoned and active mines are equally responsible for the contamination of surrounding environment by contaminating soil, surface/groundwater and plants by fine particles of tailings carrying metals transported by wind action and tailings runoff (Qin *et al*., 2012; Gong *et al*., 2014).

Heavy metals present in the soil are easily accumulated by the crops and directly impacts the human beings (Chen *et al*., 1999; Tripathi *et al*., 1997). Hence, understanding the abundance of heavy metals, identification of their source and assessment of dispersal paths are important to monitor and minimize the impact on environment and human health.

Tailings are stored and preserved in dam by following the scientific methods. The failure of tailing dam due to weak concentration, earth quake or flood can causes a major destruction of environment. The spillage due to breaking of tailing dam in Aznalcollar, Spain contaminated the surroundings of Donana park which released large amount of mud and acid water containing Co, Bi, Cd, Th, Sb and Cu. Water bodies were also contaminated by these heavy metals (Grimalt *et al*., 1999).

The major sources of pollution in copper mines is solid waste generated from mines, mine water and effluents from water treatment plants, tailings remains after froth flotation unit, gases containing high concentration of sulphur, and acid spillage from the sulphuric acid production plant. For the present study we have studied the abundance and distribution of heavy metals in the tailings, soils, water resources and vegetables of the region. The observations and assessment reports from various other mining sites and their environmental impacts are discussed in detail in the following sections.

Heavy metals in tailings

Tailings are a combination of crushed rocks and waste containing processing fluids from concentrators or mills which remain after the extraction of minerals, economic metals or mineral fuels (Hudson-Edwards *et al*., 2001). The resources are depleting at faster rate but demand is increasing continuously. It increases pressure on mining industries to extract low grade ore which further result in more tailings (Mehrabani *et al*., 2010). The ratio of tailings to concentrate is 200:1 which is very high (Lottermoser, 2007). In India also the average metal content in ore decreased from 0.96 to 0.88% of Cu during the year 2012-2013. It is different in each state i.e. 0.83% in Rajasthan, 0.90% in Madhya Pradesh and 0.93% in Jharkhand (IBM, 2013).

In case of tailings, sulphide minerals particularly pyrite produces AMD due to its oxidation in presence of water and oxygen (Atkins and Pooley, 1982).

$$\mathrm{CuFeS_2(s) + 4.25\ O_2(g) + 2.5\ H_2O = Fe(OH)_3(s) + Cu^{2+} + 2SO_4{}^{2-} + 2H^{+}} \qquad \text{--(1)}$$

$$FeS_2(s) + 3.75O_2(g) + 3.75H_2O = Fe(OH)_3(s) + 2SO_4^{2-} + 4H^+ \qquad \text{--(2)}$$

AMD and Acid Rock Drainage (ARD) have low pH with high abundance of Fe and SO_4. AMD facilitates the mobility and dissolution of toxic heavy metals from tailings (Williams, 1975).

The presence of high abundance of heavy metals in tailings is reported by several studies in India as well as in different parts of the world. Maiti *et al*. (2005) found abundant quantity of sulphides like chalcopyrite, pyrite, pyrrhotite, molybdenite, and other minerals at the copper mine tailings of Mosaboni, India. They also observed mobility of heavy metals in the order of Cu > Ni > Mn > Zn > Co > Pb.

Branson *et al*. (2004) observed higher concentration of heavy metals (Cu = 2-100 ppm, Ni = 5-500 ppm, Mn = 20-300 ppm, Zn = 10-300 ppm, Cd = 0.6-1.1ppm and Cr = 54 ppm) at the copper tailings of Ducktown, Tennessee, USA which is spread out in 800 to 900 acres of area. A study by Ramirez *et al*. (2005) shows that the coastal shores are badly affected by the copper mine and tailings at El Salvador, Chile. Along with the coastal shores the biodiversity of the area is also adversely affected by the presence of higher concentrations of Cu, Zn, Cd, Mn, Pb, Fe and Ni in the tailings.

Heavy metals in soils

The main anthropogenic sources of heavy metals in soils are industrial, urban and mining waste (Singh, 2001). Heavy metal rich tailings and waste dumps are susceptible to dispersal by wind and water and become source for heavy metal contamination to neighboring area (Lee *et al*., 2001).

Heavy metal contamination of soil due to copper mining is well reported by many researchers from different parts of the world (Ali *et al*. 2003; Wang *et al*. 2004; Meza-Figueroa *et al*. 2009; Gómez-Álvarez *et al*. 2011; Rastmanesh *et al*. 2011; Qin *et al*. 2012). In India, very little is known on the soil pollution due to copper mining (Pandey *et al*., 2007).

The impact of mines depends upon many factors such as waste management practices being followed by the authorities and the distance from mines. Tembo *et al*. (2006) reported that Cu concentration in soils decreases with increase in distance from mining sites in Kabwe of the Zambia. Similarly, Rastmanesh *et al*. (2011) also observed high heavy metal (As, Cu, Pb, Zn, Mo, Cd) contamination of soils in the prevailing wind direction of Sarcheshmeh Copper Complex.

A study by Hutchinson and Whitby (1974) confirms the enrichment of the soils surrounding the Cu and Ni smelting plant with Cu, Ni, Zn, Mn, Co and Pb. Similarly, Rosner *et al*. (1999) reported the contamination of soils near the tailings of Johannesburg region, South Africa with heavy metals such as Ni, Co and Zn. Wang *et al*. (2004) observed high concentration of Cu, Zn and Pb in the agricultural soils and stream sediments near the Cu mine of Tongling, People’s Republic of China.

Along with the active mines, the abandoned mines are also potential source for heavy metal contamination. Qin *et al*. (2012) carried out a study about the heavy metal contamination in the agricultural soils near an abandoned copper mine in eastern China. The results show high abundance of Cu, Pb, Zn and Cd and also their average concentrations are many times higher than the background values.

The two major pathways of soil contamination are point source and non point sources. The point source includes industries, metalliferous mining and smelting, and the major pathway is through the atmospheric deposition of heavy metals. The non-point source includes pesticides, fertilisers, organic manures, sewage sludge and composts (Singh, 2001; Li *et al*., 2006). The non point source mainly contaminates the agricultural soil.

Copper shows high persistence in the soil because of its strong fixation with organic matter, clay minerals and oxides of Al, Fe and Mn (Baker, 1974).

Thus, copper is one of the least mobile among heavy metals and therefore uniformly distributed in soil profiles. Cu shows little variation among the soil profiles and it is related to soil pH and oxides of Fe and Al (Kabata-Pendias and Pendias, 1992; Oliver, 1997).

Heavy metals in groundwater

Groundwater is the major source of fresh water in many countries and is widely used for domestic, agricultural and industrial purposes (Golchin and Moghaddam, 2016). It is a renewable resource with inherent advantages over the surface water for pureness, lesser evaporation and wider distribution.

The geochemistry and quality of groundwater is controlled by several processes, such as geology of the area, degree and rate of weathering of parent rock types, rock-water interaction during recharge of aquifer, and rate of groundwater flow (Domenico, 1972; Andre *et al*., 2005), apart from anthropogenic activities (Singh *et al*., 2008). Hence, the level of contamination depends upon the quantity of rainwater (leached) and the depth of groundwater.

Groundwater quality is degrading in many parts of the world due to mining as reported by Miller *et al*. (1982); Zhang and Zhao (1996); Leybourne and Cameron (2008); Nordstrom (2011); Sun *et al*. (2013); and Gong *et al*. (2014). According to WHO, 80% of diseases and 30% of infant mortality in developing countries are caused by the consumption of polluted water (Chakroborty, 1999). In India, over the last decade the adverse health impacts are increasing and about 21% of communicable diseases are caused by consumption of unsafe water (Bradon and Homman, 1995).

Hence, assessment of groundwater quality and responsible sources are important prior to its use for domestic purposes. For example, the major lithogenic sources of dissolved ions in the water are weathering of silicate, carbonate and sulfide minerals and dissolution of evaporates (Singh *et al*., 2013). The water quality assessment and hydrogeochemical characterization is also essential for effective management of groundwater resources and sustainable development of a region (Sethy *et al*., 2016).

Tailings enriched in heavy metals could easily contaminate the water bodies because of mobility of heavy metals (Jang *et al*., 2005). A study conducted by Nasrabadi (2008) shows that groundwater surrounding the Sungun mine, an open cast mine in Iran, contains high concentration of Fe and Al; more than the permissible limit prescribed by USA Environmental Protection Agency (EPA). While some studies reported, the negligible effect of mining activities on the groundwater quality in the region. In contradictory, Amari (2014) found concentration of Cu, Fe, Pb, S, Cd, Zn, Co, Cr, Ni, Se and As in groundwater within acceptable limits of Italian Standards, despite of their higher concentration in AMD of tailing (Kettara). The possible reason for the same may be the dry climatic condition which resists the metal mobility.

Acid formed by sulfide oxidation can be neutralized by the dissolution of gangue minerals. Sulfides react fastest followed by carbonates and silicates (Sherlock *et al*., 1995). Among carbonates, calcite and in silicates, olivine, wollastonite and serpentine phases offers more dissolution (Jambor *et al*., 2002; 2007). In addition, neutralization capacity of clay is less than that of calcite (Lottermoser, 2010). Hence, the sites near metallic mines are more susceptible to dissolution of minerals.

Heavy metals in vegetables

Vegetables and fruits are important diet for humans and are one of the major sources of nutrients. But along with the nutrients they also have high accumulation capacity of heavy metals from soil, water and atmosphere. Heavy metals are non-biodegradable and are persistent for long time (Wang *et al*., 2001). Hence, as they persist for long duration in soils they can easily accumulate in the animals and human beings through food chain. Punia and Siddaiah (2017) reported higher concentration of heavy metals in the vegetables grown in the Khetri copper region of Rajasthan.

Some heavy metals such as Fe, Cu, Ni, Cr, Mn and Zn are essential for organism's growth, while Cd, Pb, Ag and Hg are not essential in biological processes but are toxic. Heavy metals get accumulated in plants, mostly by two paths first by atmospheric deposition and second through uptake from soil. In case of atmospheric deposition, the heavy metals get deposited on the leaves of plants and are easily taken by plants on opening of stomata. While, heavy metal are also up taken by roots from soil and water.

The presence of heavy metals in water and food is a major threat for the health of humans and animals (Nabulo *et al*., 2010; Dong *et al*., 2011). They cause health hazards like renal failure, liver damage, kidney problems and chronic toxicity (Sathawara *et al*., 2004). Hence, health risk assessment of population is important to assess the threat caused by the consumption of vegetables containing high amount of heavy metals (Khan *et al*., 2009).

Along with the metallic mines the non ferrous metallic mines also poses a potential impact on the vegetables grown in the region. Cd concentration in the vegetables is reported 4.5 times higher than the maximum permissible limit in 3 villages neighboring the Baiyin mining and smelting and may cause health hazards on consumption (Li *et al*., 2006). Plants grown on soils with pH in neutral range and a clayey texture tend to accumulate less heavy metal than those grown on soils with an acidic pH and a coarse texture (Hooda *et al*., 1997).

1.2.2 Bioavailability and fractionation of heavy metals

Quantification of total amount of heavy metals is not sufficient in assessing their impact on environment because, their mobilization capacity and behavior into the environment depends on chemical forms in which they present (Prosi 1989; Ma and Rao 1997; Jones and Turki, 1997). Fractionation gives the information that how the heavy metals are distributed in the different fractions of solid phases and which phase retains the heavy metals more.

Among the speciation methods, single regents (EDTA, DTPA, NH_4oAc-EDTA and $CaCl_2$) could be used to identify the mobile pollutant pool in the soils and sediments (Lindsay and Norvell, 1978; Tack and Verloo, 1991; Gupta *et al*., 1996; McGrath, 1996; Ure, 1996). The fraction extracted with single reagents is considered as bio-available fraction which is available to plants.

The water soluble fraction is the most available fraction consists of soluble species made up of free ions and ions associated with soluble constituents of soils and tailings. Metals in this fraction are loosely bound and gets easily moved and dispersed in the environment. The digestion in strong acids (HNO_3, HCl or aqua regia) dissolves the heavy metals from the non-silicate bound fraction from the soil without mobilizing the heavy metals in geological and silicate parent materials (Ure, 1996; Rao *et al*., 2008). However, metals associated with oxides (reducible fraction) and organic ligands are potentially available and become available on changing the environmental conditions. Heavy metals present in crystal lattices (residue) are mainly not available or mobilized (Ma and Rao, 1997).

The sequential extraction procedures are adopted by many researchers (Sposito, 1982; Kersten and Forstner, 1986; Hirner *et al*., 1990, Silveira, 2006) for the assessment of possible fractions in the soils. Tessier *et al*. (1979) suggests five fractions such as exchangeable, bound to carbonates, bound to iron and manganese oxides, bound to organic matter and residual with which the trace metals bound in soil samples. Heavy metals bound to organic ligands or in crystal lattice are strongly bound as compared to heavy metal found in exchangeable, soluble and adsorbed forms which are easily mobilized. Anthropogenic originated metals are found mainly during the first step of fractionation while lithogenic are extracted in the last step of procedure in the residual fraction.

Tailings mainly consist of gangue minerals such as silicates along with the unrecovered sulphide minerals. pH buffering reactions lead to depletion of carbonate mineral content of the tailings to <0.01 wt. % as $CaCO_3$ as indicated by Johnson (1993). Tailings are prone to oxidation and neutralization reactions in the environment hence following fractions are expected to be found in the tailings 1) water soluble 2) acid leachable 3) reducible and 4) residue (McGreyer 1998). The information on the speciation of heavy metals is important as it provides information about the mobility and bioavailability of heavy metals in the environment.

1.2.3 Impact of Copper on humans and plants

Cu acts as a micronutrient for plants (Thomas *et al*., 1998) and plays an important role in ATP (Adenosine Tri-phosphate) synthesis and CO_2 assimilation. It is also an essential component of some proteins such as cytochrome oxidase of respiratory electron transport chain and plastocyanin of photosynthetic system (Demirevska-kepova *et al*., 2004). The presence of excess of Cu in soil plays a cytoxic role and generates oxidative stress which induces stress in the plants (Stadtman and Oliver, 1991). This results in damage to macromolecule, growth retardation and leaf chlorosis (Hegedus *et al*., 2001; Lewis *et al*., 2001) of the plants.

Excessive Cu in soil inhibits photosynthesis, affects protein and nitrogen metabolism, causes leaves chlorosis, disturbance of mineral uptake and lipid peroxidation in vegetation (Shen *et al*., 1998; Nielsen *et al*., 2003; Demirevska-Kepova *et al*., 2004).

Cu is an essential micronutrient for humans (Angelova *et al*., 2011), but is toxic at high levels. Cu is essential for neurotransmitter biosynthesis, respiration, peptide amidation, connective tissue strength and pigment formation at the cellular level (Culotta and Gitlin, 2001; Lech and Sadlik, 2007; Gybina *et al*., 2009). Cu deficiency may result in abnormalities such as degeneration of the nervous system, skeletal defects, anemia, pronounced cardiovascular lesions, impaired immunity, elevated blood cholesterol, reproductive failure and defects in the pigmentation and structure of hair. Wilson disease is a rare autosomal recessive inherited disorder caused by excessive deposition of Cu in the tissues of liver and brain. An overload of Cu leads to Fenton-type redox reactions, resulting in oxidative cell damage and cell death (Liochev and Fridovich, 2002; Prousek, 2007).

$\mathrm{Cu\ (II)} + O_2^{\bullet -} \rightarrow \mathrm{Cu\ (I)} + O_2$ --(1)

$\mathrm{Cu\ (I)} + H_2O_2 \rightarrow \mathrm{Cu\ (II)} + {}^{\bullet}OH + OH^{-}$ (Fenton reaction) --(2)

The hydroxyl radical (${}^{\bullet}OH$) is extremely reactive and can further react with any biological molecules in the near vicinity (Jomova and Valko, 2011). Cu has the capacity to break the DNA strand and causes oxidation of bases.

According to Bureau of Indian Standard (BIS) the maximum desirable limit and maximum permissible limit in concentration for Cu in drinking water is 0.05 and 1.5 mg/L respectively. Ingestion of Cu above the permissible limit causes acute and chronic disorders and various health hazards in fauna, flora and in human beings.

For normal growth 5-20 mg/kg Cu is required while concentrations below 5 mg/kg and above 20 mg/kg are considered as deficient and toxic to the plants respectively (Loneragan *et al*., 1981; Kabata-Pendias and Pendias, 1984). Kabata-Pendias and Pendias (1992) considered 100 mg/kg Cu as highly toxic to plants.

1.2.4 Khetri Copper Complex

The Khetri Copper Complex (KCC) located at Khetri Nagar (Jhunjhunu district), north eastern part of the Rajasthan is famous for Cu mining since historical times. The geology of the region is first reported by the Hackett in 1877. The mining ceased by the Britisher’s in 1872. In recent decades, the mining is resumed by the Hindustan Copper Limited (HCL) in 1967.

Along with Cu extraction unit the smelting and fertilizer plants were also installed at the KCC. The fertilizer plant was established to use the sulphur emitted from the smelter plant for the preparation of fertilizers. This was the nice step to minimize the environmental contamination and to reduce the formation of acid rain. But due to financial crisis both smelter and fertilizers plants were shutdown since 2008 (IBM, 2013).

The Khetri Nagar is new town established by the HCL for the employees of company. It is approximately 8 Km away from the old town namely Khetri. Before the establishment of mining the main occupation in the region was agriculture. But after the installation of the plant most of the people joined as mine workers. The groundwater was used for irrgitaion and the rapid depletion of groundwater resources in the region is a major cause for the shifting of occupation.

1.2.5 Previous work in Khetri Copper Mines

The extensive mining at Khetri has resulted in large quantities of sulfide rich tailings and overburden materials. Approximately 25,000 tons/year of tailings are generated and dumped in the region (Mishra *et al*., 2008). The tailings and overburden materials are prone to natural weathering agents such as wind and precipitation.

A study conducted by Thukral in 1982, approximately a decade after the installation of the KCC in 1970s shows the presence of higher concentration of Cu in the grasses of Khetri Nagar. Similarly, Sheoran *et al*. (2011) reported high concentration of Cu in soils and wild plants (*Adhatoda vasica, Aerva tomentosa* and *Tephrosia villosa* which are shrub, under shrubs and herb respectively) located along the river Kharkhara near the Khetri Copper mines. They studied soil and plants from the same location and found that soils associated with *Adhatoda vasica* and *Aerva tomentosa* have high concentration of Cu i.e. 373.88 mg/kg and 70.93 mg/kg respectively.

The mineralogy of the Cu tailings at Khetri is studied by Kundu *et al*. (2014). They reported the presence of goethite, Yoderite, Jarosite, Iron silicon (FeSi), Iron Zinc ($FeZn_7$), quartz and calcite in major quantity followed by ferric sulphate, chalcopyrite ($CuFeS_2$), nickel arsenide (Ni_5As_2) and Zangoboite ($TiFeSi_2$) in minor quantity. They also found that the concentrations of Cu, V and Al in the tailings exceed the waste acceptance screening criteria of Class A landfills for New Zealand. They carried out batch investigation studies in relation to pH, contact times and LS ratio and found high mobility of elements with organic acid in comparison inorganic acid or water.

Along with the tailings and overburden materials, the waste effluents from copper complex after the ore processing could be a source of heavy metal contamination for soil and groundwater. A high concentration of Cu, Hg, Zn and Cd is found in the waste effluent at KCC and groundwater near the effluent flow (Khicher, 2014).

Similarly, Hussain (2015) studied the groundwater quality near the wastewater outlet from the copper complex plant which joins the river Sukh. He found hardness and fluoride exceeds the maximum permissible limit i.e. 600 mg/l in some samples and it is between the maximum permissible limit and maximum desirable limit in some. Cu is also present between maximum desirable limit and maximum permissible limit in two samples.

Maharia *et al*. (2010) studied the bioaccumulation factor and heavy metal concentration for essential metals i.e. Mn, V, Co, Fe, Zn, Cu, Se and potentially toxic metals i.e. Cd, Ni, Cr, Pb, and As in medicinal plants grown at Khetri copper mining area and Gangetic fertile soil of Haridwar. They found that medicinal plants grown at Khetri contain 3-4 times higher concentration of copper compared to those at Haridwar.

Besides, high concentration of Cu in plants and water, a change in the groundwater chemistry is also reported by Gangal (2003). He compared the physiochemical parameters of the groundwater for approximately four decades. He found decrease in pH and increase in sulphate, hardness, conductivity, bicarbonate and chloride in the groundwater of the region after installation of KCC suggesting the change in the chemical composition of groundwater.

1.2.6 Definition of the Problem

Though, mining for Cu at Khetri, Rajasthan is going since historical times but no systemic and detailed study on distribution and behaviour of heavy metals in various compartments of the environment were carried out. The previous studies on this aspect are preliminary in nature and thus information is limited and scanty. Therefore, as a part of doctoral thesis, systemic study on the distribution and behaviour of heavy metals including other trace elements in various compartments of environment were planned to assess the environmental impact due to mining.

The fine particles of tailings could easily be carried to the distant places by wind and contaminate the surrounding soils. Like the tailings, the overburden materials also contain heavy metals in significant quantity that could be the major source for heavy metal contamination in the surrounding environment. As per the literature, no systematic study has been carried out to understand the abundance and distribution of heavy metals in the tailings and soils of the region. The study further assesse the pollution load using Enrichment Factor (EF), Index of Geo-accumulation (I_{geo}) and Pollution Load Index (PLI), and discuss the possible sources of heavy metals. Both single reagents (EDTA and acetic acid) and sequential extraction method were used to assess the total available content of heavy metals in the tailings and soil.

The Khetri region is also known for high rate of depletion of groundwater. This results in increase in EC and TDS, and increased infertility of land/soil. Despite, such information groundwater has been sparsely monitored in and around Khetri copper mining region and little knowledge exists about the quality of groundwater and the related hydrogeochemical processes which are important to assess the impact of the sulfide mining on human health and ecosystem.

Since, all the components of the environment are interlinked, one polluted component can pollute the other linked components as well. Therefore, a systemic study on the distribution and behaviour of heavy metals including other trace elements in various compartments of environment (groundwater/surface water, soil and vegetables) are planned to assess the environmental impact due to mining. The human health is directly influenced by the quality of water and vegetables so it is necessary to assess health risk assessment due to heavy metal pollution in the environment.

The findings of such studies would be useful to formulate action oriented policies for effective disposal of waste generated through mining. With this background, the objectives (s) of the study are as follows:

1.3 Objectives

1. Geochemical (including heavy metals) characterisation of mine tailings, soil/sediment and ground-water in and around Khetri.
2. Fractionation (physical and chemical) of Cu, Pb and Zn in tailings and soil/sediment samples to assess their behaviour.
3. Distribution of heavy metals and other trace elements in vegetables from Khetri and its surrounding areas.
4. To understand the impact of copper mining on the local environment.

Chapter 2

Study Area

2.1 Introduction

The Khetri copper mines are located in the Jhunjhunu district of Rajasthan, a western region of the country. It is 180 km southeast of Jaipur city, the state capital, and 190 km northwest of New Delhi. The altitude of the study area is 550 m above mean sea level with geographic location, latitude N 28˚04.070′ and longitude E 75˚49.294′.

The Khetri region is known for sulphide ore since historical times. The Khetri Cu belt extends about 80 km in length from Singhana (Jhunjhunu district) in the northeast to Sangarva (Sikar district) in the southwest. Presently at three locations, namely Khetri, Banwas and Kolihan with 1.13 wt.%, 1.69 wt.% and 1.34 wt.% of copper content respectively are being mined. The ore consists of ~10 volume % sulphide mainly of chalcopyrite, pyrite and pyrrhotite, and other minerals such as quartz, amphiboles, mica, chlorite and magnetite.

2.2 Climate

During summer maximum temperature reaches to 45°C and minimum is 12°C, while in winter maximum temperature hovers around 25°C and minimum is 2°C. It lies in the semi-arid region of the country with mean annual rainfall around 500 mm. During summers, in the month of May and June strong dusty wind blows in the region from the N-W and S-W direction.

2.3 Vegetation

The region comes under the sub-tropical semi-arid dry deciduous and thorny forest. Xerophytic trees and shrubs are the most common vegetation of the study area. The area is covered with sparse vegetation. *Prosopis-Capparis-Ziziphus, Prosopis-acacia, Salvadora-Prosopsis-capparis, Anogeissus-Euphorbia-Rhus and Prosopsis-Tecomella* are common trees in the area.

2.4 Regional Geology

Geologically, NW-SE transverse Kantli Fault separates the Khetri belt into northern and southern parts (Roychowdhury and Dasgupta, 1964; Gupta *et al*,. 1998) (Fig. 2.1). The rocks of the southern Khetri copper belt are made up of Delhi Supergroup, further divided into an older psammitic-dominated Alwar group and a younger pelitic-dominated Ajabgarh group (Das Gupta, 1968). The rocks of the northern Khetri copper belt (in which study area lies) are made up of feldspathic quartzites with magnetite, banded amphibole quartzites, garnetiferous chlorite schists, mica schists and quartzites, folded into number of regional synclines and anticlines (Das Gupta, 1968). Sodium-rich felsic magmatism in the form of albitites are also recorded in the region and these rocks occur along a 170 km long NNE-SSW trending lineament, named as 'albitite line' (Ray, 1990).

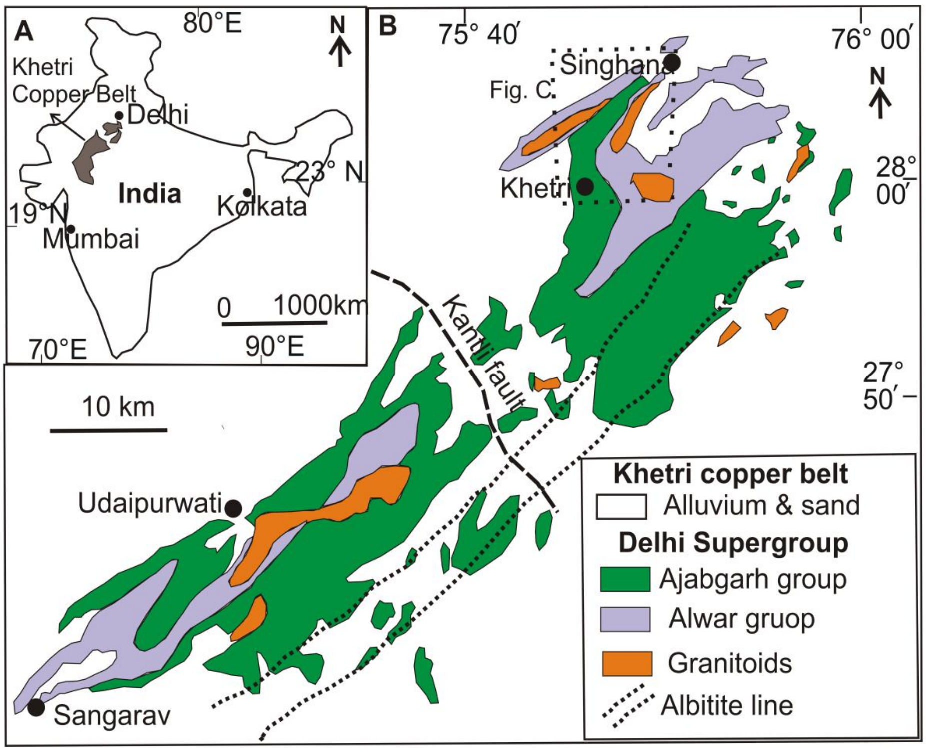


Fig. 2.1 Map of India showing (A) location of Khetri belt, Rajasthan (B) Geology of Khetri belt

2.5 Regional Hydrogeology

Hydrogeologically, the aquifer of study area is associated with quartzite, schist, phyllite, gneisses and limestone of Delhi Super Group including granites, amphibolites and pegmatites of post Delhi intrusive (Fig. 2.2). Groundwater occurs under unconfined condition in the weathered mantle (ranging in thickness from 10 to 15 m) and under unconfined to semi-confined conditions in deep seated secondary porosity i.e. fractures, joints, contacts etc. of hard formation. However, the thick (15 to 140 m) and regionally extensive alluvium (composed of gravels, sand, silt, clay and kankar) which occurs surrounding the study area holds 30-70 m thick saturated zone with unconfined and semi-confined aquifers.

The general groundwater flow is from hills (stretching southwest-northeast) of the study area to northern and eastern parts of the region (Central Groundwater Board, 2008). Water flow is fast in the study area due to steep gradient in the topography while it is considerably slow in the alluvial formations having gentle gradient. The dugwell water yield is between 150 to 600 m^3/day in alluvium and it is less than 250 m^3/day both in granites and quartzites.

2.6 Mine Waste

Milling is important part of beneficiation which results in very fine particles that allow better extraction of the metal from ore. However, milling of ore leads to production of huge quantity of fine grained tailings. From last few decades a huge quantity of mine waste (overburden materials and tailings) is being dumped openly in the environment covering a large area in the Khetri mining region. During rains heavy metals can easily be leached from these dumps and contaminate the surface and groundwater.

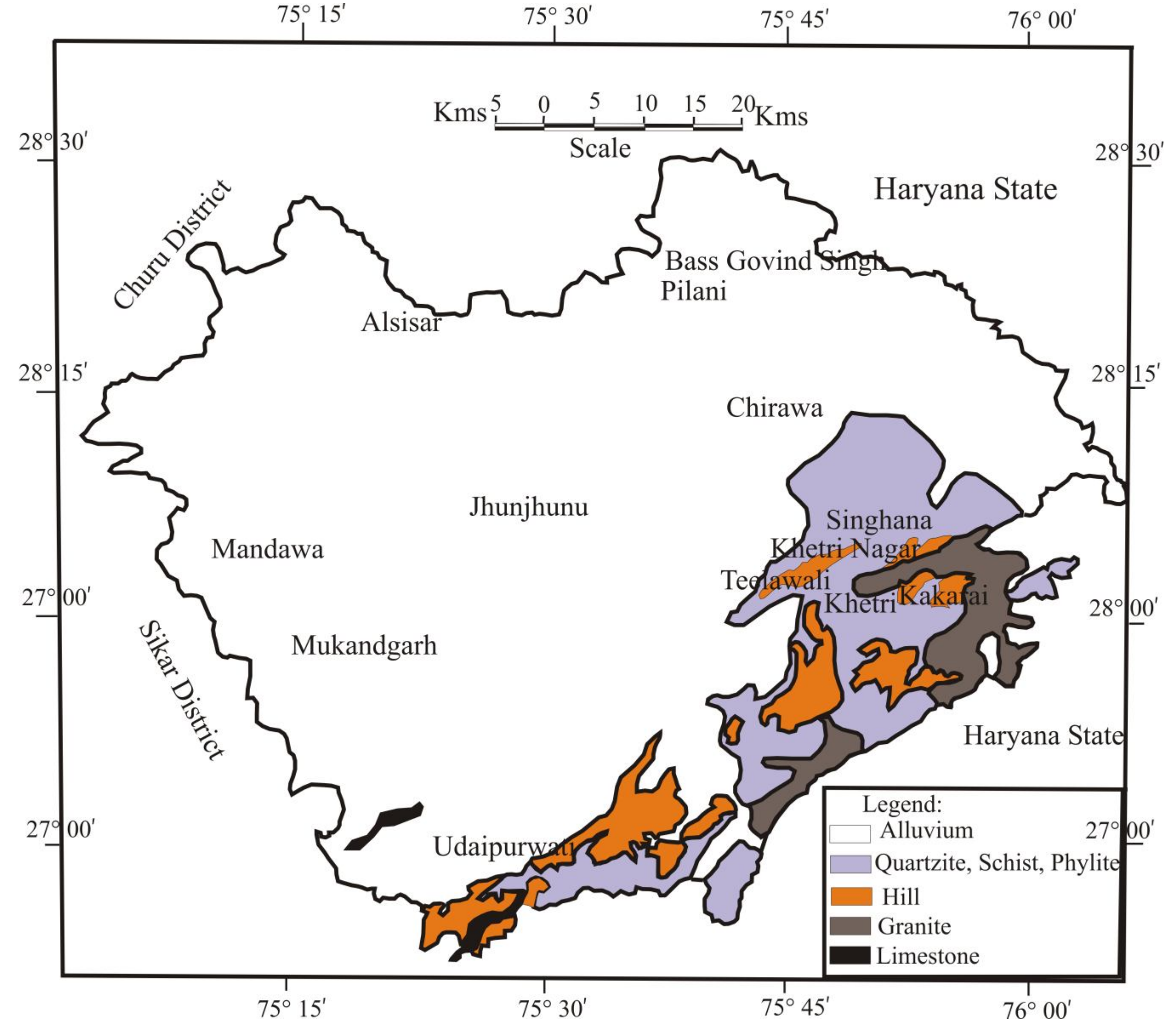


Fig. 2.2 Map of district Jhunjhunu showing hydrogeology.

The overburden materials are the rocks that contains good amount of metals but their extraction is not economically feasible. In the study area the overburden materials are observed at two locations. One dump is located near the Khetri mine and its adjoining villages (Banwas and Kanjaniyun Dhani) and is spread in ~1-2 Km of stretch (Fig. 2.3). Another dump of overburden materials is near the Chaandmari an abandoned mine (Fig. 2.4).

Fig. 2.3. Overburden materials near village Banwas

The sulphide ore is being processed till the froth flotation stage at the mining site itself, and the waste generated (~25000 tons/year) in the form of tailings is being dumped near Gothra village around 3-4 km away from the processing plant. The tailing dam is spread in an area of ~1 sq km (Fig. 2.5). On an average, to get 1 kg of Cu around 1 ton of sulphide-rich ore/rock is being mined, milled and processed and then thrown back to the environment. The tailings by virtue of their fine grained nature could easily be carried by these winds to distant places.

Fig.2.4 Overburden materials near Chaandmari mine

Fig. 2.5 Tailing dam at Khetri

In addition, Chaandmari is an abandoned mine (near Kolihan mine) since 2002, containing acidic water is a major source for heavy metal pollution in the region as shown in Fig. 2.6.

Fig. 2.6 Abandoned Chaandmari mine with acidic water (pH~ 4)

2.7 Selection of Sampling Sites

To assess the environmental impacts of mines at Khetri region, 27 sites neighboring the mines, overburden materials and tailings were selected for sampling (Fig. 2.7 (A, B & C), 2.8 & 2.9). From each location three types of samples were collected i.e. soil, water and vegetables. The sampling locations with respect to their sampling codes are given in Table 2.1 and 2.2. All the three types of samples were collected within 100-200 m of distance to assess the heavy metal distribution at each location. The details of the selected sampling locations are given in the Chapter 3 (Materials & Methods). The field photographs Fig. 2.10 to 2.16 are attached at the end of the chapter.

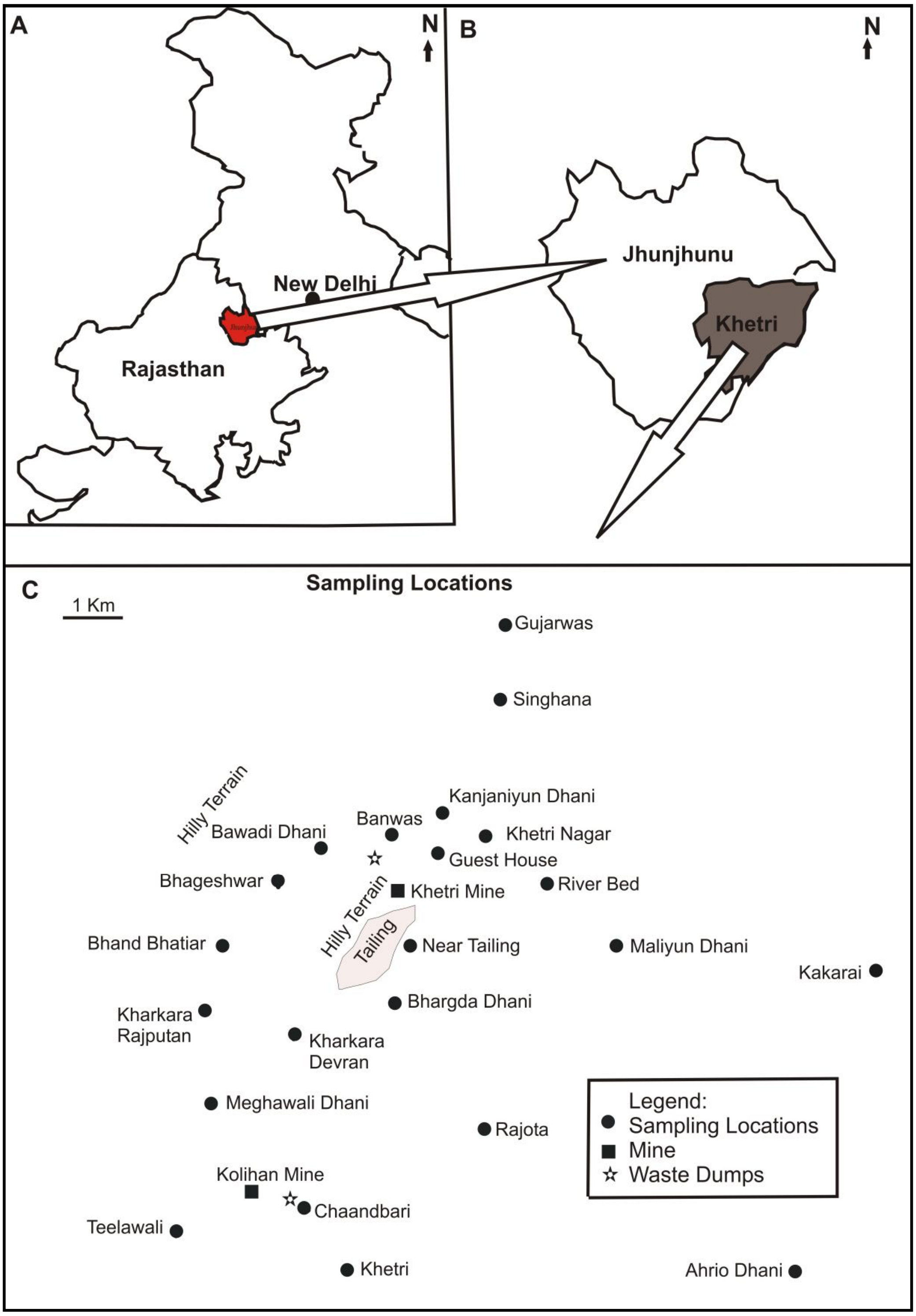


Fig. 2.7 Map of northwestern India showing (A) Jhunjhunu district in the state of Rajasthan; (B) Khetri in the Jhunjhunu district; (C) Sampling locations

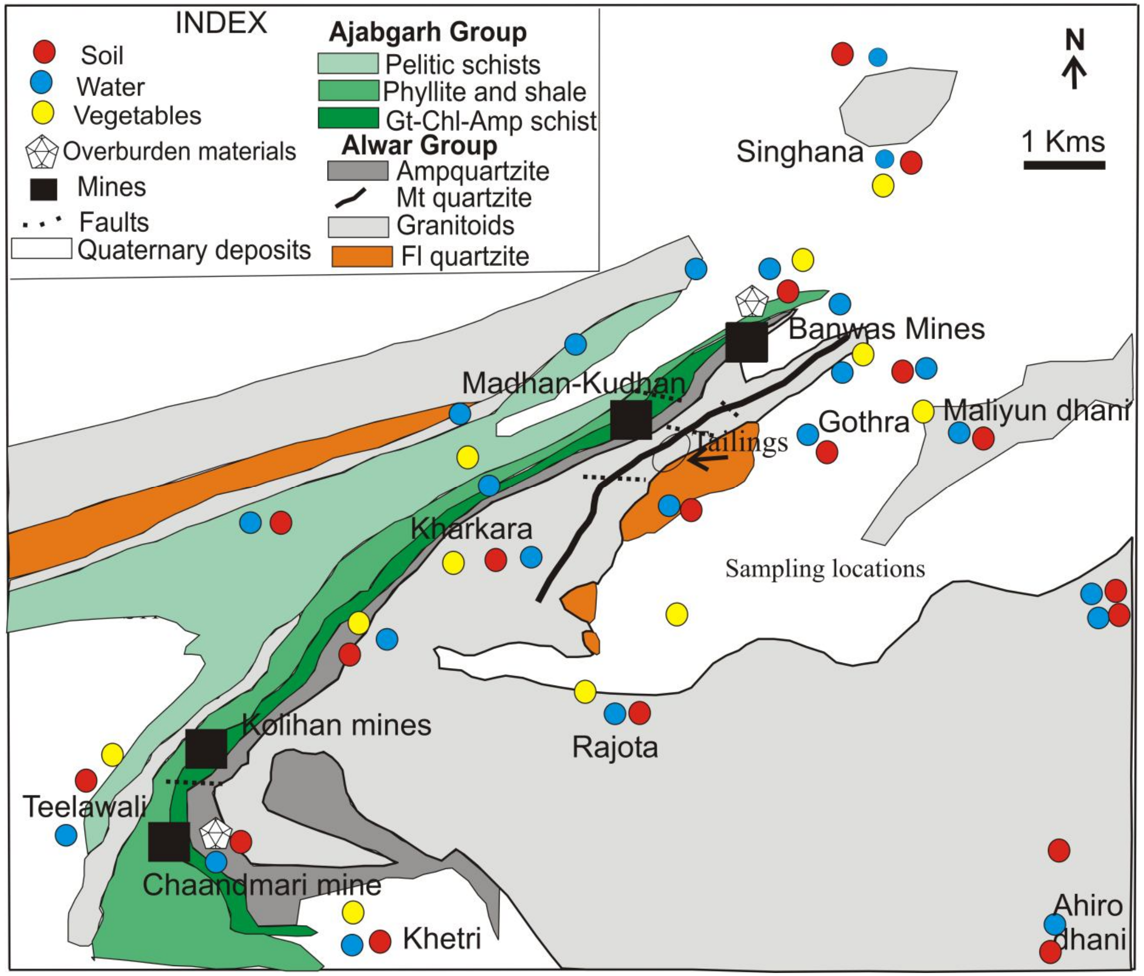


Fig. 2.8 Geological map of the study area (after Kaur and Mehta, 2005, Kaur *et al.,* 2006; Knight *et al.,* 2005) with Water, Soil and Vegetable sampling locations

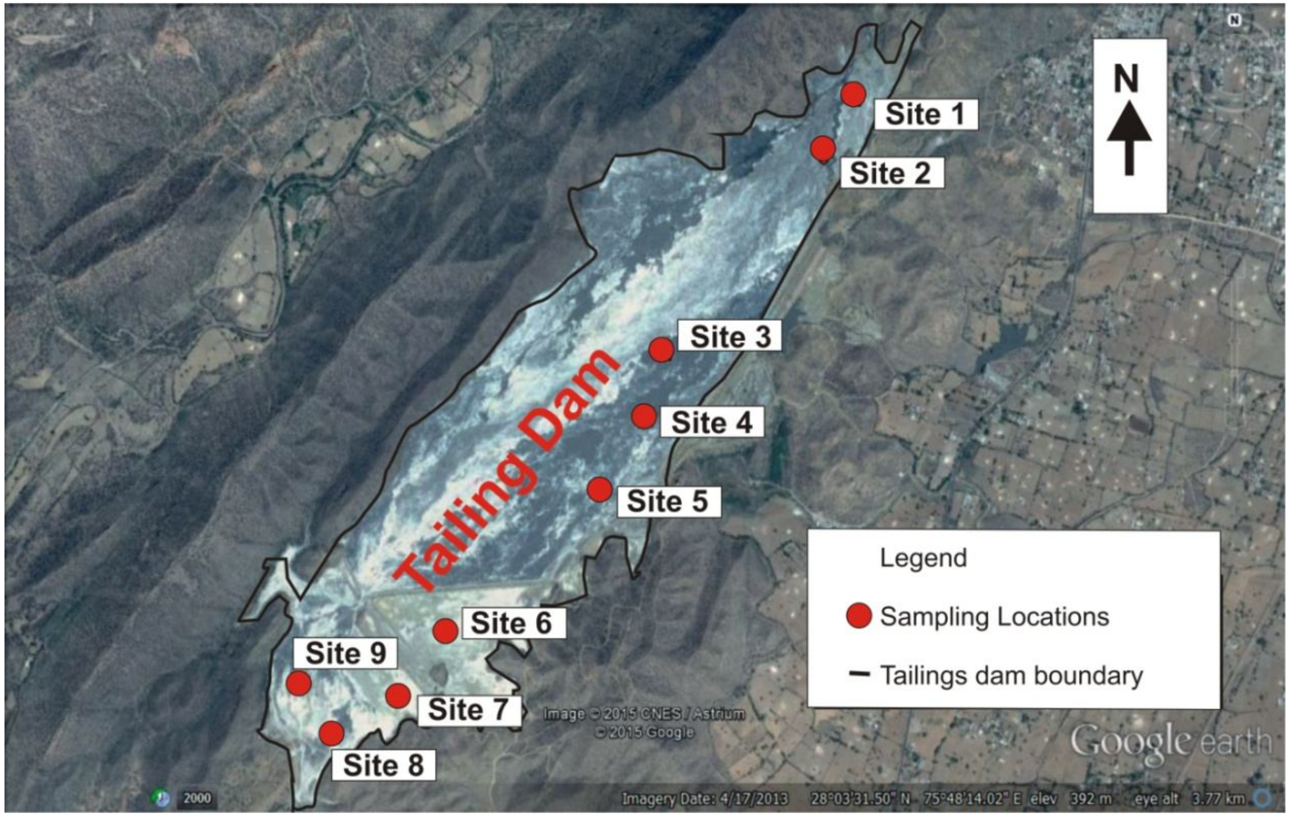


Fig. 2.9 Google earth map showing tailing dam at Khetri with sampling sites

2.8 Field Photographs

Fig. 2.10 Soil sample collection from the barren land at Maliyun Dhani

Fig.2.11 Water sample collection from the village Banwas

Fig. 2.12 Drain containing waste water from the ore processing plant at Khetri which meets dried Sukh river

Fig. 2.13 Determination of Electrical Conductivity (EC) of Water sample from Banwas

Fig. 2.14 Location of Hindustan Copper limited

Fig. 2.15 Sampling of vegetables

Fig. 2.16 Slurry at tailing dam of Khetri Copper Complex

Chapter 3

Materials and Methods

3.1 Tailings and Soils

3.1.1Sampling

A total of 24 surface soil samples, each weighing ~1kg from 17 villages located in and around the mines, overburden materials and tailings were collected from a depth 0 to 15 cm. While collecting the sample care was taken to remove plant roots and pebbles. Out of 24 samples studied, 15 samples are collected from undisturbed soils from different villages, 4 samples are from dried artificial water bodies (Ajit Sagar dam reservoir i.e. L4 and L5 and Panasagar pond i.e. L8 and L9), 5 samples are from dried river bed (dried for the last ~30 years) and one sample close to overburden material (L10). The details of the sampling locations are given Table 3.1.

In addition, we also collected two more soil samples (L25 & L26) one each from Bass Govind Singh (latitude N 28˚26.565′ and longitude E 75˚34.340′) and Pilani (latitude N 28˚22.392′and longitude E 75˚35.15′) ~50 km northwest of the mining area and these samples are considered as regional reference soil. Since the location of regional reference soil is in the northwest direction with respect to mines, thus are not affected by the mining activity.

A total of 26 tailing samples were collected from nine locations (S1-S9) covering the whole stretch of tailings. The sampling locations, S1-S6 (recent) are near the tailings entry point and S7-S9 (old) are ~1.5 km away from the entry point. The locations where tailings color changes with depth, the samples were collected from different depths i.e. 0-10 (T1), 11-20 (T2), 21-30 (T3), 31-45 (T4) and >46 cm (T5). In other cases only one sample was collected from each location. The details of the sampling locations at tailings are given Table 3.2

Table 3.1 Sampling locations (Water and Soils) with their geographic latitude and longitude

S.No	Sampling locations	Water Sample Code	Soil Sample Code	Latitude	Longitude
1	Kakarai pond	W1	L1	28˚ 03. 278′	75˚55.434′
2	Kakarai school	W2	L2	28˚ 03. 436′	75˚55.139′
3	Maliyun Dhani	W3	L3	28˚ 03. 773′	75˚51.254′
4	Ajit sagar	-	L4-L5	27˚ 59. 606′	75˚51.144′
5	Ahrio Dhani	W4	L6	27˚59. 504′	75˚50.945′
6	Rajota	W5	L7	28˚ 01. 793′	75˚48.513′
7	Khetri (Pana sagar)	W6	L8 - L9	27˚ 59. 992′	75˚46.861′
8	Suraj Dhani	-	L21	-	-
9	Teelawali	W7	L22	28˚ 00. 299′	75˚44.027′
10	Meghawali Dhani	W8	L20	28˚ 01. 731′	75˚45.272′
11	Khakara Devran	W9	L24	28˚ 02. 554′	75˚45.944′
12	Kharkara Rajputan	W10	L23	28˚ 02. 581′	75˚45.198′
13	River bed	W11	L13-L14	28˚ 03. 644′	75˚49.803′

14	Khetri Nagar	W12	-	28˚ 04. 070′	75˚49.294′
15	Bhargda Dhani	W13	L11	28˚ 02. 833′	75˚48.350′
16	Near tailing	W14	L12	28˚ 03. 799′	75˚48.732′
17	Kanjaniyun Dhani	W15	-	28˚ 05. 022′	75˚49.492′
18	Gujarwas	W16	L18	28˚ 07. 432′	75˚50.618′
19	Singhana	W17	-	28˚ 05. 989′	75˚50.057′
20	Chaandbari	W18	L10	28˚00.21′	75˚46.472′
21	Bhand bhatiar	W19	-	28˚ 02. 188′	75˚47.337′
22	Badheswar	W20	-	28˚ 03. 179′	75˚46.382′
23	Bawadi Dhani	W21	-	28˚ 03. 975′	75˚47.544′
24	Banwas	W22	L19	28˚ 05. 171′	75˚48.554′
25	Guest house	W23	-	28˚ 04. 772′	75˚49.277′
26	Bass Govind Singh	W24	L25	28˚ 26. 565′	75˚34.340′
27	Pilani	W25	L26	28˚ 22. 392′	75˚ 35.15′

Table 3.2 Sampling locations at tailings dam

Sampling location	**Sample code**	**Depth (cm)**
Site 1 (S1)	T1[*]	0-10
	T2[*]	10-20
	T3[*]	20-30
Site 2 (S2)	T1[*]	-
Site 3 (S3)	T1[*]	0-10
	T2[*]	10-20
	T3[*]	20-30
	T4[*]	30-45
	T5[*]	45-55
Site 4 (S4)	T1[*]	0-10
	T2[*]	10-20
	T3[*]	20-30
Site 5 (S5)	T1[*]	0-10
	T2[*]	10-20
	T3[*]	20-30
	T4[*]	30-45
Site 6 (S6)	T1[*]	0-10
	T2[*]	10-20
Site 7 (S7)	T3[#]	0-10
	T4[#]	10-20
	T5[#]	20-30
Site 8 (S8)	T1[#]	0-10
	T2[#]	10-20
	T3[#]	20-30
Site 9 (S9)	T1[#]	0-10
	T2[#]	10-20

[*] New

[#] Old

3.1.2 Sample preparation

Samples were dried in natural condition for two days. The particles having grain size >2 mm were discarded. By coning and quartering, tailing and soil samples were homogenized and ~100 gm of each sample was selected from bulk and stored for analysis. Around 50 gm from dried bulk sample was grinded to pass through the 60 mesh size sieves using agate mortar and pestle. From this 60 mesh sample, 25 gm of sample was grinded to pass through 200 mesh. This -200 mesh sample was used for total organic carbon, loss on ignition, mineralogical and geochemical analysis.

3.1.3 pH

pH of soils and tailings were measured using pH electrode meter (CL 46+) by mixing sample and distilled water in 1:2 ratio (Hendershot *et al*., 1993). pH meter was standardised by buffer solutions of pH 4.0, 7.0 and 9.2 prior to analysis.

3.1.4 Total organic carbon

In soil carbon is found in different forms (organic, inorganic or elemental) and these forms control various chemical and physical properties of the soil. The total organic carbon (TOC) can be determined by many procedures. For the present study, Walkley Black (1934) method was followed to determine total organic carbon of the soils. It involves the oxidation of organic matter by the Potassium Dichromate ($K_2Cr_2O_7$) solution. The remaining oxidizing agent is titrated by ferrous sulphate ($FeSO_4$). The process is based on the oxidation of chromic acid (H_2CrO_4).

3.1.5 Loss on ignition

Loss on ignition (LOI) is analyzed to know the volatile matter (water, weakly bound organic matter and carbonate bound carbon) present in samples. The sum of LOI and major oxides give an accurate estimation of geochemical composition of soils. The single step process was used to determine the loss on ignition (LOI in wt.%) in the tailings and soil. For LOI, 2 gm of -200 mesh size sample was weighed and put in silica crucible. The initial weight of sample and crucible was noted. The samples in silica crucible were burnt at 1000 °C for 1 hour in muffle furnace (Heiri *et al.*, 2001). Then the difference in final and initial weight multiplied by 100 gives the total loss of weight in percentage.

$$\mathrm{LOI} = \frac{\{\mathrm{Weight(crucible + sample)_{beforeheating}}\} - \{\mathrm{Weight(crucible + sample)_{afterheating}}\}}{\{\mathrm{Weight(crucible + sample)_{beforeheating}}\}}$$

3.1.6 Mineralogical analysis

The mineralogical analysis of soils and tailings were done using X-ray Diffraction (XRD) spectroscopy (Philip X-pert pro diffractometer). The XRD data was analyzed using X'pert High Score software. The minerals in the soils and tailings samples were identified by comparing d spacing and 2θ values of the samples with the reference values given by Lindolhm (1987).

3.1.7 Geochemical analysis

The X-ray Fluorescent spectroscopy is widely used for the determination of the major and trace elements in the soils and sediments. A secondary X-ray beam excites from the sample on exposure to primary X-ray beam. The intensity and wavelength of the secondary X-ray beam are used to identify the elements present in the sample in reference to calibrated standards. Before the analysis the instrument was calibrated with the standard to avoid error. The major oxides in the soils and tailings were analysed using X-Ray Fluorescent spectroscopy (XRF) (PANalytical). Three soil reference materials SDO-1, GSP-2 and SDC-1 of USGS were used during XRF analysis.

For the analysis of heavy metals, the soil and tailing samples were digested in a mixture of acids (HNO_3, HF and $HClO_4$) and were analysed using Atomic Absorption Spectroscopy (AAS). In the digestion process 0.5 gm of 200 mesh samples were taken in a Teflon crucible. Then add 10 ml of Hydrofluoric Acid (HF) + 5 ml of Nitric Acid (HNO_3) + 1 ml of Perchloric Acid ($HClO_4$), this was put on a hot plate with lid at a temperature between 80-90°C. After 4hr the lids were removed and heating was continued until the whole acid mixuture gets evaporated and dried.

After evaporation the crucibles were allowed to cool. Then added 5 ml of HF + 10 ml HNO_3 and again put on hot plate to evaporate and dry. Then add 10 ml of HNO_3 and kept on hot plate to evaporate completely. If solution becomes transparent then this is the final evaporation process. After this add 25 ml of 2N HCl solution in the teflon crucibles and heat up to 100°C for 1hr to dissolve the digested materials from the crucibles. The solution from Teflon crucibles were transferred into 100ml volumetric flask and volume was made to 100ml with Millipore water. Then the solution was transferred in to a 125ml poly bottles for further analysis.

During acid digestion, to monitor the chemical analysis and accuracy of the method three soil reference materials such as SGR-1 (Green River Shale) issued by United States Geological Survey (USGS), and JSO-1 (Black Forest soil) and JSD-1 (Sedimentary rocks) issued by Geological Survey of Japan were used.

3.2 Groundwater

3.2.1 Sampling

A total of 17 and 22 groundwater samples were collected in the months of March (pre monsoon) and October (post monsoon) 2015 respectively. During both the seasons samples were collected from the same hand pump in case of groundwater at each sampling location, except two locations in north direction i.e. Gujarwas and Singhana where hand pumps were dried off during post monsoon season sampling. In addition, one (Kakarai pond) and two (Kakarai pond and Badheswar) number of surface water samples were also collected during pre and post monsoon respectively.

To assess the effect of mining on water quality, the sampling sites were selected in the periphery of mining areas, namely, near the mining area (W23), overburden materials (W12, W15 & W22), tailing dam (W21, W13 & W14), abandoned mine (W6) and also distant places from the mines (Fig. 2.8). Seven new sampling sites were added during post monsoon season compared to the pre-monsoon. Along with soil, groundwater samples were also collected from two sites (relatively less affected by the mining activity) namely Bass Govind Singh (W24) and Pilani (W25). Sample was also collected from the flowing slurry on the tailings and was analyzed for heavy metals.

The water samples were collected in narrow mouth polypropylene bottles, double rinsed with sample before sampling. The first twenty-twenty five strokes of water was discarded before filling the sample bottles in order to minimize the impact of iron pipes. From each location sample was collected in three polypropylene bottles i.e one sample in 1 litre bottle and two samples in 125 ml of bottles.

3.2.2 Analytical methods

The pH (Hanna instrument, H196107), EC and temperature (Aquapro water tester, model AP-2) were measured *in-situ*. All the collected water samples were preserved by adding few drops of concentrated Supra-pure HNO_3 (Radojevic and Bashkin, 1999) followed by filtration and vice versa. The samples were filtered using 0.45 µm Millipore filter paper and stored below 4°C.

1 litre non-acidified and unfiltered samples were used for analysis of anions namely bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{2}), dissolved silica (H_4SiO_4) and nitrate (NO_3^-) following the APHA (2012) protocol. 125 ml filtrated and acidified samples were used for analysis of cations such as sodium (Na^+), magnesium (Mg^{2+}), potassium (K^+) and calcium (Ca^{2+}) along with the heavy metal (Cu, Zn, Cd, Pb, Mo, Ni, Fe, Cr and Mn) using Atomic Absorption Spectrophotometer (AAS, ThermoScientific M series) using air-acetylene gas as a fuel.

For the calibration of instrument, standard solutions for each heavy metal were prepared by diluting the 1000 ppm certified standard solution issued by Merck. After every 10 samples, standard solution was measured to test the accuracy and stability of the instrument. The calculated relative error was below 5% indicating the high efficiency of the heavy metal analysis. During the analysis the samples were handled carefully to avoid the contamination. Properly cleaned glassware and analytical grade reagents were used.

3.3 Vegetables

3.3.1 Sampling

Vegetable samples were collected in the month of September, 2015 from 10 different localities (Kharkhara Devran, Teelawali, Manota, Banwas, Khetri Nagar, Maliyun Dhani, Meghawali, Khetri, Bhand Bhaitar and Rajota) from the

Khetri copper mine region. One reference sample was collected from Chirawa situated far away from copper mine region and assumed to be less effected by the mining activities

Eight species namely *Capsicum annuum* (Chilli pepper), *Solanum melongena* (Brinjal or eggplant), *Abelmoschus esculentus* (Lady;s Finger or Okra), *Spinacia oleracea* (Spinach), *Raphanus sativus var. Longipinnatus* (Daikon), *Luffa* (Ridged gourd), *Lagenaria siceraria* (Bottle gourd) and *Cyamopsis tetragonoloba* (Guar), each weighting ~200-500 gm were collected. The samples are from home gardens avoiding the commercial farms where fertilizers could be applied.

3.3.2 Analytical methods

The vegetable samples collected were washed first in running tap water for 10 minutes and rinsed with distilled water. They were cut into small pieces by stainless steel knife and dried off in oven at 70°C for 48-72 hours.

The dried samples were crushed to pass through 60 mesh size sieve using porcelain motor and pestle. The crushed samples were acid digested for heavy metals analysis by Atomic Absorption Spectroscopy. 1 gm of crushed samples were digested by 15 ml of acid mixture (70 % HNO_3, 65% $HClO_4$ and 70% H_2SO_4 in 5:1:1 ratio) and heated at 80°C till the solution become transparent (Allen *et al*., 1986). The digested samples were diluted to 50 ml in volumetric flask with distilled water. In each batch of acid digestion one reagent blank was prepared to monitor glassware contamination and analysis error.

3.4 Extraction and Fractionation of Heavy Metals

For extraction of heavy metals 5 samples each from soils and tailings were selected. Soil samples surrounding the mines, overburden materials (L19), abandoned mine (L10), river bed (L13) and distant areas (L4 and L6) were selected. In case of tailings, both types new (S1-T2, S2-T1 and S5-T3) and old (S7-T1 and S9-T1) were selected for extraction. To assess the impact of grain size of the samples on the mobility of heavy metals, two grain size samples were used. For grain size, 100 g of bulk sample was sieved into two fractions +63 mesh size and -63 mesh size using sieve shaker. For analysis bulk and -63 mesh size fractions were used.

3.4.1 Single reagent extraction

EDTA or Ammonia method

For preparation of 0.05 mol/L EDTA, an ammonium salt solution, 146±0.05 gm of EDTA was added in 800±20 ml of distilled water along with 130±5 ml of saturated ammonia solution while stirring continuously. The prepared solution is diluted with distilled water to 9+0.5 L and pH was adjusted to 7±0.05 either by ammonia or HCl as appropriate. In extraction bottles, 5 gm of sample was taken and added 50 ml 0.05 mol/L EDTA and shaken (Rotary Shaker, Selec RC5100) for 1 hr at 30 rpm (McGrath, 1996). Then the mixture was transferred to centrifuge tubes and centrifuged (R8C Laboratory Centrifuge, REMI Equipments) the mixture at 3000 rpm for 20 minutes. The separated supernatant was stored at 4°C for heavy metal analysis.

Acetic Acid

Acetic acid solution (0.43 M) was prepared by adding the 250±2 ml of glacial acetic acid in 5 L of distilled water in 10 L of polyethylene container. The prepared solution was diluted to 10 L with distilled water and stored in polyethylene container. For extraction 200 ml 0.43 M acetic acid was added to

5 gm of sample and shake for 16 hr at 30 rpm (Das and Maiti 2008). The supernatant was separated by centrifugation and stored at 4 °C.

3.4.2 Sequential fractionation

Four fractions were extracted namely distilled-water soluble, acid-leachable, reducible fractions and residue fraction of each sample using Ribet *et al*. (1995) method. The distilled-water fraction of the tailings was extracted by dissolving 2 gm sample in 100 ml of distilled water for 24 h at room temperature while undergoing constant agitation. The acid-leachable fraction was extracted by dissolving supernatant from the step first in 30 ml of 20% (v/v) HCl for 20 min at room temperature. The reducible fraction was extracted using 30 ml of 2M hydroxylamine hydrochloride ($NH_2OH.HCl$) and 25% (v/v) acetic acid (CH_3COOH) for 24 h at 95 °C. The residue fraction was determined following the above mentioned acid digestion method.

3.5 Statistical Analysis

For geochemical analysis of soil and tailings the descriptive statistical parameters (range, average, standard deviation and median) were calculated. The degree of association between two parameters i.e. among heavy metals was evaluated by calculating coefficient of correlation (r) (Meyer, 1975). Pearson correlation matrix was generated to identify the relationship between the elements and the possible sources. For inference of hypothetical source of heavy metal i.e. natural or anthropogenic, the principal component analysis (PCA) was used. For factor analysis in PCA, a varimax rotation was used because orthogonal rotation minimizes the number of variables with high loading on each component and facilitates the interpretation of PCA results. PCA and correlation matrix was generated using IBM SPSS 19 version. All analytical steps followed and the important parameters analysed are shown in Fig. 3.1.

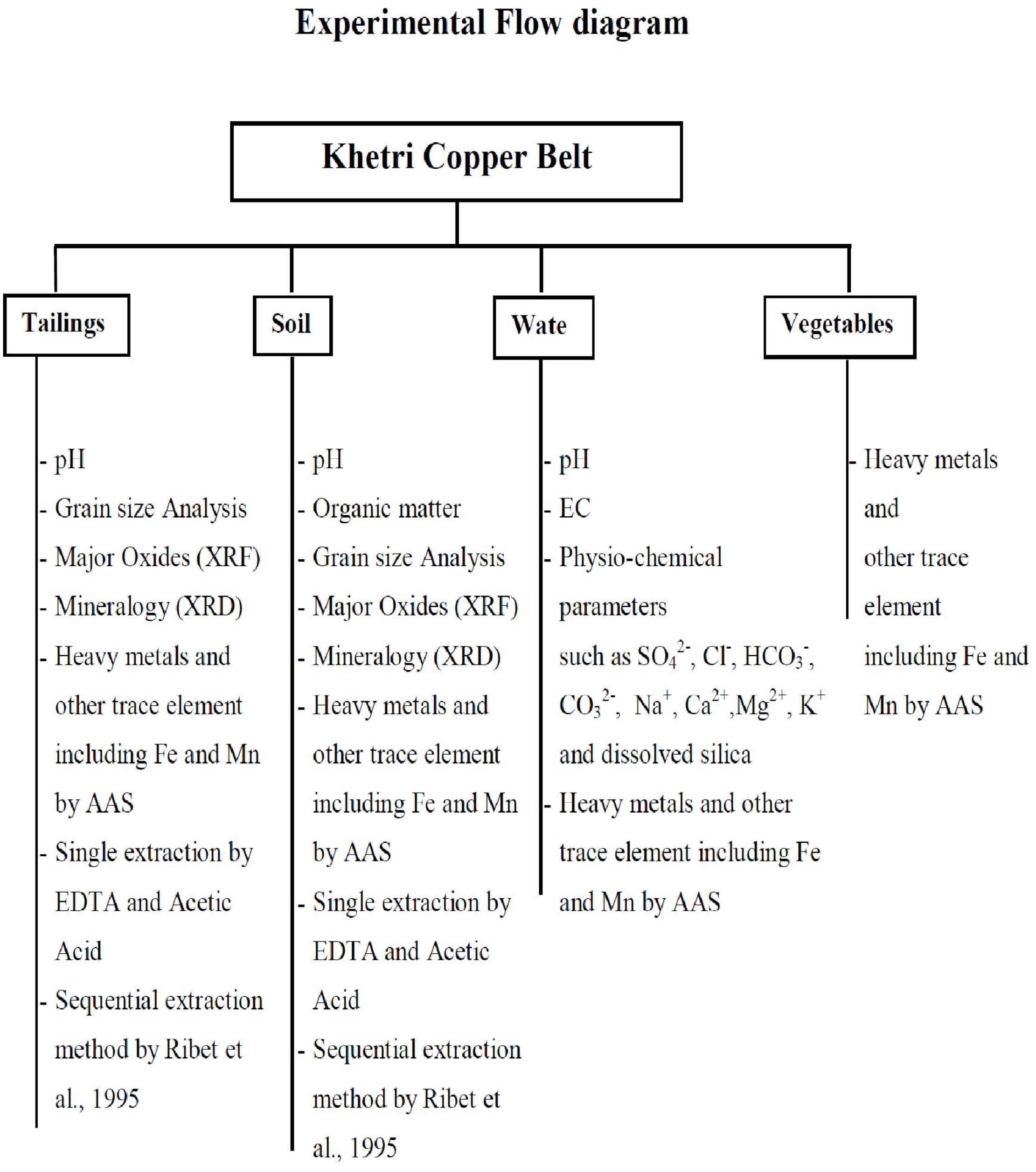


Fig. 3.1 Experimental flow diagram

Chapter 4

Results and Discussions

Section I

Abundance and Behaviour of Heavy Metals

4.1 Abundance and Behaviour of Heavy Metals

To assess the environmental impacts of copper mines at Khetri region, the concentration of heavy metals (Cu, Zn, Pb, Cr, Ni, Co and Fe) along with physio-chemical parameters in tailings, soils, groundwater, surface water and vegetables of the region were studied. Various indices using heavy metal concentration were calculated to assess the accumulation and enrichment of heavy metals in tailings, soils, groundwater, surface water and vegetables. To better understand the heavy metal contamination in the region each component (tailings, soil, groundwater/surface water and vegetables) of the environment is discussed separately for heavy metal abundances followed by pollution indices and health risk assessment. The availability of heavy metal depends upon the association of the heavy metal with different species of soil. Hence, the heavy metals are extracted with single reagent and multiple reagents (sequential extraction) to understand the mobility and behavior of heavy metals (Cu, Zn, Pb, Ni and Cr) in tailings and soils. The results are summarized in the following sections.

4.1.1 Geochemical Assessment of Tailings

Tailings were analyzed for pH and geochemical parameters (major oxides and heavy metals) along with the mineralogy to assess the environmental impact of tailings at the Khetri copper mine region.

4.1.1.1 pH

pH is one of the important parameters in controlling the mobility and toxicity of the heavy metals (Chuan *et al*., 1996). Tailings lie in acidic range from 2.7 - 6.7 (Fig. 4.1), with an average of 4.6 ± 1.4. On comparing pH of new (S1-S6) and old tailings (S7-S9), it is found that pH of old tailings lies more towards the acidic (varies from 2.66 to 4.03 with an average of 3.3) range compared to that of new tailings which lies towards the alkaline range (varies from 4.24 to 6.71

with an average of 5.64). The old tailings get oxidized with time and lead to oxidation of sulphides in presence of water and generate sulphuric acid which is known as AMD. Hence, pH lies in acidic range in the old tailings (Fig.4.2).

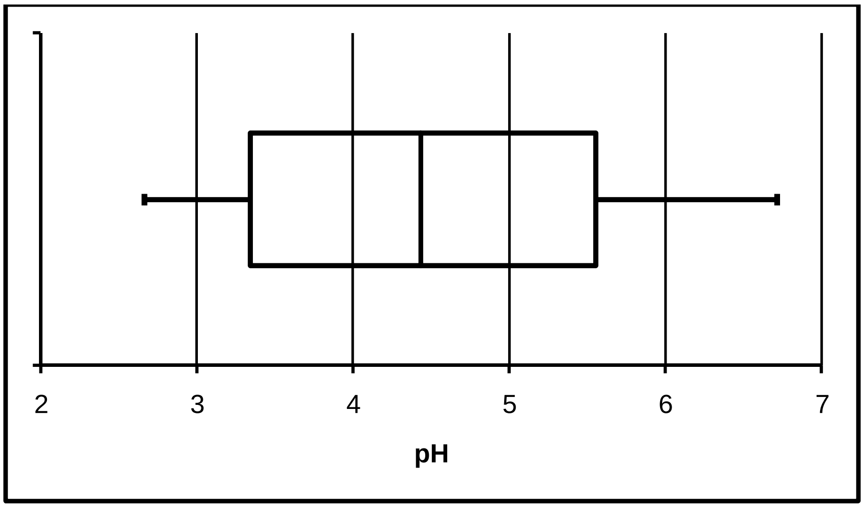


Fig. 4.1 Box plot showing pH variation in the tailings at Khetri

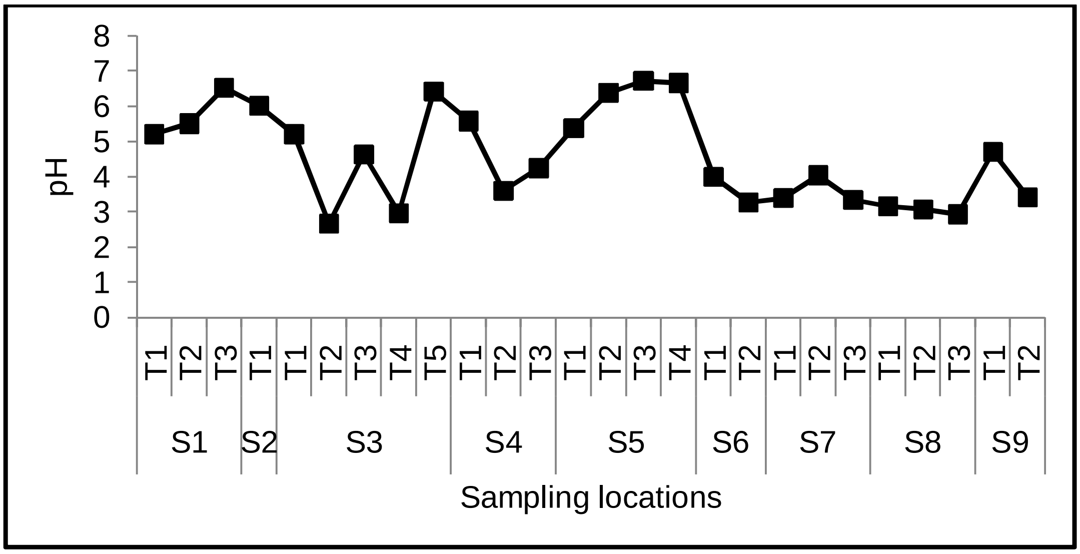


Fig. 4.2 pH of each tailings sample, S1-S5 (new tailings) and S6-S9 (old tailings)

4.1.1.2 Loss on ignition

Loss on ignition (LOI) in tailings ranges from 2.89 to 13 wt. % with an average of 5.49 wt. % and range is shown in box plot (Fig. 4.3). High LOI suggests the presence of more clay content or adsorption of volatile matter on the surface. In old tailings, the LOI is found in higher ranges varying from 5.08 to 13 wt.% with an average of 7.9 wt. % (Fig. 4.4) and in new tailings it ranges from 2.89 to 8.28 wt.% with an average of 4.41 wt.% (Fig. 4.5).

Old tailings have high LOI compared to new tailings as the old tailings are more oxidized and precipitated to secondary minerals (Dubrovsky *et al*., 1984; Morin *et al*., 1988; Nicholson *et al*., 1990), and hence have more sites for adsorption of volatile matter.

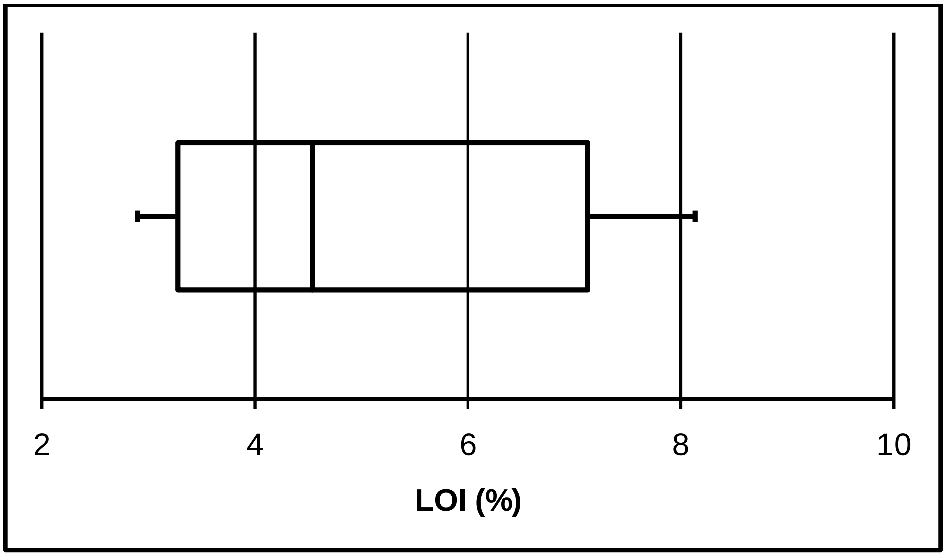


Fig. 4.3 Box plot showing LOI (wt.%) variation in the tailings

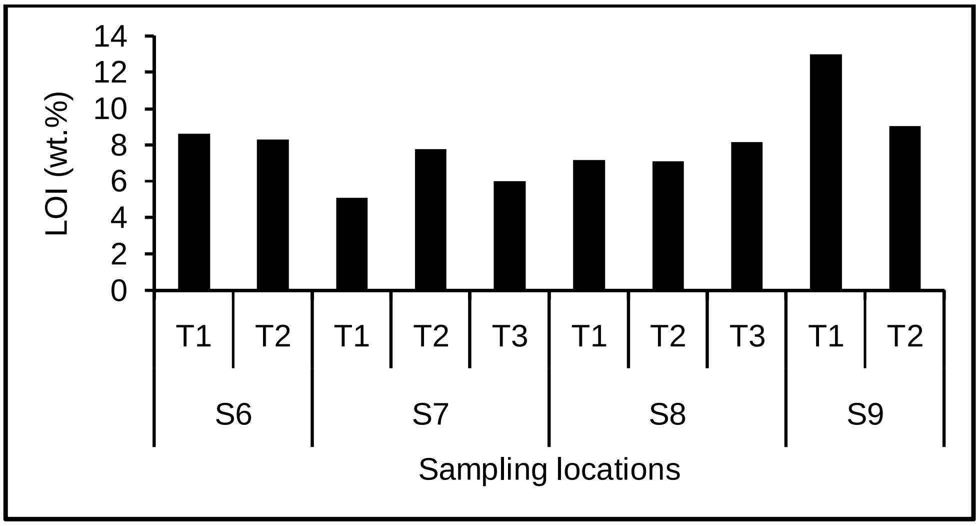


Fig. 4.4 LOI in old tailings with an average of 7.9 wt. %

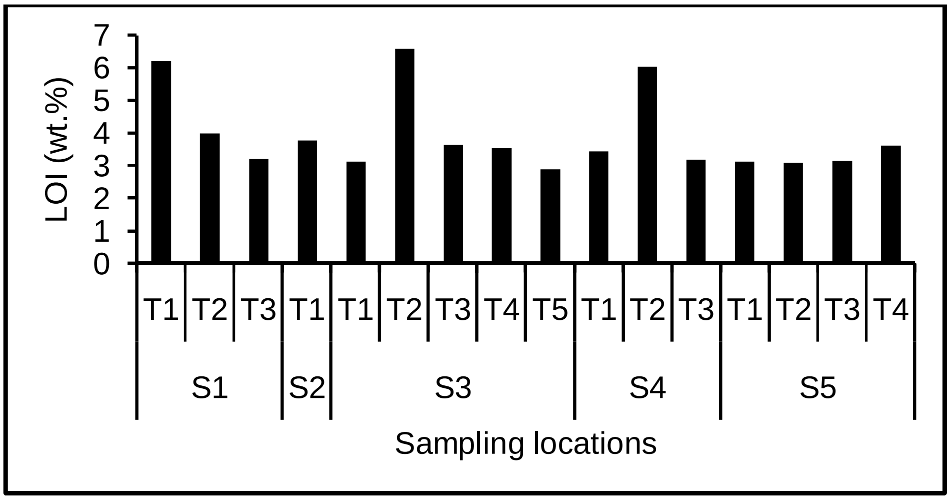


Fig. 4.5 LOI in new tailings with an average of 4.41 wt. %

4.1.1.3 Major oxides

Among the major oxides, silica (SiO_2) dominates in tailings. It ranges from 50.81 to 63.04 wt. % with an average of 55.83 ± 3.81 wt. % (Table 4.1). The dominance of silica in tailings of Khetri confirms the presence of gangue minerals in abundant quantity. Concentration of silica is followed by the concentration of FeO which ranges from 13.94 to 21.05 wt. % with an average of 16.79 ± 1.75 wt. %. The high enrichment of FeO compared to UCC (Fig. 4.6) in the tailings confirms the presence of sulphides namely pyrite and pyrrhotite in association with copper ore i.e. chalcopyrite. The enrichment of MgO could be attributed to the presence of amphiboles in the region.

Al_2O_3 does not show much variation among the samples as it is least mobile and it ranges from 9.90 to 11.76 wt. % with an average of 10.57 ± 0.41 wt. %. MgO follows Al_2O_3 and range from 3.88 to 7.59 wt. % with an average concentration of 5.68 ± 0.89 wt. %. The variation in the MgO may be due to its mobility and leaching or neutralization capacity with sulphides present in tailings. CaO follows MgO in major oxide concentration, it ranges from 0.97 to 1.93 wt. % with an average of 1.4 ± 0.26 wt. %. No major difference is found in the major oxide concentration between the new and old tailings. The detail description of major oxides for each sample is given below in the Table 4.1.

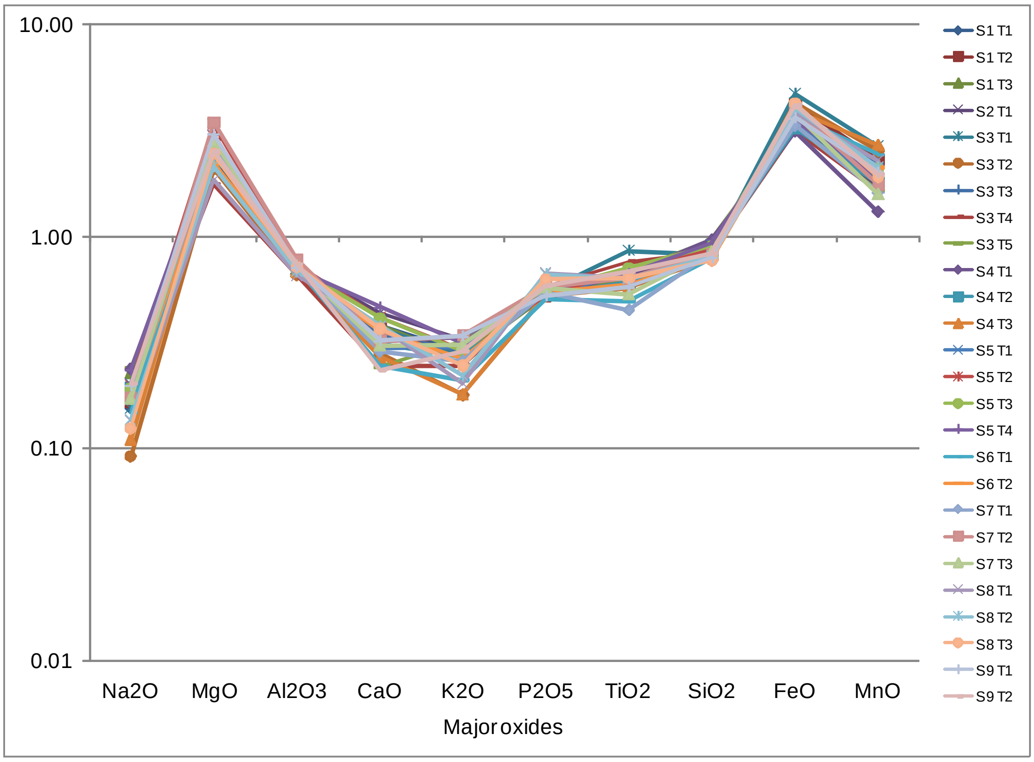


Fig. 4.6 UCC normalized plot for major oxides of tailings

Table 4.1 Major oxide composition (in wt.%) of tailings along with LOI content

Sample location	**Samples (at different depths)**	**Major Oxides**										**LOI**
		SiO_2	**FeO**	**Al_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**TiO_2**	**MnO**	
S1	T1	51.30	19.19	10.06	5.17	1.58	0.60	0.95	0.11	0.30	0.16	6.21
	T2	55.00	18.85	10.31	6.00	1.54	0.64	0.94	0.10	0.30	0.16	4.00
	T3	60.96	16.05	10.33	5.86	1.59	0.89	0.90	0.11	0.31	0.14	3.22
S2	T1	59.44	15.61	10.78	6.56	1.80	0.78	1.10	0.11	0.33	0.12	3.78
S3	T1	54.09	21.05	10.44	5.94	1.53	0.60	0.92	0.11	0.43	0.19	3.14
	T2	51.12	18.95	10.01	4.55	1.17	0.36	0.61	0.11	0.29	0.18	6.59
	T3	58.91	16.96	10.47	5.70	1.42	0.79	0.98	0.11	0.34	0.15	3.63
	T4	55.59	14.12	9.95	3.88	1.04	0.67	0.84	0.12	0.38	0.12	3.54
	T5	63.04	14.78	10.86	5.51	1.02	0.93	1.09	0.11	0.34	0.11	2.89

S4	T1	62.85	13.94	10.73	6.14	1.34	0.91	1.13	0.11	0.33	0.09	3.44
	T2	55.33	14.44	10.41	4.82	1.31	0.74	0.92	0.11	0.31	0.13	6.05
	T3	57.69	17.49	10.33	5.39	1.13	0.43	0.61	0.11	0.29	0.19	3.19
S5	T1	59.78	15.47	10.66	6.23	1.25	0.78	1.02	0.11	0.34	0.13	3.13
	T2	56.70	16.19	10.96	7.38	1.73	0.78	0.98	0.11	0.34	0.13	3.09
	T3	59.05	16.80	10.55	5.95	1.72	0.75	0.97	0.11	0.35	0.15	3.15
	T4	61.10	15.74	10.44	6.28	1.93	0.90	1.05	0.11	0.33	0.13	3.62
S6	T1	51.34	16.37	10.56	5.72	1.03	0.58	0.71	0.10	0.25	0.17	8.60
	T2	51.04	16.69	10.49	4.86	1.50	0.69	0.90	0.11	0.30	0.15	8.28
S7	T1	54.27	14.88	10.68	5.82	1.19	0.66	0.87	0.11	0.22	0.11	5.08
	T2	54.42	17.81	11.76	7.59	1.35	0.67	1.16	0.12	0.32	0.12	7.76
	T3	55.51	16.77	10.96	6.15	1.28	0.67	1.05	0.11	0.27	0.11	6.00

S8	T1	52.14	17.09	9.90	4.04	1.57	0.53	0.69	0.13	0.32	0.16	7.14
	T2	53.11	17.95	10.37	4.69	1.58	0.53	0.75	0.13	0.31	0.15	7.09
	T3	50.81	18.77	10.85	5.36	1.53	0.49	0.83	0.13	0.32	0.13	8.14
S9	T1	52.23	16.17	10.86	6.65	1.35	0.77	1.15	0.11	0.29	0.14	13.00
	T2	54.71	18.49	11.18	5.53	0.97	0.78	0.97	0.12	0.34	0.14	9.06
	Minimum	50.81	13.94	9.90	3.88	0.97	0.36	0.61	0.10	0.22	0.09	2.89
	Maximum	63.04	21.05	11.76	7.59	1.93	0.93	1.16	0.13	0.43	0.19	13.00
	Average	55.83	16.79	10.57	5.68	1.40	0.69	0.93	0.11	0.32	0.14	5.49
	STDEV	3.81	1.75	0.41	0.89	0.26	0.15	0.16	0.01	0.04	0.02	2.58
	Median	55.17	16.73	10.52	5.77	1.38	0.68	0.94	0.11	0.32	0.14	4.54

4.1.1.4 Heavy metal concentration

Tailings contain heavy metal bearing fine grained sulphides. Weathering and oxidation of sulphides in the tailings produce sulphuric acid by the reaction with water, and the toxic metals associated with the sulphides easily get transported and distributed in soil-water-plant-air system. This phenomenon is known as AMD and constitutes one of the main environmental problems for the mining industry (Akcil and Koldas, 2006). Hence, the tailings were analysed for heavy metal concentration and the results are discussed here.

Cu concentration is relatively high in tailings ranging from 395 - 4388 ppm with an average of 2047 ± 1222 ppm, which is 82, 46 and 280 times higher than that of the average Upper Continental Crust (UCC), World Average Shale (WAS) and regional soil (LS) values respectively (Table 4.2). Zn varies from 82.3 to 732.4 ppm with an average of 299.2 ± 176.2 ppm in tailings.

In tailings, Co is found in higher concentration as Co minerals are also present in association with Cu ore at Khetri as reported by GSI, 1997. The concentration vary from 24 to 102 ppm with an average of 53.4 ± 18.7 ppm, which is 10, 3 and 25 times higher than that of average UCC, WAS and LS respectively. The average concentration of Pb in tailings is 1.2 ± 1.3 ppm which is very low compared to soils of the region.

The order of abundance of heavy metals in tailings is Cu > Cr > Zn > Co > Ni > Pb. The observed higher concentration of heavy metals in the tailings reflects the poor efficiency of Cu extraction unit and the heavy metal bearing tailings in the region are the potential source of pollutants.

Table 4.2 Average concentration (in ppm) of heavy metals in tailings along with the average concentration in UCC, WAS and LS

Elements	**Range**	**Average±Stdev**	**Median**	**UCC***	**WAS#**	**LS**
Cu	394.6-4388.4	2046.6±1221.6	1586.0	25	45	7.3
Zn	82.3-732.4	299.2±176.2	253.9	71	95	47.3
Cr	88.0-272.7	152.9±45	143.4	35	90	34.6
Cd	-	-	-	-	0.3	Nd
Co	24.0-102.0	53.4±18.7	52.1	10	19	2.1
Ni	9.9-83.6	44.4±16.6	45.0	20	68	22.6
Pb	0.0-3.8	1.2±1.3	1.0	20	20	23.6
Mn	1108.7-1848.1	1492.2±183.1	1462.9	600	850	411.5

*Taylor and McLennan 1985

#Turekian and Wedepohl, 1961

NdNot determined

On comparing the heavy metals in new and old tailings, Cu, Zn, Co and Fe are found in higher concentration in the new tailings compared to older tailings. The lowest concentrations of Cu (average = 1253 ± 470 ppm) are found in comparatively old tailings (S7-S9) located in southwestern part of tailing dam (Table 4.3). Over a time oxidation of sulphides could lead to leaching of heavy metals (McGregor *et al.*, 1998). While, new tailings (S1-S6) close to tailings entry point have high concentration of Cu (average 2542 ± 1293ppm).

The observed lower abundances of heavy metals in the old tailings may be due to oxidation and leaching. The difference in average concentration of Cu between old and new tailings is ~1200 ppm, which also indicates that ~1200 ppm of Cu got leached from tailings. The average concentration of Zn in new and old tailings is 360 ± 196 ppm and 202 ± 69 ppm respectively.

The results shows that old tailings have pH in strong acidic range, high LOI and low heavy metal concentration, while new tailings have a pH more towards alkaline range, low LOI and high abundance of heavy metals. It suggests that on exposure to air and water sulphides got precipitated which generate AMD and results in decrease in pH and leaching of heavy metals in old tailings.

The UCC normalized plot for heavy metals in tailings shows the high enrichment of heavy metals (Cu, Ni, Co, Zn and Cr) in the tailings (Fig. 4.7).

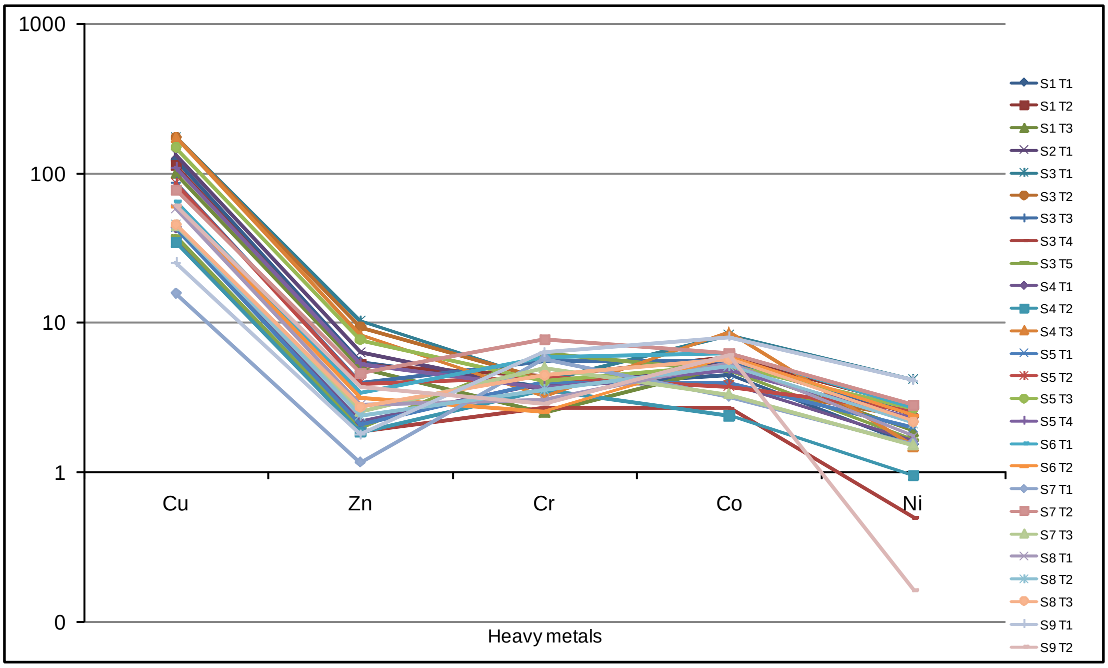


Fig. 4.7 UCC normalized plot for heavy metals of tailings

Table 4.3 Heavy metals concentration (ppm) in new and old tailings with respect to their locations

	Sample location	**Cu**	**Zn**	**Cr**	**Co**	**Ni**	**Pb**	**Mn**	**Fe**
New tailings									
S1	T1	3082.49	387.61	131.51	45.33	30.49	0.00	1654.43	149171.64
	T2	2837.81	374.26	155.15	59.69	56.19	3.84	1697.67	146505.50
	T3	2499.40	356.50	88.04	51.59	37.45	0.00	1560.70	124772.20
S2	T1	3347.95	450.39	124.06	54.42	48.62	0.32	1323.23	121359.85
S3	T1	4374.64	732.44	144.17	83.35	83.61	0.00	1848.09	163652.74
	T2	4388.43	666.98	148.50	38.60	46.85	0.00	1834.11	147259.49
	T3	2191.19	282.22	194.83	55.57	49.27	0.00	1768.20	131845.63
	T4	928.48	133.35	95.38	26.90	9.90	0.91	1439.82	109785.85

	T5	952.57	139.46	218.57	47.55	32.79	0.00	1372.66	114869.39
S4	T1	1092.09	154.11	138.05	38.94	32.19	2.95	1108.71	108355.62
	T2	868.35	132.69	124.93	24.04	19.07	1.44	1420.18	112218.80
	T3	4380.73	587.59	112.56	86.80	29.98	0.00	1450.00	135910.91
S5	T1	1084.67	149.01	141.63	39.96	39.88	0.00	1475.36	120232.76
	T2	2162.21	281.54	152.72	37.98	52.28	0.00	1507.04	125829.32
	T3	3746.77	547.19	142.59	52.43	53.19	0.00	1584.75	130570.85
	T4	2738.96	382.28	130.78	48.58	46.23	1.10	1477.18	122339.25
	Minimum	868.35	132.69	88.04	24.04	9.90	0.00	1108.71	108355.62
	Maximum	4388.43	732.44	218.57	86.80	83.61	3.84	1848.09	163652.74
	Average	2542.30	359.85	140.22	49.48	41.75	0.66	1532.63	129042.49
	STDEV	1293.42	196.68	32.41	17.03	17.01	1.18	195.91	15895.58

	Median	2619.18	365.38	139.84	48.06	43.06	0.00	1492.11	125300.76
	Old tailings								
S6	T1	1634.02	242.92	208.59	63.03	53.87	0.08	1587.82	127228.46
	T2	1520.71	226.40	89.93	59.58	48.10	2.35	1450.47	129754.69
S7	T1	394.62	82.29	202.60	32.20	31.11	1.01	1259.27	115693.33
	T2	1949.30	327.11	272.70	62.44	56.74	1.33	1342.88	138452.68
	T3	1122.37	182.26	175.76	33.34	30.49	1.53	1257.98	130376.53
S8	T1	1457.23	201.76	107.33	53.60	34.75	3.15	1710.49	132817.25
	T2	1142.27	171.87	125.84	51.85	42.63	2.52	1534.38	139533.12
	T3	1143.25	195.72	156.65	57.41	43.77	3.20	1362.24	145875.89
S9	T1	632.02	127.42	221.99	80.65	82.63	2.20	1433.42	125704.96
	T2	1537.98	264.95	101.96	61.52	3.27	13.37	14375.39	143753.86

Minimum	394.62	82.29	89.93	32.20	3.27	0.08	1257.98	115693.33
Maximum	1949.30	327.11	272.70	80.65	82.63	13.37	14375.39	145875.89
Average	1253.38	202.27	166.34	55.56	42.73	3.08	2731.43	132919.08
STDEV	470.03	69.21	60.37	14.32	20.68	3.75	4093.78	9172.90
Median	1300.24	198.74	166.20	58.49	43.20	2.27	1441.94	131596.89

4.1.2 Geochemical Assessment of Soils

By virtue of fine disseminations of sulphides, the tailings are susceptible to travel distant places hence the soils neighbouring the mines, tailings and overburden materials are analyzed for heavy metal contamination. Along with heavy metal contamination, pH, geochemical parameters (organic matter and major oxides) and mineralogy of soils were also analyzed to assess the chemical composition. The results of the physio-chemical parameters are discussed here.

4.1.2.1 pH

The soil of the Khetri copper mine region lies in acidic to alkaline range with pH 5.1 - 8.2 (Fig. 4.8), with an average of 7.5 ± 0.8. The lowest pH 5.1 is found in the soils (L10) near (~20 m near) the overburden materials of abandoned Chaandmari mine (Table 4.4). The low pH in the soils near overburden materials of surface Chaandmari mine can be attributed to the oxidation of sulphides which results in decrease in pH. Similarly, pH 6.14 is found in the soils of Banwas (L19) which is near Khetri mine and overburden materials.

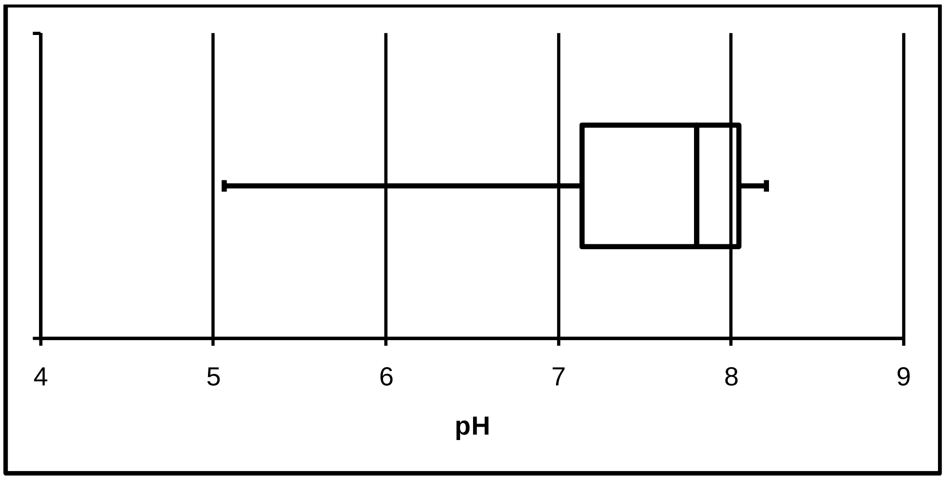


Fig. 4.8 Box plot showing the range of pH in soil samples of Khetri

4.1.2.2 Total organic carbon

The organic carbon varies from 0 to 2.88 wt. % with an average of 1.22 wt. % with a standard deviation of 0.88% (Fig. 4.9). The total organic carbon content is found low in the soils of Khetri region may be because the soils were collected from barren land with no agricultural activities. The major parts of the region are covered with aeolian (Sandy), and more sand content in soils could be the reason for low organic carbon (Jobbágy and Jackson, 2000).

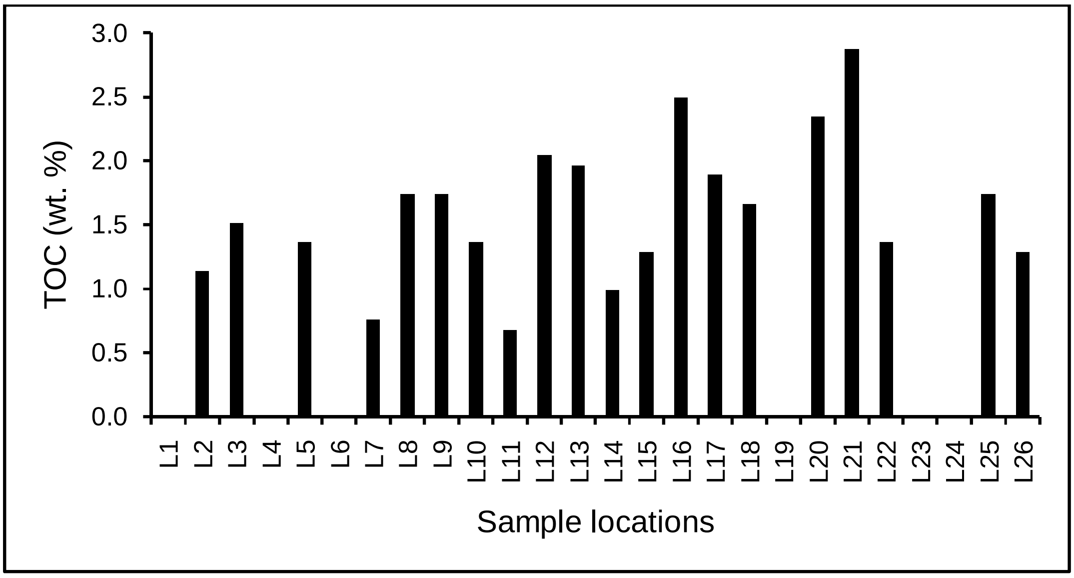


Fig. 4.9 Total organic carbon content in the soils

4.1.2.3 Loss on ignition

LOI ranges from 1.6 to 12.1 wt. % (Fig. 4.10) with an average of 5.14 wt. %. LOI shows wide variation in the values may be due to presence of different types of soil chosen for analysis such as river bed sediments and aeolian soil. The minimum LOI i.e. 1.6 wt. % is found in the aeolian soil of the Surj ki Dhani (L21), as the soil is coarse grained thus the adsorption capacity for volatile substances is less (Table 4.4). While the soils from dried reservoir of Ajit Sagar dam (L4 and L5) and the Pannasagar talab i.e. artifical pond (L8 and

L9) has the maximum LOI i.e. 10 and 12 wt. % respectively. The soils from dried water bodies have more clay content and clay has more size to volume ratio so the adsorption capacity is more in clay.

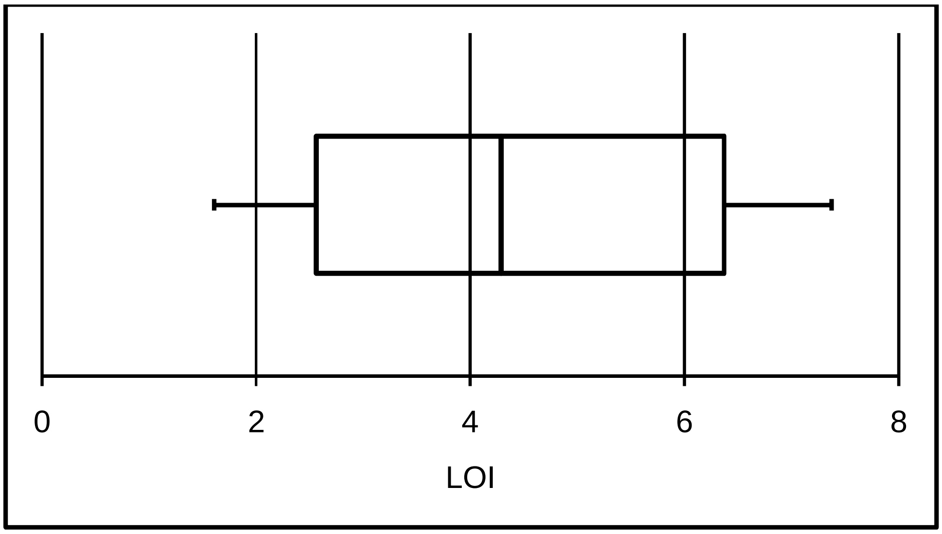


Fig. 4.10 Box plot showing LOI (wt. %) in soils

4.1.2.4 Major oxides

The silica (SiO_2) dominates in the soil of Khetri copper region and ranges from 47.16 to 77.59 wt. % with an average of 65.93 ± 9.42 wt. % (Table 4.4). The soils dried bed of *Ajit sagar* (L4 and L5) and *Panasagar talab* (L8 and L9) are depleted in SiO_2 due to silica dilution effect. The soil near the overburden materials soil (L10) also contain low silica may be due to presence of high sulphides and other associated minerals. The soils are dominated by the Al_2O_3 after silica with an average of 12.78±1.06 wt. %.

Table 4.4 Physio-chemical parameters of soil samples

Sample location	Sample location	pH	OC	Major Oxides (wt. %)										LOI (%)
				SiO_2	Al_2O_3	MgO	FeO	CaO	K_2O	Na_2O	TiO_2	P_2O_5	MnO	
L1	Kakariya (mountain bed)	8.1	0.00	70.66	12.27	5.62	4.39	1.84	1.33	1.01	1.01	0.11	0.05	4.14
L2	Kakariya (sand)	8.16	1.14	69.36	13.33	5.21	3.84	1.98	1.75	1.31	0.50	0.09	0.05	2.74
L3	Maliyun Dhani	7.43	1.51	73.05	12.92	5.83	3.23	1.24	1.84	2.01	0.56	0.08	0.04	2.69
L4	Ajit sagar (upper)	7.94	0.00	52.47	14.77	3.27	7.18	2.50	2.54	0.92	0.75	0.20	0.06	9.43
L5	Ajit sagar (below 10 cm)	6.97	1.36	51.39	15.06	2.57	7.99	2.96	2.62	0.77	0.77	0.22	0.07	10.23
L6	Ahiro Dhani	7.29	0.00	61.45	14.23	2.19	6.40	0.83	1.44	3.75	0.70	0.14	0.06	4.38
L7	Rajota	7.57	0.76	63.98	13.37	3.33	4.60	1.21	1.79	1.05	0.69	0.16	0.05	7.05
L8	Pana sagar (upper surface)	7.8	1.74	47.35	14.27	3.92	9.05	2.86	2.48	0.77	0.78	0.25	0.06	11.45
L9	Pana sagar (below 10 cm)	7.95	1.74	47.16	14.38	4.01	8.53	3.09	2.45	0.88	0.72	0.26	0.06	12.14

L10	Chaandmari	5.06	1.36	54.21	12.52	5.05	13.79	1.18	0.74	1.67	0.56	0.11	0.06	5.25
L11	Bhargada Dhani	7.14	0.68	75.93	12.26	5.92	3.11	1.61	1.60	1.88	0.32	0.10	0.04	2.15
L12	Near tailings (Gothra)	8.17	2.04	66.51	12.52	7.98	4.78	5.41	0.95	3.00	0.48	0.07	0.03	5.09
L13	River bed (upper surface)	8.15	1.97	69.44	11.96	5.88	3.65	5.22	1.57	1.63	0.44	0.10	0.05	4.2
L14	River bed (10 cm depth)	8.04	0.98	77.59	11.66	6.07	3.01	2.32	1.60	1.76	0.38	0.08	0.04	1.75
L15	River bed (20 cm)	8.06	1.29	74.45	11.90	5.93	3.58	3.08	1.56	1.74	0.48	0.10	0.05	2.65
L16	River bed (30 cm)	7.95	2.50	75.08	11.13	6.46	4.49	2.48	1.20	1.64	0.60	0.08	0.05	1.9
L17	River bed (45 cm)	7.12	1.89	65.05	12.33	5.54	3.87	4.70	1.70	1.27	0.40	0.10	0.05	5.49
L18	Gujarwas	7.8	1.67	73.92	12.32	5.70	3.35	1.66	1.70	1.72	0.42	0.13	0.05	2.24
L19	Banwas	6.14	0.00	61.59	11.65	1.16	7.84	1.18	1.30	0.98	0.58	0.31	0.04	5.98
L20	Meghawali Dhani	8.2	2.35	61.50	12.28	6.26	3.27	9.62	1.10	2.26	0.33	0.09	0.04	8.79
L21	Suraj Dhani	6.86	2.88	73.16	12.02	0.58	1.94	1.45	1.66	1.77	0.29	0.10	0.04	1.6

L22	Teelawali	6.09	1.36	76.23	12.05	5.51	2.91	1.55	1.66	1.67	0.33	0.12	0.05	2.3
L23	Kharakara Rajputan	7.81	0.00	70.19	13.01	3.05	3.94	1.08	1.82	0.80	0.52	0.23	0.05	6.14
L24	Kharkra Devran	7.54	0.00	70.63	12.55	4.02	4.11	1.33	1.91	1.21	0.53	0.24	0.06	3.59
Min		5.1	0.00	47.16	11.13	0.58	1.94	0.83	0.74	0.77	0.29	0.07	0.03	1.60
Max		8.2	2.88	77.59	15.06	7.98	13.79	9.62	2.62	3.75	1.01	0.31	0.07	12.14
Average		7.5	1.22	65.93	12.78	4.63	5.12	2.60	1.68	1.56	0.55	0.14	0.05	5.14
STDEV		0.8	0.88	9.42	1.06	1.82	2.71	1.97	0.48	0.71	0.18	0.07	0.01	3.19
Median		7.8	1.36	69.40	12.42	5.36	4.02	1.91	1.66	1.63	0.52	0.11	0.05	4.29

FeO is very low in soil compared to tailings due to absence of pyrite and pyrrhotite. It varies from 1.94 to 13.79 wt. % with an average of 5.12 ± 2.71 wt. %. Maximum FeO (13.79 wt. %) is found in the soil (L10) very near ~20 m the overburden materials of Chaandmari mine. Soils (L4, L5, L8 and L9) from dried bed of water bodies are also having high content of FeO i.e. 7.2, 8.0, 9.2 and 8.8 wt. % respectively may be due to silica dilution effect. On excluding the extremes of FeO content samples (L4, L5, L8, L9 and L10) the average FeO is 4 wt. %. Meghawali Dhani (L20) has 9 wt. % of CaO may be due to presence of calcite or dolomite. White colour powder was observed in the area during the sampling and on analyzing with HCl, the white fumes came out which indicates the presence of carbonates.

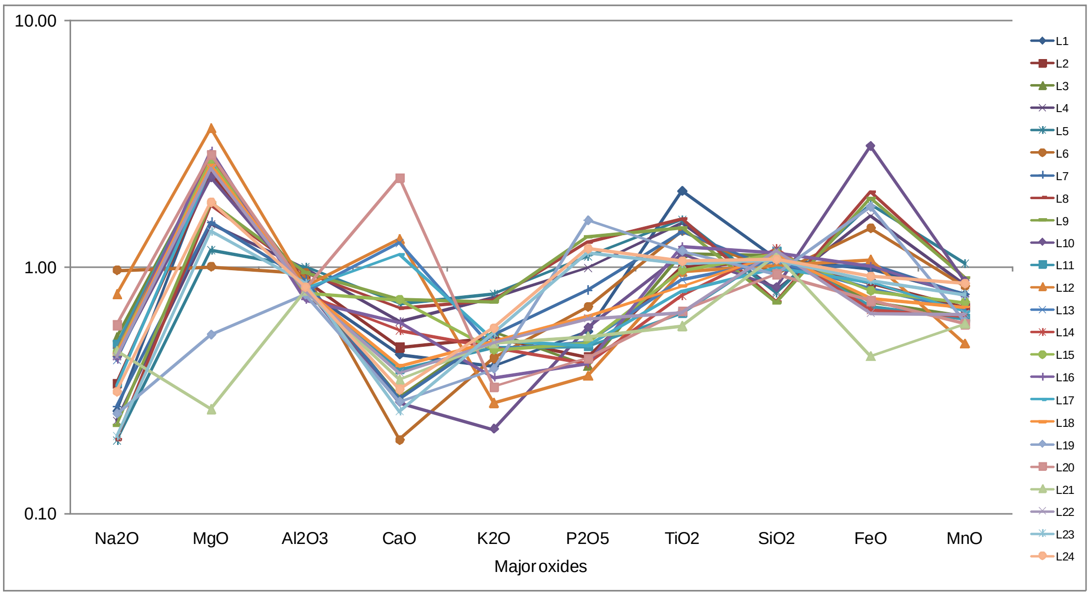


Fig. 4.11 UCC normalized plot for major oxides of soils

The soils are enriched of MgO indicating the moderate weathering or due to presence of amphiboles (Fig. 4.11). The soils have depleted concentrations of CaO (2.6 wt. %), K_2O (1.68 wt. %), P_2O_5 (0.14 wt. %), MnO (0.05 wt. %) and LOI (5.1 wt. %). Thus these soils are typical of those found in sub-tropical semi-arid regions, being leached, low in nutrient and of poor fertility.

4.1.2.5 Weathering

To analyse the intensity of chemical alternation in the soils of the region the chemical index of alternations (CIA) (Nesbitt and Young, 1982) and chemical index of weathering (CIW) (Harnois, 1988) were calculated. For the calculations of indices the major oxide composition of the samples were used.

$$CIA = \frac{Al_2O_3}{Al_2O_3 + CaO^* + Na_2O + K_2O} \times 100$$

$$CIW = \frac{Al_2O_3}{Al_2O_3 + CaO + Na_2O} \times 100$$

Where CaO* represent the CaO in the silicate fraction only.

The increase in CIA and CIW values indicate the increase in weathering intensity. CIA values from 45 to 55 indicate virtually no weathering whereas the maximum value 100 represents intense weathering with complete removal of Ca^{2+}, K^+ and Na^+ compared to residual components such as Al^{3+} and Ti^{4+}. The molar proportions of Al_2O_3, $CaO+Na_2O$ and K_2O are plotted on triangular plot commonly known as A-CN-K plot for better representation of weathering (Nesbitt and Young, 1984; 1989). Similarly, the molar proportion of Al_2O_3, $CaO+Na_2O$, K_2O and FeO+MgO are also plotted which is known as A-CN-K-FM plot.

The calculated CIA values indicate the moderate weathering in the soils of Khetri region. The average values of CIA and CIW values of soil (CIA = 69 and CIW = 76) are higher than those of UCC (CIA = 56.92 and CIW = 65.24). The soils near the overburden materials, L10 (CIA = 78) and L19 (CIA = 77) have high values of CIA. This may be due to presence of sulphides that facilitated the chemical weathering intensity (Dang *et al*., 2002). The average of major oxides along with the CIA and CIW values are given in the below table 4.5.

Table 4.5 Average major oxide composition of soils compared with that of UCC and WAS

Parameters	**Soil**			**UCC**[*]	**WAS**[#]
	Range	**Average±Stdev**	**Median**		
SiO_2	47.16-77.59	65.93±9.42	69.40	66	58.50
Na_2O	0.77-3.75	1.56±0.71	1.63	3.9	1.30
MgO	0.58-7.98	4.63±1.82	5.36	2.2	2.50
Al_2O_3	11.13-15.06	12.78±1.06	12.42	15.2	15.00
CaO	0.83-9.62	2.60±1.97	1.91	4.2	1.30
K_2O	0.74-2.62	1.68±0.48	1.66	3.4	3.10
P_2O_5	0.07-0.31	0.14±0.07	0.11	-	0.16
TiO_2	0.29-1.01	0.55±0.18	0.52	-	0.77
Fe_2O_3	-	-	-	5	4.72
FeO	1.94-13.79	5.12±2.71	4.02	-	-
MnO	0.03-0.07	0.05±0.01	0.05	-	-
CIA	48.62-77.88	69.30±6.95	70.74	56.92	66.66
CIW	50.84-87.38	76.35±8.54	78.91	65.24	77.31

[*] Taylor and McLennan, 1985

[#] Turekian and Wedepohl, 1961

A-CN-K diagram (Fig. 4.12) shows that some of the points lie near to WAS and some near the loess. Hence, the area has both types of soil. A-CN-K shows that the samples have high content of K_2O compared to CaO and Na_2O due to leaching of these elements during the weathering. Soils near the overburden materials of Chaandmari mine (L10) lies below the plagioclase and feldspar suggesting the low content of Al_2O_3 and high content of CaO and Na_2O. It indicates less weathering, as the soil (L10) at overburden materials were generated after the manual crushing.

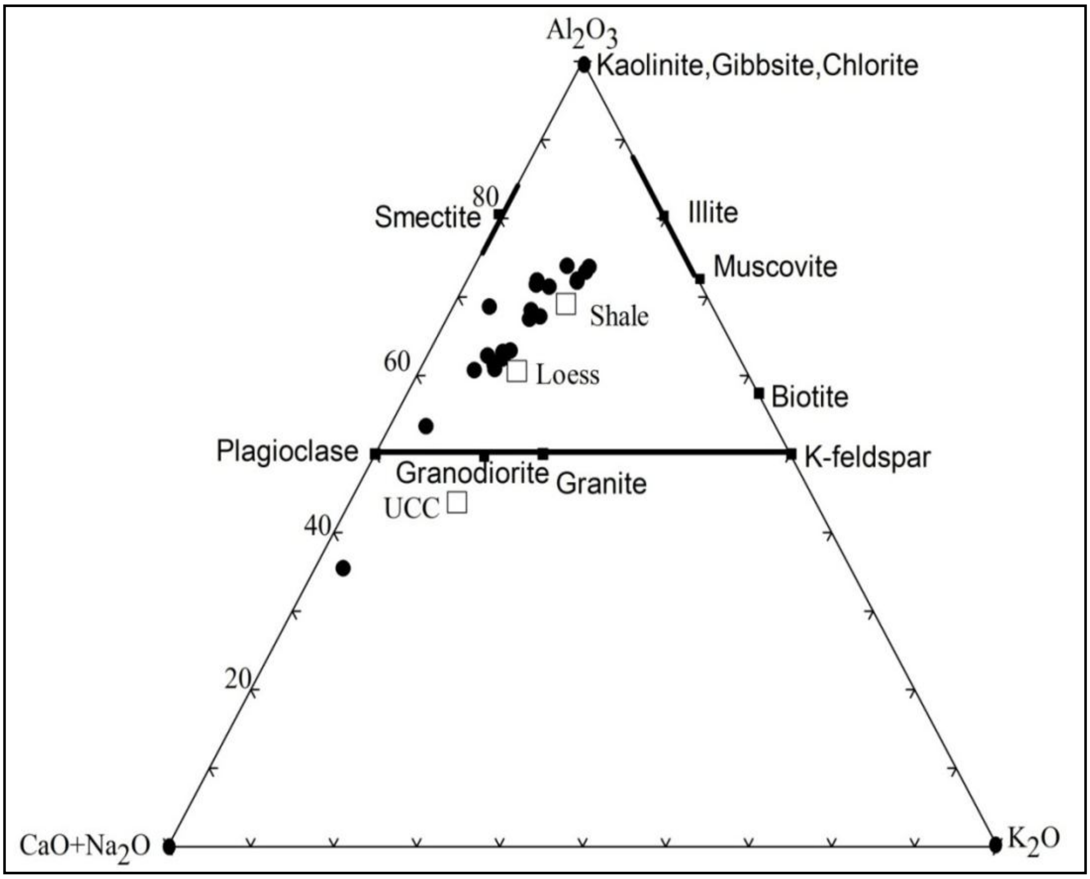


Fig. 4.12 A-CNK diagram for soils

In A-CNK-FM plot most of the sampling points lies between the granodiorite and basalt indicating the presence of both felsic and mafic rocks as shown in Fig. 4.13.

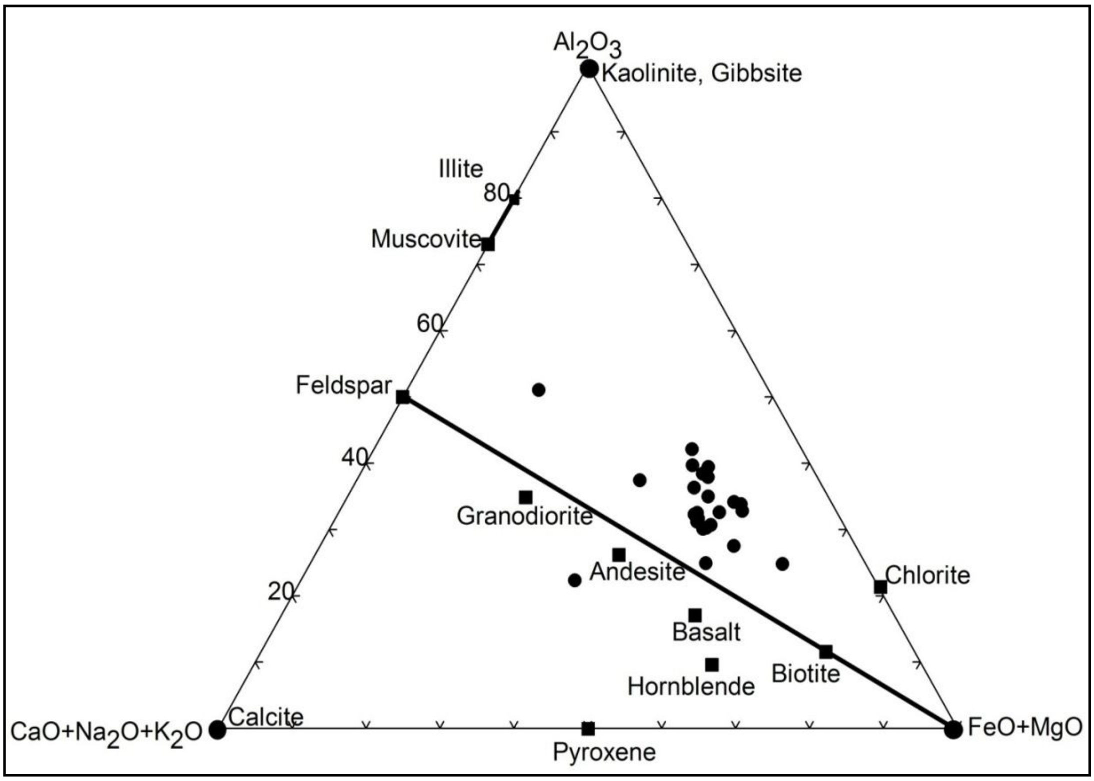


Fig. 4.13 A-CNK-FM diagram for soils

4.1.2.6 Correlation among major oxides

LOI shows a significant positive correlation (0.73, p>0.05 level) with Al_2O_3 indicating absorption of water on the clays. SiO_2 has negative correlation with Al_2O_3 (0.76, p>0.05), P_2O_5 (0.59, p>0.05), TiO_2 (0.56, p>0.05), FeO (0.81, p>0.05) and MnO (0.59, p>0.05) and indicates the dilution effect on these elements (Table 4.6). The positive correlation among CaO and MgO (0.45, p>0.01) indicates their mobility in association with each other or may be due to their similar geochemical behavior.

Table 4.6 Correlation among the major oxides in soils

	LOI	**Na_2O**	**MgO**	**Al_2O_3**	**CaO**	**K_2O**	**P_2O_5**	**TiO_2**	**SiO_2**	**FeO**	**MnO**
LOI	1	-0.41*	-0.29	0.73**	0.32	0.53**	0.64**	0.52**	-0.92**	0.60**	0.49*
Na_2O		1	0.28	-0.19	0.19	-0.56**	-0.57**	-0.34	0.29	-0.22	-0.39
MgO			1	-0.40	0.45*	-0.40	-0.66**	-0.25	0.37	-0.27	-0.36
Al_2O_3				1	-0.09	0.72**	0.48*	0.57**	-0.76**	0.47*	0.66**
CaO					1	-0.17	-0.27	-0.25	-0.17	-0.15	-0.25
K_2O						1	0.56**	0.35	-0.43*	0.08	0.56**
P_2O_5							1	0.44*	-0.59**	0.48*	0.49*
TiO_2								1	-0.56**	0.52**	0.56**
SiO_2									1	-0.81**	-0.59**
FeO										1	0.57**
MnO											1

* Correlation is significant at the 0.05 level (2-tailed)

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

4.1.2.7 Heavy metal concentration

The average heavy metal concentration in soils of Khetri region are compared with the average of UCC, WAS and LS to assess the accumulation of heavy metals. It is found that Cu is accumulated more in the soils compared to other heavy metals i.e. Zn, Co, Ni, Pb and Cr.

In soils, Cu concentration varies from 3 (leeward direction and away from mining area) to 2533 (near overburden materials) ppm with an average of 231±543 ppm and is 9, 5 and 32 times higher than that of the UCC, WAS and LS respectively (Table 4.7). The average concentration of Zn is 87.6±74.98 ppm which is relatively lower when compared with the studies carried out in other copper mining sites (Khorasanipour and Aftabi, 2011; Qin *et al*., 2012). This could be due to low abundance of sphalerite. The heavy metal concentration varies with respect to location and sites neighbouring the mine, tailings and overburden materials. These are more contaminated with heavy metals compared to distant locations (Table 4.8). Similar results were reported from parts of the Zambia (Tembo *et al*., 2006).

Maximum Cu concentration is found in the soils near overburden materials i.e. 2533 ppm at L10 and 1224 ppm at L19 (~1 km away from overburden materials). The soil (L12) close (~1 km) to tailing dam has 111 ppm of Cu. The tailing dam is surrounded by hills from three directions i.e. western, southern and northern. The wind direction during summer and winter season is from S-W and N-W respectively hence the wind direction is parallel to the trends of the hills. Thus, the dispersal of tailing particles due to wind is comparatively minimal. While, the overburden materials with fine disseminations of sulphide are not surrounded by the hills hence it supports their dispersal and thus the soils in the vicinity of overburden material contain comparatively high amount of heavy metals. Hence, the overburden spread in the area has relatively higher environmental impact compared to tailings at Khetri.

Table 4.7 Average heavy metal concentration in the soils of Khetri alongwith that of UCC, WAS and LS (all concentration are in ppm)

Parameters	**Soils**			**UCC**[*]	**WAS**[#]	**LS**
	Range	**Average±Stdev**	**Median**			
Cu	3.1-2532.5	230.6±542.6	47.3	25	45	7.3
Zn	43.1-365.6	87.6±74.98	53.7	71	95	47.3
Cr	25.0-145.5	82.8±32.7	80.4	35	90	34.6
Cd	0.0-0.8	0.1±0.2	0.0	-	0.3	Nd
Co	0.0-62.4	13.5±17.5	5.8	10	19	2.1
Ni	8.6-76.8	32.0±21.9	23.3	20	68	22.6
Pb	0.0-44.3	21.6±8.9	22.2	20	20	23.6
Mn	48.9-702.2	469.0±130.7	466.5	600	850	411.5

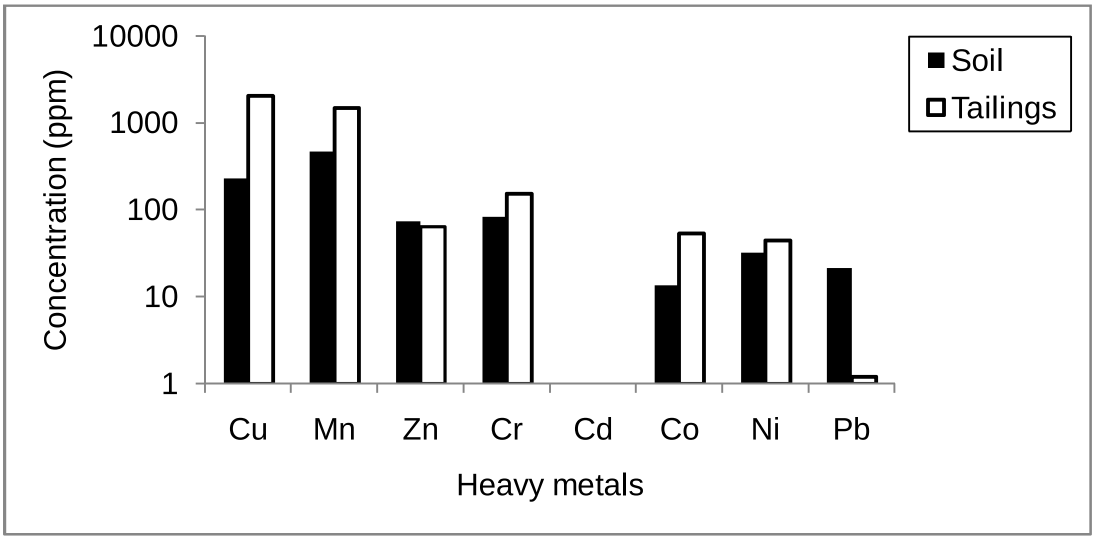
[*] Taylor and McLennan 1985
[#] Turekian and Wedepohl, 1961

Similarly, Zn (L10 = 365 ppm; L19 = 228 ppm), Co (L10 = 62 ppm; L19 = 6), and Ni (L10 = 77 ppm; L19 = 26 ppm) are also present in higher concentration in the soils near overburden materials (L10 and L19) compared to concentration of Zn (73 ppm), Co (13 ppm), and Ni (36 ppm) in soils near the tailings (L12). Among L10 and L19, concentration of Co and Ni is high at L10 compared to L19, may be because L10 is ~ 20 m while L19 is ~1 km away from overburden materials. Pb is high in L19 compared to L10 due to vehicular pollution as L19 is close to road.

Along with strong dusty winds, temperature also plays an important role in the dispersion of tailing particles during summer. Meza-Figueroa *et al*. (2009) found high abundance of heavy metals (Zn, Cu, Mn and Ba) in the efflorescence salts formed by the evaporation on the upper surface of tailings and due to their fine grained nature are the source for the contamination of neighbouring soils. Since, Khetri lies in the semi-arid region with scarce vegetation and high temperature during summer which further accelerates the heavy metal mobility from overburden materials and tailings.

Soils (L4, L5, L8 and L9) from dried water bodies have high heavy metal content compared to soils from other sites properly due to presence of fine size of clay, which adsorbs more heavy metals. Soils (L6) near the mountain of Ahrio Dhani (near Ajit Sagar dam reservoir) is having high concentration of Cu, Zn, Cr, Co and Ni i.e. 786, 136, 98, 62 and 63 ppm may be due to oxidation of sulpides in the presence of reservoir water. GSI, 1977 confirms the presence of Cu deposits at Ajit Sagar and the presence of sulphides veins and red color vertical veins can easily be seen at site.

The order of abundance of heavy metals in soils is Cu > Cr > Zn > Ni > Pb > Co. The heavy metals (Cu, Zn, Cr, Co, Mn and Fe) those found in high concentration in tailings are also found in high concentration in soils (Fig. 4.14). Pb and Cd which are present in lower concentration in tailings are found in lower concentration in soils with comparison to UCC, WAS and LS.



*Cd is below 1 ppm

Fig. 4.14 Comparison of heavy metals among tailings and soils of Khetri region

The UCC normalized plot for heavy metals (Cu, Zn, Cr, CO, Ni and Pn) indicates the enrichment of Cu in the soils of the region (Fig. 4.15)

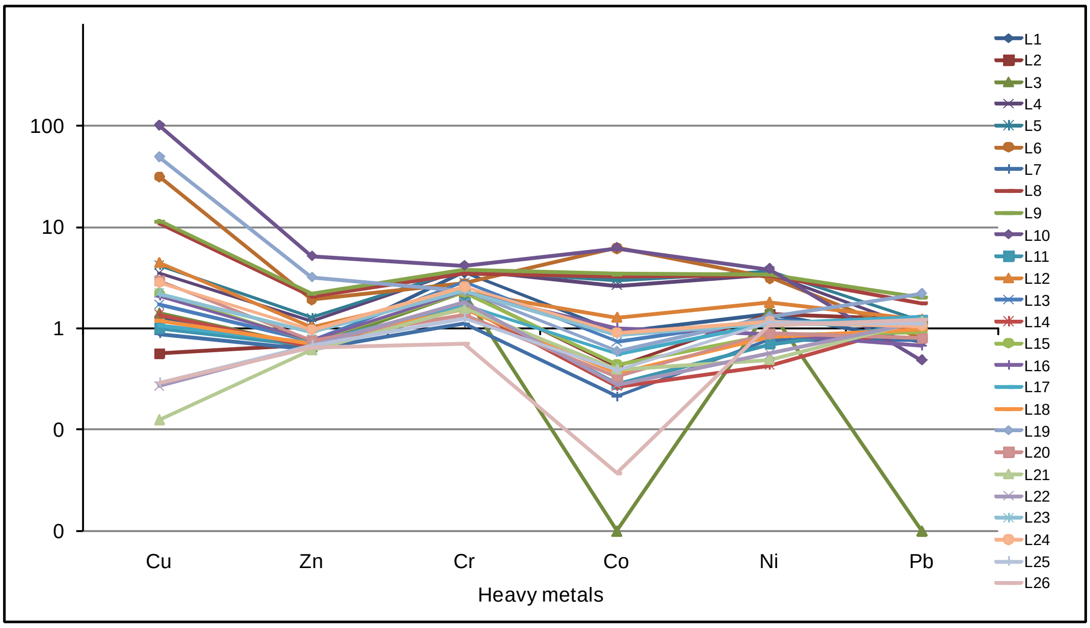


Fig. 4.15 UCC normalized plot for heavy metals of soils

Table 4.8 Heavy metal concentration (ppm) in the soils for each sampling location

Sample Code	**Sample location**	**Cu**	**Zn**	**Cr**	**Cd**	**Co**	**Ni**	**Pb**	**Mn**	**Fe**
L1	Kakariya (mountain bed)	32.75	48.21	123.88	0.17	9.19	27.85	14.90	590.26	34107.92
L2	Kakariya (sand)	14.30	48.65	80.13	0.50	4.20	27.81	24.11	464.22	29871.64
L3	Maliyun Dhani	35.50	46.87	78.40	0.00	0.00	31.04	0.00	340.00	25130.11
L4	Ajit sagar (upper)	86.09	83.52	132.79	0.00	26.36	68.13	19.24	571.90	55810.14
L5	Ajit sagar (below 10 cm)	103.93	89.13	133.68	0.10	30.13	73.20	23.23	702.16	62098.50
L6	Ahiro Dhani	785.76	136.36	98.23	0.00	62.16	63.03	15.77	501.30	49723.88
L7	Rajota	22.15	43.89	39.32	0.00	2.12	15.39	15.36	316.09	37162.71
L8	Pana sagar (upper surface)	270.78	146.76	121.91	0.26	32.75	66.93	35.36	575.79	71705.93
L9	Pana sagar (below 10 cm)	286.69	154.82	132.01	0.36	34.46	67.83	40.28	561.07	68620.04
L10	Chaandmari	2532.49	365.62	145.53	0.00	62.37	76.77	9.64	613.95	106194.73
L11	Bhargada Dhani	25.10	47.61	62.44	0.77	2.81	13.91	22.58	403.80	24150.71
L12	Near tailings (Gothra)	110.51	72.57	81.14	0.44	12.84	35.93	24.56	468.77	35771.35
L13	River bed (upper surface)	43.00	53.69	99.59	0.00	7.36	24.56	19.87	518.25	28363.68
L14	River bed (10 cm depth)	34.19	47.31	58.26	0.00	2.68	8.65	22.84	477.33	23381.18

L15	River bed (20 cm)	55.98	53.11	79.67	0.00	4.41	17.42	18.54	533.23	27827.34
L16	River bed (30 cm)	51.67	53.70	80.61	0.00	10.04	17.58	13.45	567.58	34877.45
L17	River bed (45 cm)	27.00	51.66	59.55	0.00	5.62	22.43	26.01	458.65	30104.83
L18	Gujarwas	30.15	50.68	54.87	0.00	3.58	16.70	19.89	453.50	26024.00
L19	Banwas	1224.37	228.44	82.28	0.00	5.96	26.32	44.34	386.80	60885.91
L20	Meghawali Dhani	73.82	53.75	48.06	0.01	3.27	17.90	15.98	386.08	25378.85
L21	Suraj Dhani	3.11	43.05	55.07	0.00	3.94	9.71	23.54	358.24	20909.37
L22	Teelawali	6.79	48.01	62.71	0.00	2.76	11.23	23.04	430.12	22619.43
L23	Kharakara Rajputan	55.66	65.86	83.05	0.00	8.70	22.62	21.86	48.89	30625.62
L24	Kharkra Devran	70.46	68.40	89.83	0.00	9.05	23.32	20.95	642.75	31939.26
L25	Bass Govind Singh	7.28	48.48	44.16	0.00	3.84	23.36	22.54	456.09	5840.00
L26	Pilani	7.36	46.22	24.98	0.00	0.37	21.82	24.70	366.94	5816.00
	Minimum	3.11	43.05	24.98	0.00	0.00	8.65	0.00	48.89	5816.00
	Maximum	2532.49	365.62	145.53	0.77	62.37	76.77	44.34	702.16	106194.73
	Average	230.65	84.47	82.77	0.10	13.50	31.98	21.64	468.99	37497.71
	STDEV	542.61	72.75	32.69	0.20	17.47	21.89	8.85	130.73	22086.93
	Median	47.33	53.40	80.37	0.00	5.79	23.34	22.20	466.50	30365.22

4.1.2.8 Mineralogy of tailings and soils

The mineralogical study of the soil provides the presence of silicate and non-silicate groups (Fig. 4.16 A & B). The silicate minerals include quartz, mica, chlorite, K-feldspars, Na-plagioclases, amphiboles, pyroxene and garnet, and the non-silicates are calcite and dolomite. The mineralogy of the soil is showing presence of minerals of metamorphic origin, which indicate metamorphic origin of parent materials. The tailings show mineralogical similarity with the soils of the region.

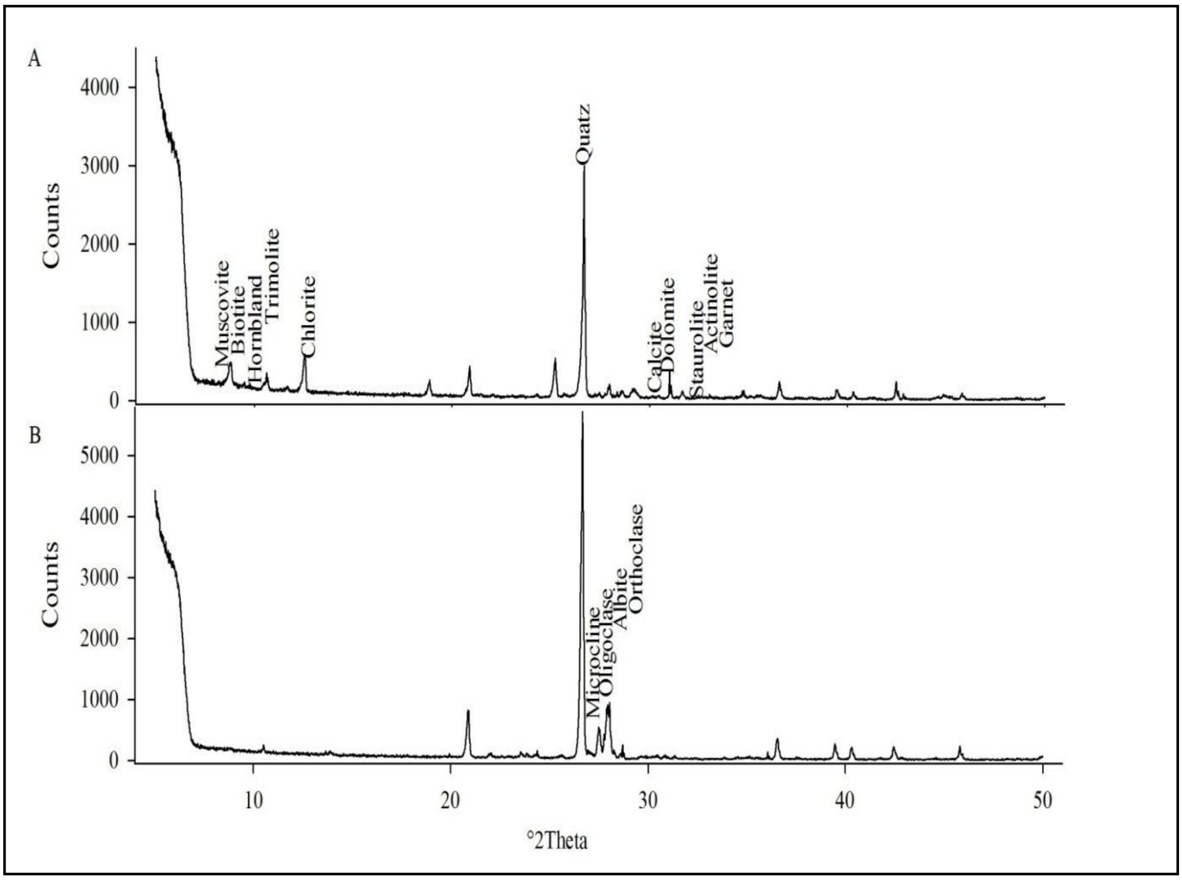


Fig. 4.16 X-ray diffractogram showing the mineralogy of A) tailings B) soils

4.1.3 Hydrogeochemical Characterization of Groundwater

Chemically groundwater evolves by interacting with aquifer minerals or by internal mixing of different groundwater along the flow paths in the subsurface (Domenico 1972; Wallick and Toth 1976; Andre *et al*., 2005; Kumar *et al*., 2012). The aerial exposure of overburden materials and tailings may lead to dissolution of minerals present in them on reacting with oxygen and water. This section presents the results of the analysis of water samples of different locations around the Khetri copper mine region.

4.1.3.1 Physio-Chemical parameters

Seasonal variation in major ions

The chemical composition of surface and groundwater samples for post monsoon and pre monsoon are shown in Table 4.9 and 4.10 respectively. Average pH of surface water and groundwater samples is 7.3 ± 0.7 (varies from 4.6 to 8.3) and 7.1 ± 1.1 (varies from 4.30 to 10.30) in post monsoon and pre monsoon respectively. The minimum pH is found at Chaandmari mine (W18) during both the seasons. The maximum pH 10.30 is found in the surface water of Kakaria artificial pond (W1) during pre monsoon. The observed high pH may be due to mixing of soaps due to bathing and washing at the pond. While, during post monsoon pH decreases to 7.3 (W1) may be due to dilution during rainy season. pH 8.3 and 7.7 is observed at Teelawali (W7) during post monsoon and pre monsoon respectively is due to dissolution of carbonates.

EC is the capacity of a solution or substance to conduct a current. EC ranges from 170-5350 µs/cm and 350-3543 µs/cm with an average of 2075 ± 1162 µs/cm and 1974 ± 1057 µs/cm in post and pre monsoon respectively. The observed increase in EC during post monsoon is attributed to the dissolution of minerals and anthropogenic influence in the region. The EC at surface water (W1) decreases in post monsoon (170 µs/cm) compared to pre monsoon (350 µs/cm) due to dilution effect.

The maximum EC 3543 µs/cm is found at Gujarwas (W16) during pre monsoon and 5350 µs/cm at Singhana (W17) during post monsoon season. Both Gujarwas and Singhana lies in the northern direction of mines, and groundwater table is depleting at the faster rate as both the tube wells from the area were found dried during second (post monsoon) season sampling. The sampling sites close to mines have high EC in both the seasons. During pre monsoon 2900 µs/cm of EC is found at Khetri Nagar (W12) and during post monsoon 3067, 2744 and 2813 µs/cm of EC is observed near tailings (W14), guest house of Khetri Nagar (W23) and Khetri Nagar (W12) respectively. Zhao et al. (2012) found high EC in AMD affected water and suggested it as an a indicator of contamination degree.

The order of concentration of cations during post monsoon is $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ and during pre monsoon is $Ca^{2+} > Na^+ > Mg^{2+} > K^+$. The concentration of Na^+ varies from 7 - 601 mg/L with an average of 243 ± 155 mg/L in post monsoon season and 16 - 453 mg/L with an average of 166 ± 119 mg/L in pre monsoon. The concentration of Ca^{2+} and Mg^{2+} ranges from 25 to 508 mg/L and 6 to 514 mg/L respectively in post monsoon season. Similarly, the concentration of Ca^{2+} and Mg^{2+} ranges from 10 to 488 mg/L and 2 to 334 mg/L respectively in pre monsoon season. The low concentration of dissolved silica i.e. 7 and 9 mg/L is observed in the surface water (W1) during post and pre monsoon respectively. During pre monsoon, 37 mg/L of dissolved silica is observed in the reference water sample (W24) which is comparatively lesser concentration than the groundwater from the Khetri region indicating the lack of mining influence on W24.

During post monsoon the anion dominance order is $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ and during pre monsoon the order is $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$. The dominance of Cl^- during pre monsoon could be due to evaporation or anthropogenic activities, and this might get diluted during monsoon (Fig. 4.17).

The observed higher concentrations of SO_4^{2-} in groundwater samples of post monsoon season could be due to leaching of sulphides during monsoon. During post monsoon Mg^{2+} and Na^+ + K^+ are the dominant cations in the groundwater over Ca^{2+}, while in pre monsoon Ca^{2+} is predominant**.**

Relatively higher concentrations of major ions in groundwater are found in the close vicinity of mining area (W23), overburden materials (W12, W15 & W22), tailings (W21, W13 & W14) and near the abandoned mine (W6) (Table 4.9 & 4.10). The groundwater sample (W11) from the Sukh river bed which receives wastewater from the Khetri mines through channels also show high concentrations of major ions.

The mining has been going on in the hilly region of study area and mining waste is also being dumped in the hills. The groundwater flow is from hills (stretching southwest-northeast) to northern and eastern parts, the sampling location falling in the eastern (W5, W13, W14, W23, W15) and northern (W16, W17) direction shows higher concentration of major ions compared to the western sampling locations (W19, W7, W8, W10). Thus relatively high concentration of ions are found near the mining activities (mine, tailings, overburden materials and abandoned mine) and in the downstream direction of groundwater flow.

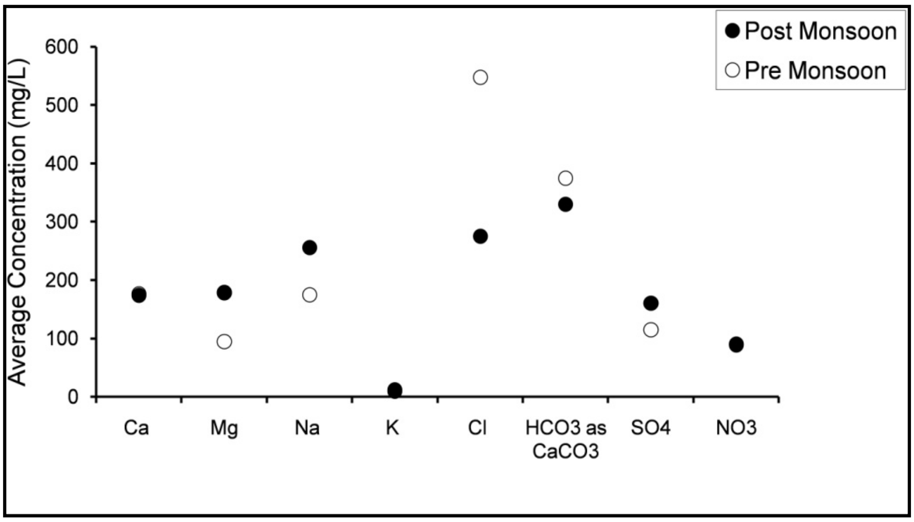


Fig. 4.17 Average concentration of major cations and anions in water samples during post and pre monsoon

Table 4.9 Physio-chemical parameters of water samples for post monsoon season

Site code	**Location Name**	**pH**	**EC$^{\#}$**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**HCO$_3^-$**	**SO$_4^{2-}$**	**Cl$^-$**	**NO$_3^-$**	**Silica**
W1	Kakarai pond	7.3	170	25	6	7	11	174	17	9	10	7
W2	Kakarai	7.5	3534	123	85	601	21	192	157	910	30	28
W3	Maliyun dhani	7.2	1876	159	170	239	3	354	157	222	182	87
W4	Ahiro dhani	7.7	1035	58	54	208	3	323	70	75	2	38
W5	Rajota	7.1	2207	190	182	244	12	439	226	200	202	81
W6	Khetri	6.9	2499	219	209	244	37	415	174	288	202	52
W7	Teelawali	8.3	590	52	80	30	2	180	17	31	131	30
W8	Meghawali Dhani	7.9	680	51	80	51	1	241	52	31	81	48
W9	Khakara Devran	7.7	1088	105	124	60	0	281	70	102	91	56
W10	Kharkara Rajputan	7.5	1827	63	73	459	8	564	122	160	61	56
W11	River bed	8.2	1975	139	132	322	6	180	157	297	71	27
W12	Khetri Nagar	7.5	2813	203	313	264	3	287	174	364	202	78
W13	Bhargda Dhani	7.3	1969	142	229	163	0	311	226	213	192	86

W14	Near tailing	7.2	3067	440	242	290	5	235	331	231	51	86
W15	Kanjaniyun Dhani	7.2	2730	239	232	379	4	348	226	430	71	58
W16	Gujarwas	7.3	1160	50	60	210	2	293	87	129	51	48
W17	Singhana	7	5350	508	419	435	32	354	209	861	212	52
W18	Chandmari	4.6	3546	465	514	129	24	37	261	67	10	60
W19	Bhand bhatiar	7.6	929	98	82	60	2	244	122	49	40	70
W20	Badheswar	7.6	1613	130	146	200	15	439	122	173	20	66
W21	Bawadi Dhani	8.2	2495	142	207	222	72	982	244	186	0	67
W22	Banwas	7.6	1285	136	90	141	11	409	104	93	0	44
W23	Guest house	7.2	2744	147	180	426	3	351	209	506	20	67
W24	Bass govind singh	6.6	2614	81	160	439	5	229	122	595	71	37
	Minimum	4.6	170	25	6	7	0	37	17	9	0	7.0
	Maximum	8.3	5350	508	514	601	72	982	331	910	212	87.0
	Average± STDEV	7.3± 0.7	2075 ±1162	165± 131	170± 118	243± 155	12± 17	328± 139	152± 80	259± 245	83± 75	55± 21

[#] unit is μs/cm

Table 4.10 Physio-chemical parameters of water samples for pre monsoon season

Site code	**pH**	**EC#**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**	**NO_3^-**	**Silica**
W1	10.3	350	10	2	29	37	124	18	31	34	9
W2	7.3	2715	115	62	343	14	376	140	1065	85	71
W3	7.2	933	69	32	91	3	372	58	213	74	77
W4	7.2	1006	62	24	133	5	432	38	355	11	77
W5	7	1882	184	76	123	9	428	115	430	180	77
W6	6.7	2394	234	106	158	25	480	127	506	177	63
W7	7.7	615	67	35	16	3	360	54	160	131	74
W8	7.6	715	75	42	30	2	388	81	213	93	65
W9	7.3	1006	92	54	52	3	352	187	297	101	75
W10	7.3	1850	67	32	312	5	804	70	497	54	53
W11	7.6	1801	113	48	212	30	228	137	861	51	74
W12	7	2900	269	178	188	2	380	110	923	170	67
W13	7.2	3061	356	206	110	1	340	69	497	175	75

W14	7.2	1398	94	34	180	3	412	170	506	2	77
W15	7.5	2638	205	121	256	3	340	120	710	4	75
W16	7.2	3543	164	35	453	20	300	159	1207	10	59
W17	7.1	3228	330	186	229	5	344	108	497	168	51
W18	4.3	3501	488	334	79	20	20	202	364	18	76
Minimum	4.3	350	10	2	16	1	20	18	31	2	9
Maximum	10.3	3543	488	334	453	37	804	202	1207	180	77
Average± STDEV	7.1±1.1	1974±1057	166±124	89±86	166±119	10±11	360±157	109±51	518±321	85±67	66±17

[#] unit is μs/cm

4.1.3.2 WHO and BIS permissible limits

In majority of samples, ion concentrations are above the permissible limits prescribed by the WHO (2011) and BIS (2012) suggesting the unsuitability of groundwater for human consumption (Table 4.11).

EC exceeds the WHO permissible limit in 15 out of 18 samples in pre monsoon and in 21 out of 24 samples. During pre monsoon, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, NO_3^{-} and Cl^{-} exceeds the WHO permissible limit in 12, 9, 6, 6, 16 and 15 number of samples respectively. Similarly during post monsoon, the Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, NO_3^{-} and Cl^{-} exceeds in 18, 23, 14, 6, 23, 19 and 8 number of samples respectively. Excessive Na^{+} in drinking water can increase blood pressure in neonates (Avishalom *et al*., 2002). Presence of excess of Cl^{-} in water gives salty taste and increases the risk of bladder and rectal cancer (Clark *et al*., 1986; Morris *et al*., 1992).

NO_3^{-} concentration is also in the higher range and exceeds the permissible limits in 7 number of samples during both post and pre monsoon season. Excessive consumption of NO_3^{-} might lead to gastric cancer, methaemoglobinaemia in infants, goiter, birth malformations and hypertension (Yang *et al*., 1998; Majumdar and Gupta, 2000). The SO_4^{2-} is found within the permissible limit except in the sample collected near tailings. This may be due to leaching of sulphides during rainy season.

On comparing with the BIS permissible limit, 6 samples for each Ca^{2+} and Mg^{2+} exceeds the permissible limit during post monsoon. It is 6 and 15 samples for Ca^{2+} and Mg^{2+} respectively during pre monsoon. It suggests that during post monsoon the Mg^{2+} concentration increases in the samples as compared to pre monsoon. Both Ca^{2+} and $Mg^{2+}$are important in biological system particularly for the develpoment of bones and nervours system but excess consumption of Ca^{2+} for long duration can lead to formation of kidney stones (Maragella *et al*., 1996).

Table 4.11 Comparison of concentration of major ions of water samples from Khetri copper mine region with WHO and BIS standards (all concentrations are in mg/L)

Parameters	**WHO (2011) Desirable**	**BIS Desirable Limit**	**BIS Permissible Limit**	**No. of samples exceeds WHO limit**		**No. of samples exceeds the BIS limit**			
						Pre-Monsoon (n=18)		**Post-Monsoon (n=24)**	
				Pre (n=18)	**Post (n=24)**	**Desirable**	**Permissible**	**Desirable**	**Permissible**
pH	6.5-8.5	6.5-8.5	-	2	1	2	-	1	-
EC	750	-	-	15	21	-	-	-	-
Alkalinity	-	200	600	-	-	14	1	17	1
TDS	600	500	2000	15	21	12	3	18	3
Ca^{2+}	75	75	200	12	18	6	6	12	6
Mg^{2+}	50	30	100	9	23	10	6	7	15
Na^{+}	200	-	-	6	14	-	-	-	-
K^{+}	12	-	-	6	6	-	-	-	-
HCO_3^{-}	120	-	-	16	23				
SO_4^{2-}	250	200	400	0	1	1	-	8	-
NO_3^{-}	10	45	100	15	19	5	7	8	7
Cl^{-}	250	250	1000	14	8	13	2	8	-

Number of samples in pre monsoon = 18 and post monsoon = 24

4.1.3.3 Hydrogeochemical evaluation

The ion exchange processes play an important role in controlling the concentration of ions in groundwater. The ion exchange chemistry between sub surface waters and the surrounding environment is a major phenomenon that controls distribution and occurrence of the former (Senthilkumar and Elango, 2013). The hydrogeochemical processes of a region is evaluated by employing chloro-alkaline indices (CAI-1 and CAI-2) as proposed by Schoeller (1965) and shown in equations (12) & (13).

$$\mathrm{CAI-1} = \left[\mathrm{Cl^-} - \left(\mathrm{Na^+} + \mathrm{K^+}\right)\right] / \ \mathrm{Cl^-} \qquad \text{---(12)}$$

$$\mathrm{CAI-2} = \left[\mathrm{Cl^-} - \left(\mathrm{Na^+} + \mathrm{K^+}\right)\right] / \ \left[\mathrm{SO_4{}^{2-}} + \mathrm{HCO_3{}^-} + \mathrm{CO_3{}^{2-}} + \mathrm{NO_3{}^-}\right] \qquad \text{---(13)}$$

The CAIs are positive, when Na^+ and K^+ ions present in the groundwater are exchanged with Ca^{2+} and Mg^{2+} ions present in the surrounding rock and the exchange is known as direct. The reaction is also named as base-exchange reaction and the resulting condition is chloro-alkaline equilibrium. Whereas, in reverse process the CAIs are negative and the exchange is called as indirect. The reaction is called as cation-anion exchange reaction and the resulting condition is chloro-alkaline disequilibrium (Aghazadeh and Mogaddam, 2011; Bhardwaj and Singh, 2011).

In post monsoon season, there is an indirect exchange of Na^+ and K^+ ions with the Ca^{2+} and Mg^{2+} as CAIs is negative except in two samples (W10 & W18) may be due to leaching of Na^+ during monsoon season. In pre monsoon, CAI is positive (Fig. 4.18) hence there is a direct exchange between Na^+ and K^+ ions present in the groundwater with the Ca^{2+} and Mg^{2+} and the water is base exchange softened.

Presence of acids (carbonic acid or sulphuric acid) enhances the weathering intensity (Das and Kaur, 2001). The ratio of Ca^{2+}: SO_4^{2-} is almost

1:1 indicating sulphuric acid as a weathering agent. The scatter plot (Ca^{2+} + Mg^{2+}) vs (SO_4^{2-} + HCO_3^-) shows that most of the samples lie below the 1:1 equliline suggesting excess of SO_4^{2-} + HCO_3^- over alkaline earth elements which could be due to dissolution of sulphide minerals during the rainy season (Fig. 4.20). The excess SO_4^{2-} + HCO_3^- are required to be balanced by alkalies (Na^+ + K^+) suggesting the silicate weathering in the region.

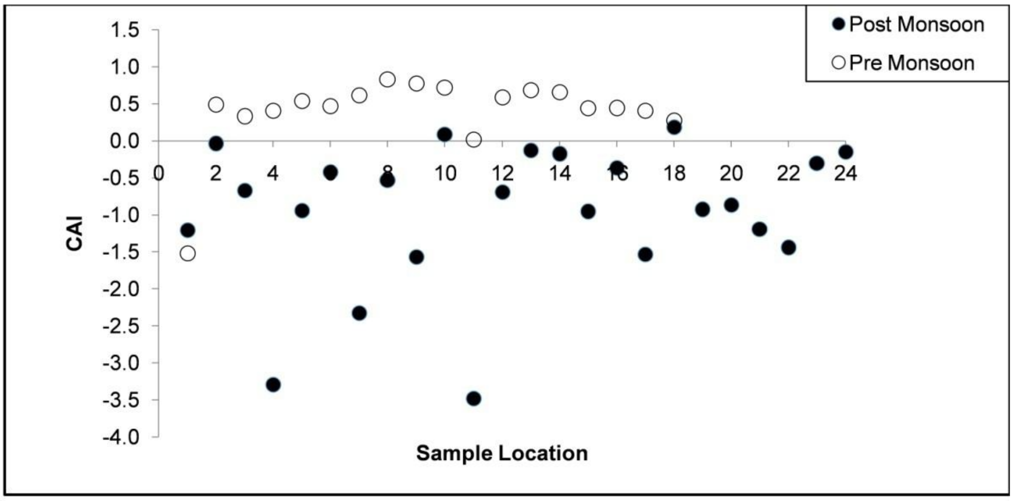


Fig. 4.18 CAI plot for water samples of post and pre monsoon

During pre monsoon, most of the sample points fall above the equiline (1:1) suggesting the presence of excess Ca^{2+} + Mg^{2+} over SO_4^{2-} + HCO_3^-, and the excess Ca^{2+} + Mg^{2+} must be balanced by dominating anion (Cl^-) which suggests the weathering of silicates (chlorite) and influence of anthropogenic activities. In scatter plot, the point falls below the equiline indicates the dominance of ion exchange or weathering process and point fall above the equiline indicate the reverese ion exchange process (Cerling *et al*., 1989; Fisher and Mulican, 1997).

The scatter plot Na^+ + K^+ vs Cl^- shows that the sample points of pre monsoon season lie below the equiline (1:1) confirming the excess of Cl^- over alkalies (Na^+ + K^+) that may have been derived from weathering of silicates (chlorites) and anthropogenic activities (Fig. 4.21). Whereas, most of the sample points of post season fall above the equiline in the scatter plot (Na^+ + K^+) vs Cl^- suggesting excess of alkalies (Na^+ + K^+) which may be due to dilution of chloride ions in rainy season.

The scatter plots Ca^{2+} + Mg^{2+} and Na^+ + K^+ as a function of total cations show that all the sample points fall below the equiline suggesting equal contribution of Ca^{2+} + Mg^{2+} and Na^+ + K^+ ions to total cation concentrations in both the seasons (Fig. 4.19 & 4.22). The presence of excess of Na^+ + K^+ ion in the groundwater suggests the silicate weathering and influence of anthropogenic activities in the region.

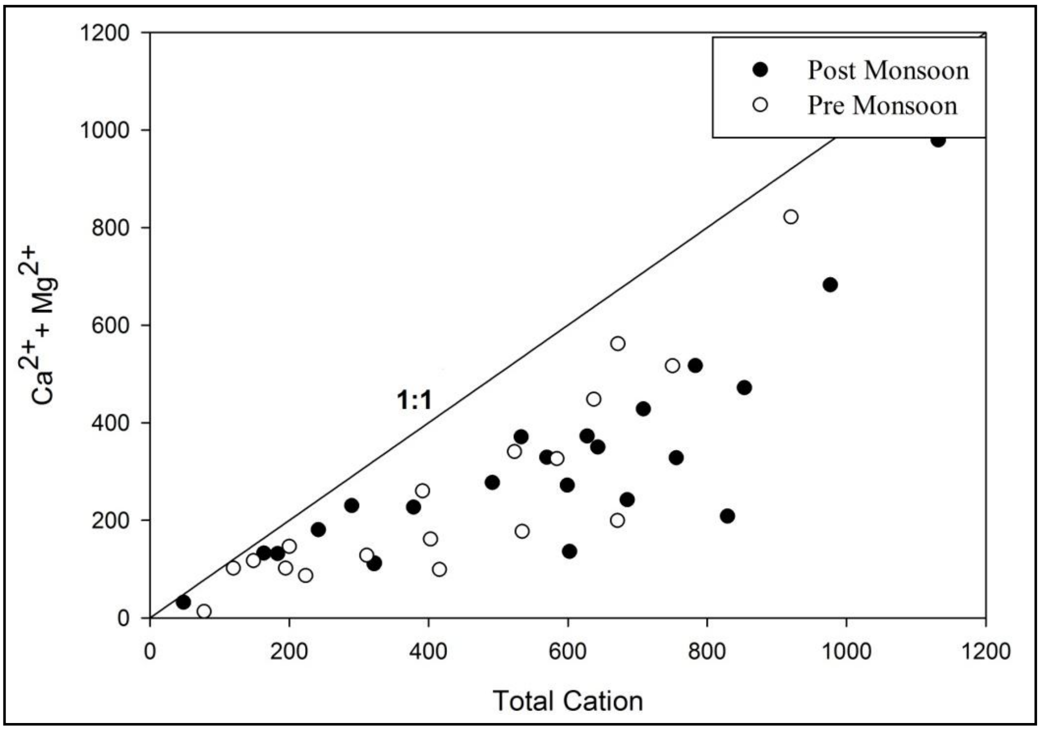


Fig. 4.19 Scatter plot of Ca^{2+} + Mg^{2+} vs total cations for post and pre monsoon water samples

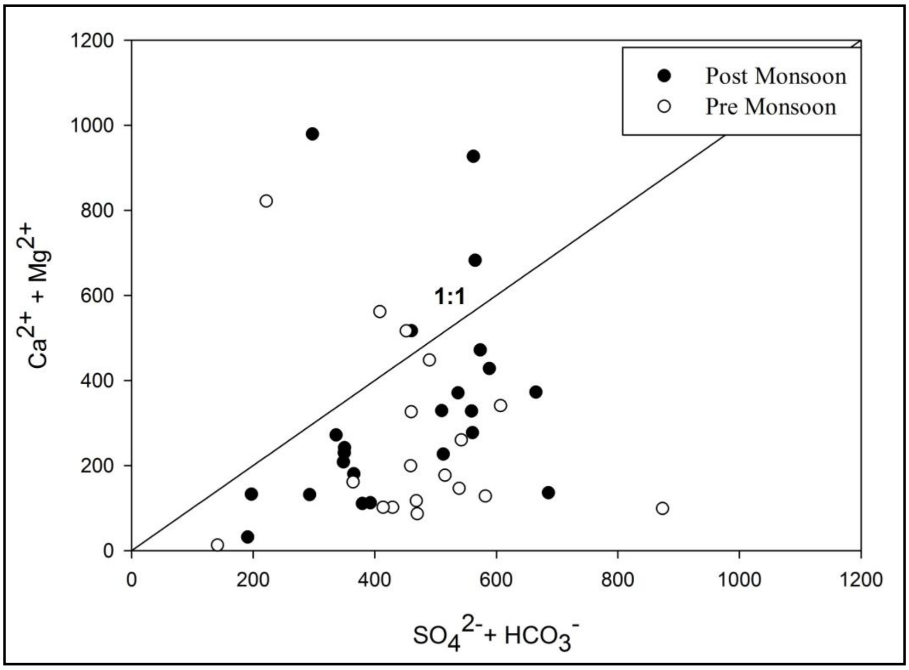


Fig. 4.20 Scatter plot of Ca^{2+} + Mg^{2+} vs SO_4^{2-} + HCO_3^- for post and pre monsoon water samples

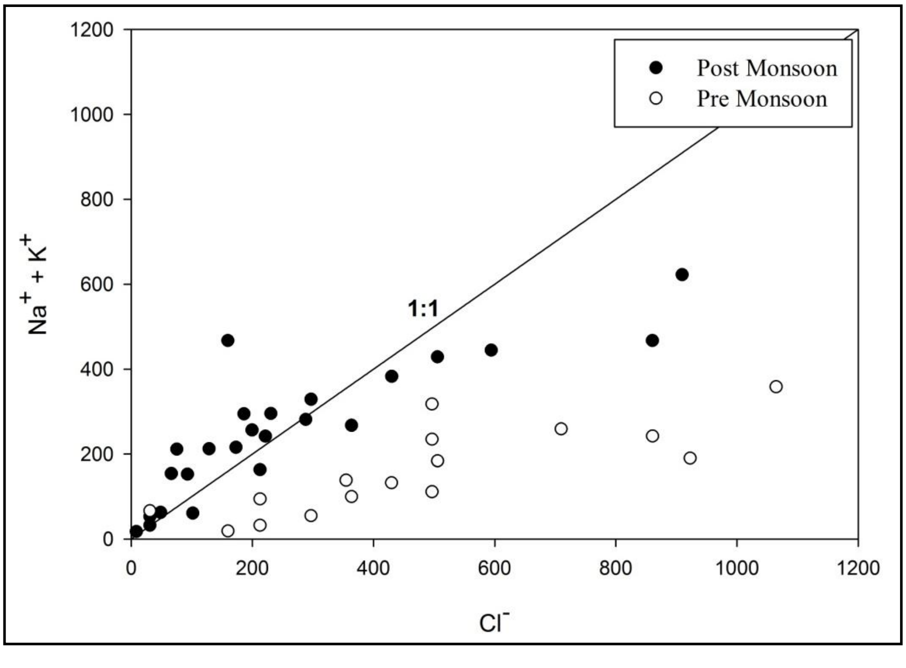


Fig. 4.21 Scatter plot of Na^+ + K^+ vs Cl^- for post and pre monsoon water samples

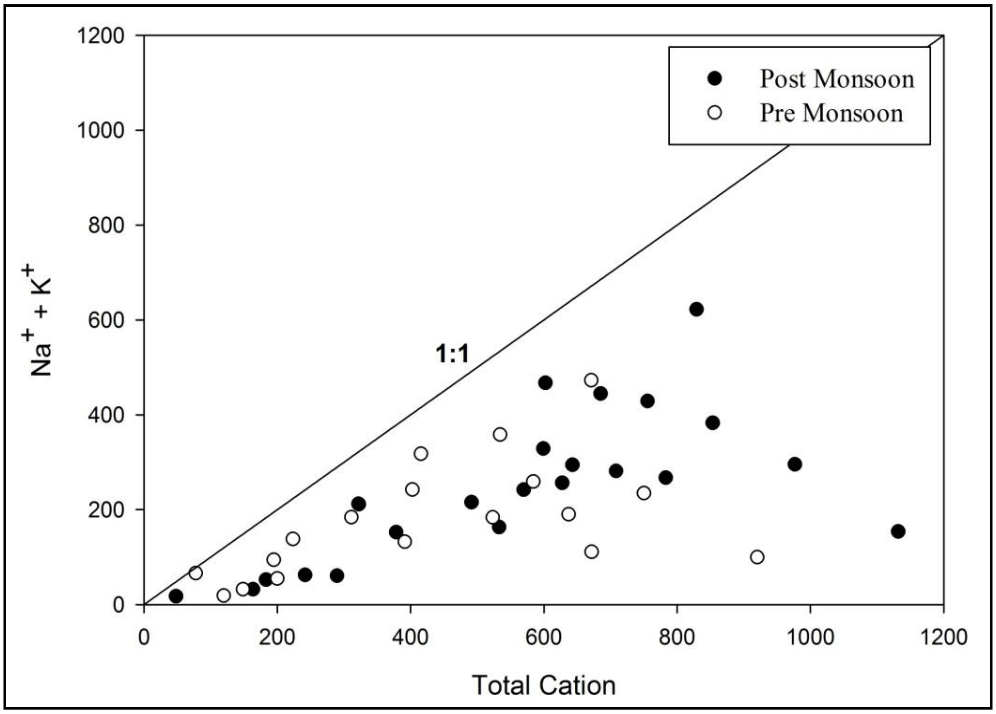


Fig. 4.22 Scatter plot of Na^+ + K^+ vs total cations for post and pre monsoon water samples

Further, the low concentration of HCO_3^- and lower ratio of HCO_3^-/SO_4^{2-} + Cl^- i.e. 0.57 and 0.79 during pre and post monsoon respectively reveals that the major source for ions in the groundwater may be anthropogenic activities rather than rock weathering (Rose, 2002; Singh *et al*., 2013).

4.1.3.4 Gibbs plot

The Gibbs diagram (Gibbs, 1970) is widely used to assess the sources of geochemical constituents in groundwater from the processes of precipitation, evaporation and rock-water interaction (Fig. 4.23 and 4.24). The ratios of $[Na^+/(Na^+ + Ca^{2+})]$ and $[Cl^-/(Cl^- + HCO_3^-)]$ as a function of TDS shows that most of the geochemical data falls in the rock weathering dominance zone for both the seasons.

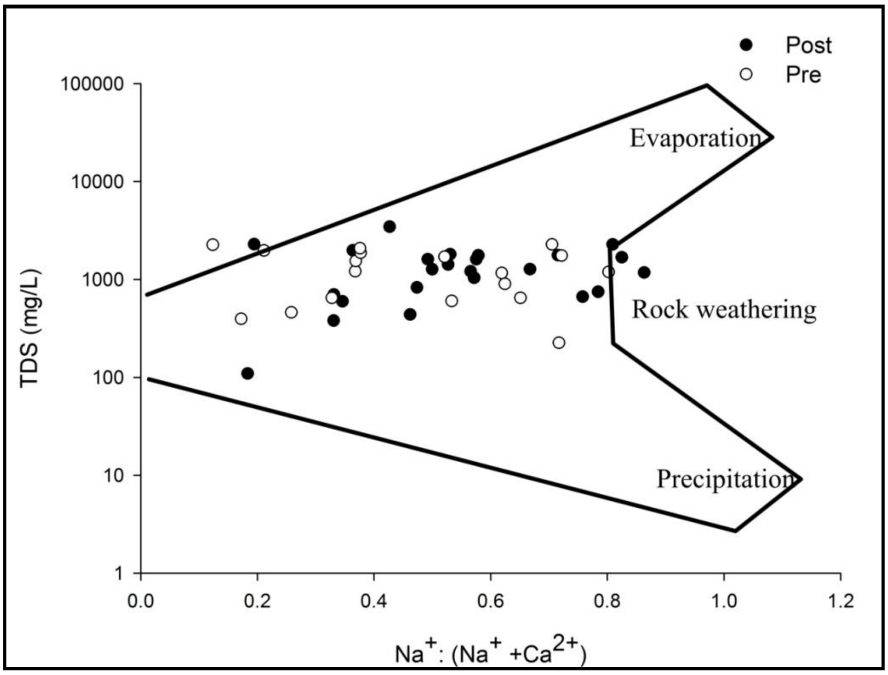


Fig. 4.23 Gibbs plot for TDS versus [$Na^+/(Na^+ + Ca^{2+})$] for post and pre monsoon water samples

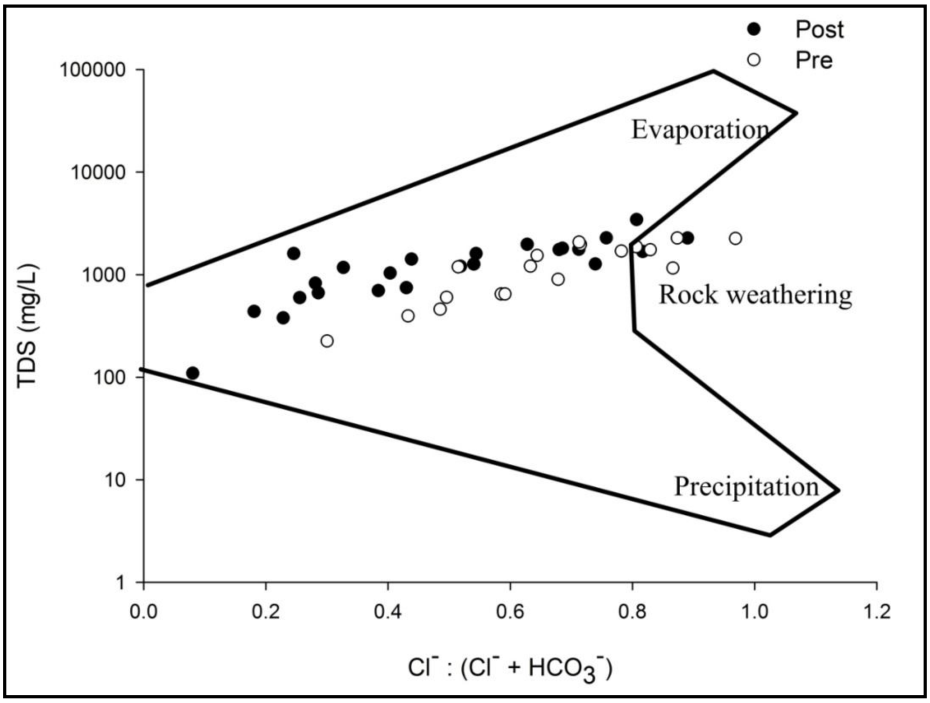


Fig. 4.24 Gibbs plot for TDS versus [$Cl^-/(Cl^- + HCO_3^-)$] post and pre monsoon water samples

4.1.3.5 Hydrogeochemical facies

The Piper diagram (1944) is a widely used trilinear plot to understand the hydrogeochemical evolution of groundwater by plotting measured concentration of major cations and anions (Fig. 4.25 & 4.26). In the anionic triangular, Cl^- ion shows dominance over HCO_3^- ion in pre monsoon, while HCO_3^- shows dominance in post monsoon.

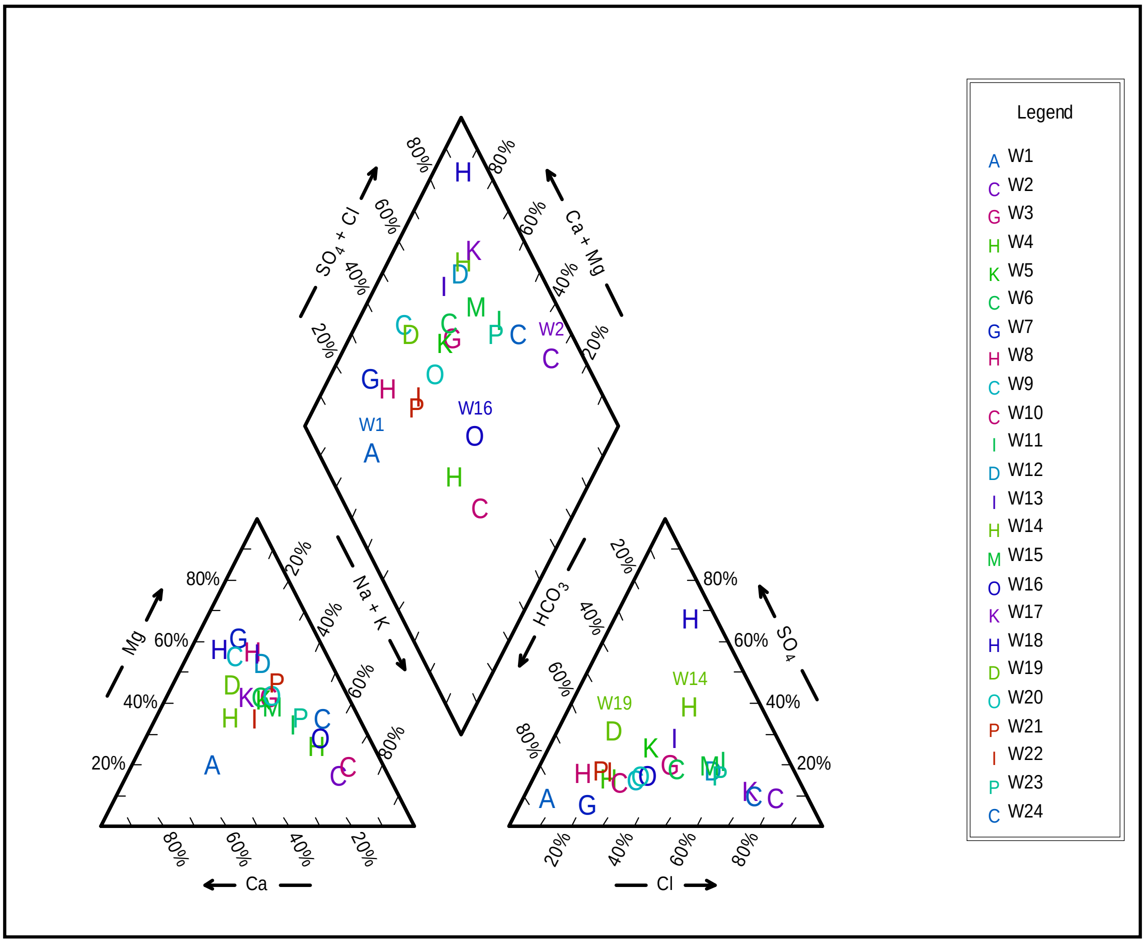


Fig. 4.25 Piper triangular diagram showing the hydrogeochemical facies of water samples from Khetri region for post monsoon season

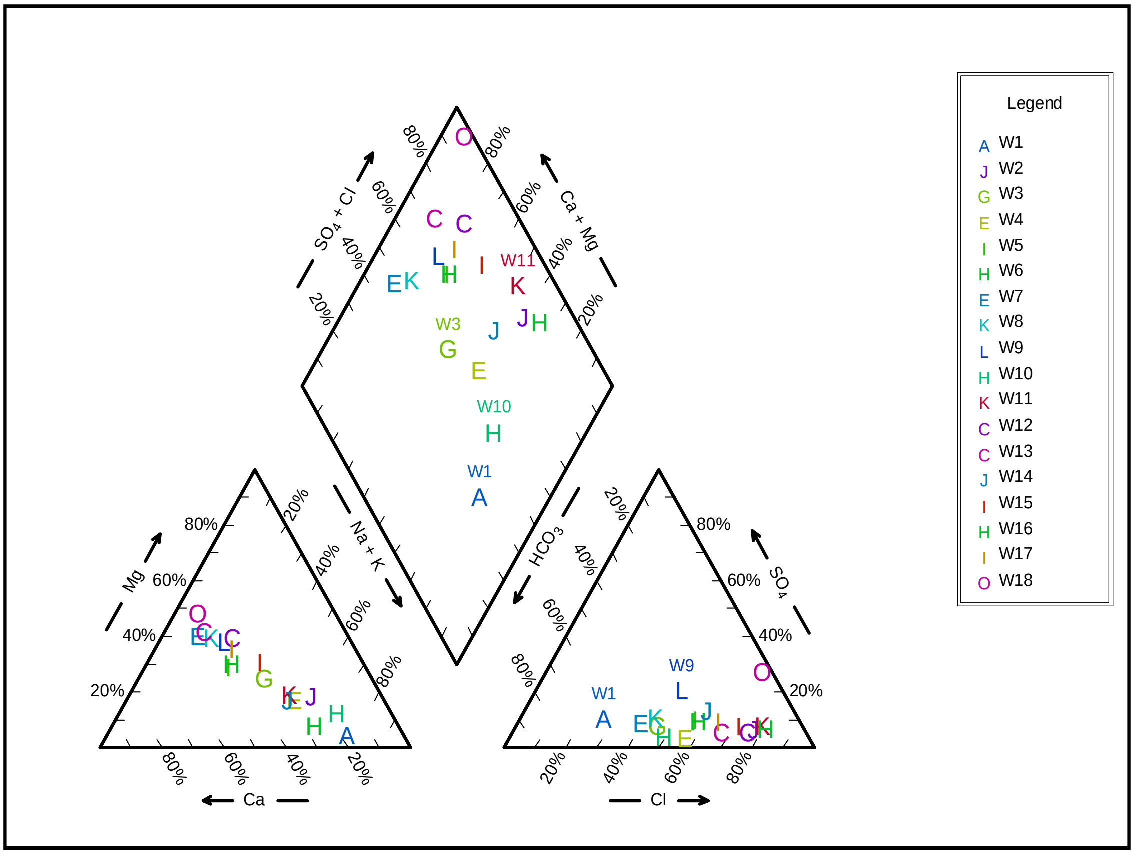


Fig. 4.26 Piper triangular diagram showing the hydrogeochemical facies of water samples from Khetri region for pre monsoon season

In pre monsoon, the hydrogeochemical facies namely NaCl (33%), CaCl (28%) and mixed CaMgCl (28%) dominant the groundwater chemical composition. Whereas, in post monsoon $CaHCO_3$ (29%), CaMgCl (33%) and CaCl (17%) are dominant in groundwater. Hence, the alkaline earths (Ca^{2+} + Mg^{2+}) and strong acid (Cl^{-}) dominate the groundwater chemistry of the region in both the seasons.

The CaMgCl causes permanent hardness in the water and its presence in groundwater (both seasons) of Khetri copper mining region confirms its unsuitability for irrigation purposes. Some samples also shows the dominance of NaCl which creates salinity problem and thus water is not suitable for both drinking and irrigation purposes.

4.1.3.6 Heavy metal concentration

AMD leads to leaching of heavy metals in the groundwater thus the concentration of heavy metals in groundwater were analyzed. The results show that the sites close to mining area (W23), tailings (W13 & W14) and overburden materials (W15 & W22) have high concentration of heavy metals. The further details are discussed here.

Concentration of Cu ranges from 0.17 to 8.19 ppm with an average of 0.66 ppm during pre monsoon and from 0.09 to 9.04 ppm with an average of 0.49 ppm during post monsoon (Table 4.12 & 4.13). At Bhargada Dhani (W13) which is near the tailings have high concentration of Cu i.e. 0.38 and 0.19 ppm during pre and post monsoon may be due to leaching of Cu from tailings dam.

The Fe concentration at Kanjayion Dhani (W15) near the overburden materials is 10.40 and 6.53 ppm and Zn is 2.29 and 3.29 ppm during pre and post monsoon respectively. The Fe ores namely pyrite and pyrrhotite are also present in association with chalcopyrite at Khetri copper belt and are probable source of Fe at W15. It is observed that, the concentration of Fe and Zn in groundwater neighboring the overburden materials are much higher compared to Cu. The Cu has low mobility as it can be easily absorbed by the carbonates, phylosilicates and organic matter (Kabata-Pendias and Pendias, 2001).

The average concentration Ni during pre and post monsoon is 0.19 and 0.17 ppm respectively. According to GSI, 1977 nickeliferous pyrrhotite along with Cu ore is present at Khetri Copper belt. Hence high concentration of Ni in water is attributed to mining activities. The Ni has high leaching capacity through the soil compared to Cu (Toribio and Romanyà, 2006).

Heavy metals in Chaandmari mine water

The Chaandmari mine water (W18) has high concentration of Cu (pre monsoon = 8.19 & post monsoon = 9.04 ppm) and Mn (pre monsoon = 7.38 & post monsoon = 6.74 ppm) and shown in Fig. 4.27. The high concentration of

Cu is due to leaching because of oxidation of exposed sulphides. Concentration of Fe (0.28 and 0.26 ppm during pre and post monsoon respectively) is low compared to Cu and Mn may be due to presence of sulphides which generate reducing conditions. In the acid mine drainage, iron is present as ferric ion and Fe^{3+} ions get precipitated at pH 3-4. Hence the present iron gets precipitated in acidic conditions (Balintova and Petrilakova, 2011).

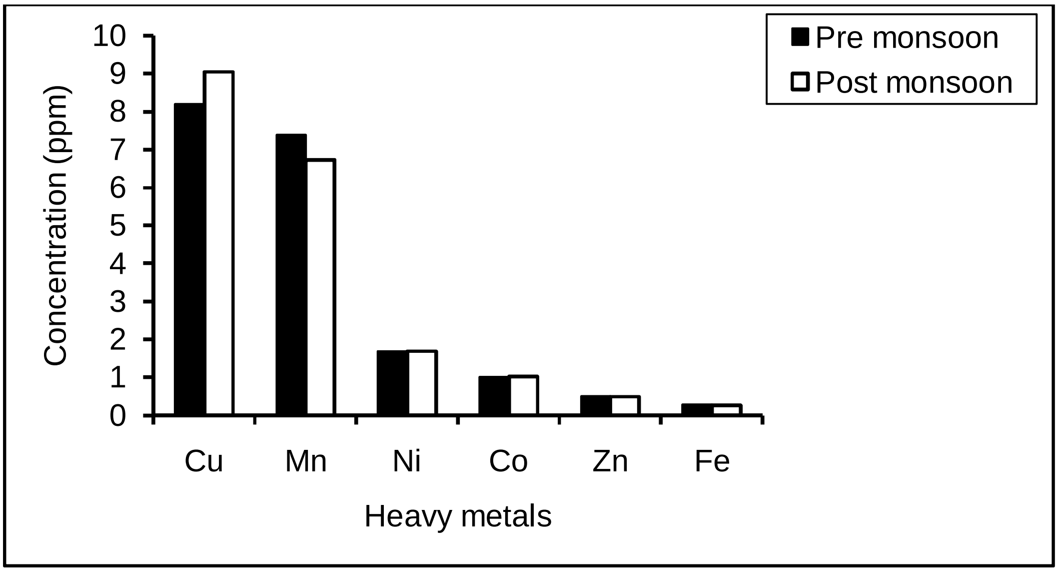


Fig. 4.27 Concentration of heavy metals in water (W18) from Chaandmari

Comparison of heavy metal concentration with permissible limits

The measured concentrations of each element (Cu, Zn, Fe, Co, Ni, Mn and Pb) are compared to those set by the Bureau of Indian Standards (BIS) 2012 and WHO (2011) water quality standards (Table 4.14) which revealed that heavy metal concentration in majority of the water samples exceeds the permissible limits.

Table 4.12 Details of sample locations along with concentration (in ppm) of heavy metals for pre monsoon

Sample Code	Sample Location	Cu	Zn	Fe	Co	Ni	Mn	Pb
W1	Kakarai Pond	0.17	0.06	0.42	0.08	0.09	0.21	0.04
W2	Kakarai School	0.18	2.49	0.16	0.03	0.11	0.11	0.05
W3	Maliyun Dhani	0.19	0.37	0.63	0.10	0.10	0.09	0.00
W4	Ahiro Dhani	0.17	1.12	1.22	0.06	0.09	0.12	0.00
W5	Rajota	0.19	0.15	1.37	0.08	0.11	0.12	0.00
W6	Khetri	0.19	0.31	1.95	0.07	0.11	0.16	0.03
W7	Teelawali	0.23	2.92	1.05	0.09	0.08	0.14	0.07
W8	Meghawali Dhani	0.22	0.46	1.35	0.07	0.09	0.11	0.02
W9	Khakara Devran	0.23	0.11	0.32	0.13	0.10	0.09	0.00
W10	Kharkara Rajputan	0.23	1.62	0.50	0.06	0.08	0.13	0.01
W11	River bed	0.21	2.31	0.19	0.03	0.10	0.11	0.01
W12	Khetri Nagar	0.21	0.89	1.15	0.09	0.07	0.12	0.01
W13	Bhargda Dhani	0.38	7.14	2.65	0.04	0.08	0.16	0.03

W14	Near tailing	0.20	1.76	2.29	0.08	0.12	0.21	0.05
W15	Kanjaniyun Dhani	0.24	0.77	10.40	0.10	0.11	0.23	0.00
W16	Gujarwas	0.21	0.34	0.34	0.39	0.07	0.53	0.01
W17	Singhana	0.22	1.31	2.25	0.07	0.12	0.13	0.01
W18	Chaandbari	8.19	0.51	0.28	1.00	1.70	7.38	0.00
	Minimum	0.17	0.06	0.16	0.03	0.07	0.09	0.00
	Maximum	8.19	7.14	10.40	1.00	1.70	7.38	0.07
	Average	0.66	1.37	1.58	0.14	0.19	0.56	0.02
	Median	0.21	0.83	1.10	0.08	0.10	0.13	0.01
	STDEV	1.88	1.68	2.34	0.23	0.38	1.71	0.02

Table 4.13 Details of sample locations along with the concentration (in ppm) of heavy metals for post monsoon

Sample Code	**Sample Location**	**Cu**	**Zn**	**Fe**	**Co**	**Ni**	**Mn**	**Pb**
W1	Kakarai pond	0.09	0.04	0.39	0.08	0.10	0.30	0.04
W2	Kakarai school	0.09	1.81	0.33	0.08	0.09	0.14	0.03
W3	Maliyun Dhani	0.11	1.16	1.78	0.09	0.11	0.16	0.00
W4	Ahiro Dhani	0.10	0.40	9.42	0.09	0.13	0.24	0.00
W5	Rajota	0.13	0.37	2.13	0.06	0.05	0.23	0.00
W6	Khetri	0.11	0.22	0.61	0.09	0.13	0.14	0.00
W7	Teelawali	0.11	1.66	2.16	0.09	0.11	0.25	0.00
W8	Meghawali Dhani	0.12	0.32	4.43	0.06	0.09	0.23	0.00
W9	Khakara Devran	0.13	0.62	0.43	0.08	0.10	0.22	0.00
W10	Kharkara Rajputan	0.13	1.36	0.59	0.08	0.10	0.23	0.00
W11	River bed	0.14	3.15	0.37	0.08	0.10	0.23	0.00
W12	Khetri Nagar	0.15	1.11	2.41	0.09	0.12	0.24	0.00
W13	Bhargda Dhani	0.19	6.69	1.04	0.05	0.09	0.24	0.00
W14	Near tailing	0.17	8.51	3.29	0.11	0.09	0.32	0.00

W15	Kanjaniyun Dhani	0.15	0.46	6.53	0.10	0.12	0.29	0.00
W16	Gujarwas	0.16	0.72	0.27	0.06	0.09	0.19	0.00
W17	Singhana	0.17	4.21	1.62	0.10	0.08	0.30	0.00
W18	Chaandbari	9.04	0.49	0.26	1.01	1.69	6.74	0.00
W19	Bhand bhatiar	0.11	0.41	0.18	0.06	0.10	0.18	0.00
W20	Badheswar	0.14	0.14	0.19	0.10	0.09	0.26	0.00
W21	Bawadi Dhani	0.12	0.05	0.29	0.09	0.10	0.70	0.00
W22	Banwas	0.14	6.12	1.20	0.06	0.11	0.29	0.00
W23	Guest house	0.20	0.67	4.07	0.08	0.11	0.34	0.00
W24	Bass Govind Singh	0.16	0.03	0.21	0.09	0.11	0.23	0.00
W25	Pilani	0.16	0.06	0.17	0.06	0.09	0.17	0.00
	Minimum	0.09	0.03	0.17	0.05	0.05	0.14	0.00
	Maximum	9.04	8.51	9.42	1.01	1.69	6.74	0.04
	Average	0.49	1.63	1.78	0.12	0.17	0.51	0.00
	Median	0.14	0.62	0.61	0.08	0.10	0.24	0.00
	STDEV	1.78	2.32	2.28	0.19	0.32	1.30	0.01

6 and 4% of samples during pre and post monsoon respectively exceeds the Cu, Ni and Co permissible limits prescribed by the BIS (2012) for drinking water. An overload of Cu in the liver, brain and other tissues leads to Wilson disease which is a rare autosomal recessive inherited disorder (Bull *et al*., 1993). High concentration of Co in humans can leads to excessive erythrocytosis and further results in chronic mountain sickness (Jefferson *et al*., 2002). In addition to this, excessive inhalation of Co in association with metal carbides can result in hard metal disease or cobalt lung (Lison *et al*., 1996). Fe exceeds the BIS desirable limit which is also a permissible limit for Fe, in 89 and 85 % of samples during pre and post monsoon respectively. The overload of Fe in humans body can leads to colorectal cancer and liver cancer (Huang, 2003).

Mn exceeds the permissible limits in 11 and 31 % of samples during pre and post monsoon while for Pb it exceeds in 56 and 8 % of samples during pre and post monsoon. High concentration of Pb can leads to inhibition of haemoglobin synthesis and problems related to kidney, reproductive systems, cardiovascular system, central nervous system and peripheral nervous system (Ogwuebgu and Muhanga, 2005).

Seasonal variation in heavy metal concentration

Cu concentration is relatively higher in pre monsoon samples compared to post monsoon samples at all the sampling locations which may be due to dilution effect during monsoon season (Fig. 4.28). Fe, Ni and Mn concentration increases during the post monsoon compared to pre monsoon may be due to leaching of sulphides and mineral dissolution (Fig. 4.29, 4.30 & 4.31). Fe dissolves in Fe^{2+} state below pH 8 in anaerobic condition (Xinchao *et al*., 2005). Similar to Fe, Mn concentration is also high due to its high sensitivity to pH and redox potential, and started dissolving below pH 5.5 (Balintova and Petrilakova, 2011).

Table 4.14 Comparison of heavy metal concentration from Khetri copper mine region with that of BIS 2012 and WHO 2011 water quality standards

Parameters	**WHO limit (2011)**	**BIS Desirable Limit**	**BIS Permissible Limit**	**% of samples exceeding the limit**			
				Pre-Monsoon(n=18)		**Post-Monsoon (n=25)**	
				Desirable	**Permissible**	**Desirable**	**Permissible**
Cu	2	0.05	1.5	94	6	96	4
Zn	3	5	15	6	-	15	-
Fe	-	0.3	No relaxation	89	-	85	-
Co	-	0.03	0.2	94	6	96	4
Ni	0.07	0.02	No relaxation	94	6	96	4
Mn	0.4	0.1	0.3	89	11	69	31
Pb	0.01	0.01	No relaxation	-	56	-	8

The sampling sites close to mines (W23), tailings (W14) and overburden materials (W15) have high concentration of Fe comparative to those at distant locations indicating the high mobility of Fe as it is more susceptible to environmental conditions. The mining has been going on in the hilly region of region and overburden materials along tailings in the nearby areas. The sampling sites (W9, W10, W19, W20 & W21) located in the western direction have low Fe concentration compared to eastern and northern direction as the groundwater flow is from hills (stretching southwest-northeast) to towards northern and eastern parts. Pb is detected in few samples (W1, W2, W6, W7, W13 & W14) and is more in pre monsoon compared to post monsoon samples may be due to dilution effect (Fig. 4.32).

Variation in the heavy metal concentration in AF (acidification before filtration) and FA (acidification after filtration) samples

The samples were preserved by two methods *first* acidification followed by filtration (AF) and *second* filtration followed by acidification (FA) methods. The analyzed heavy metal concentrations for both AF and FA during post and pre monsoon season are discussed here (Fig. 4.33 & 4.34). The difference in concentration of AF and FA indicates the dissolution of solids (precipitates or nodules) during the acidification followed by filtration in AF compared to FA (filtration followed by acidification). While in FA solids gots removed during filtration.

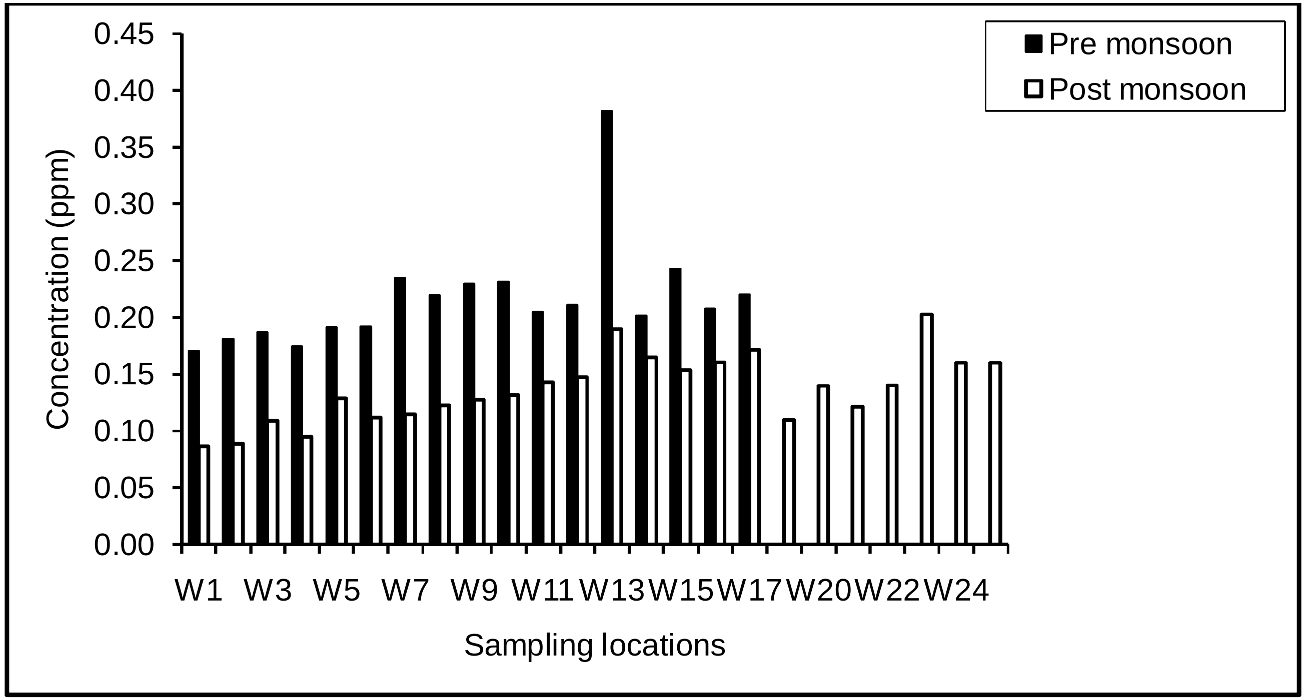


Fig. 4.28 Bar diagram showing the seasonal (pre and post monsoon) variation in Cu concentration in water samples at each location

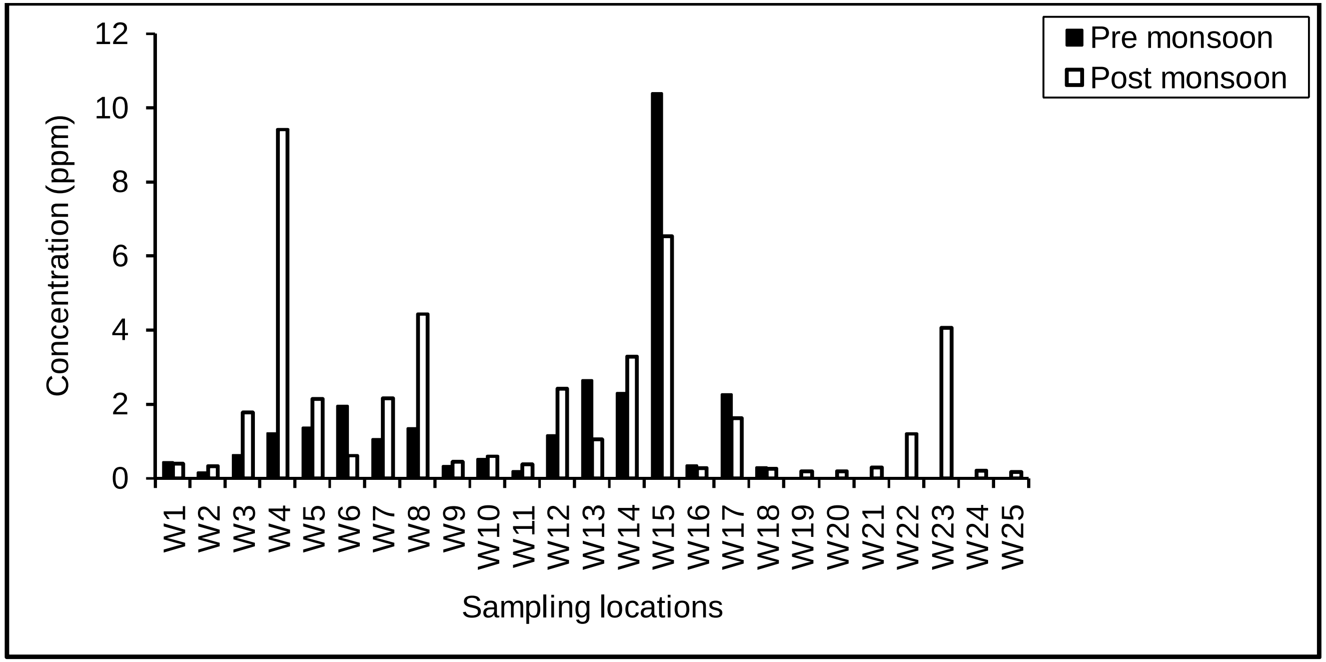


Fig. 4.29 Bar diagram showing the seasonal (pre and post monsoon) variation in Fe concentration in water samples at each location

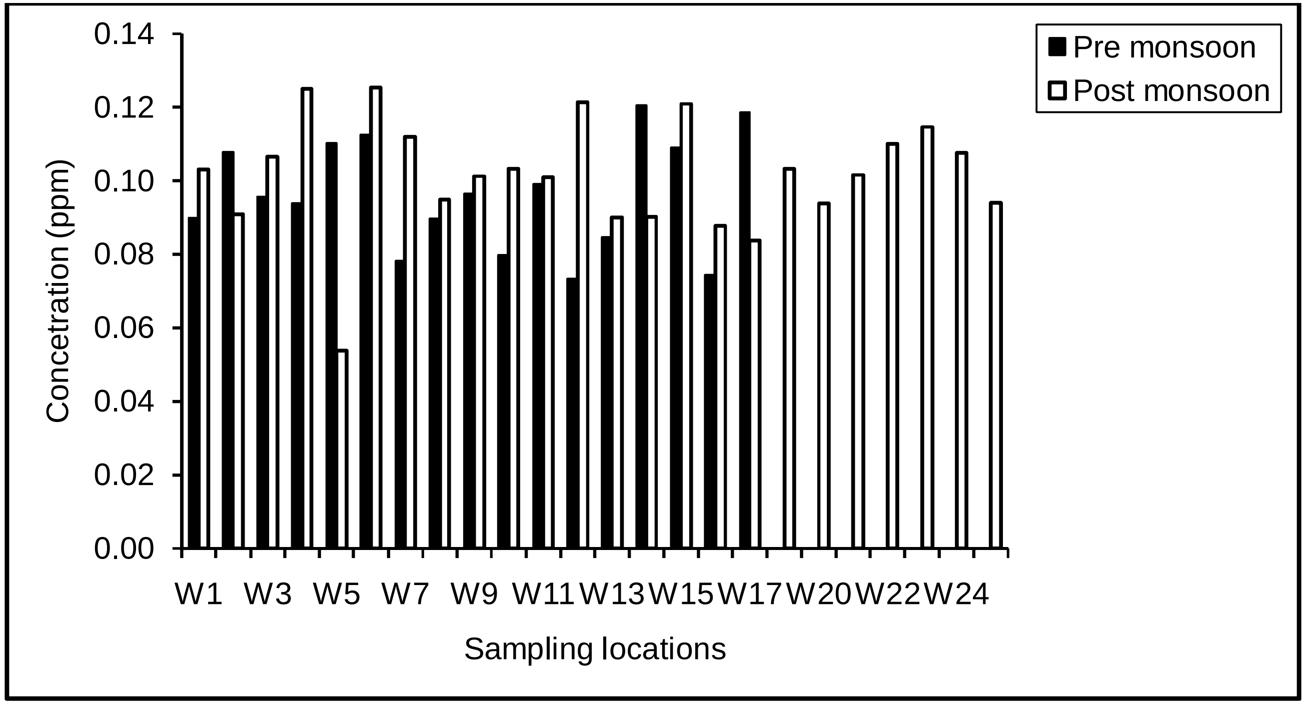


Fig. 4.30 Bar diagram showing the seasonal (pre and post monsoon) variation in Ni concentration in water samples at each location

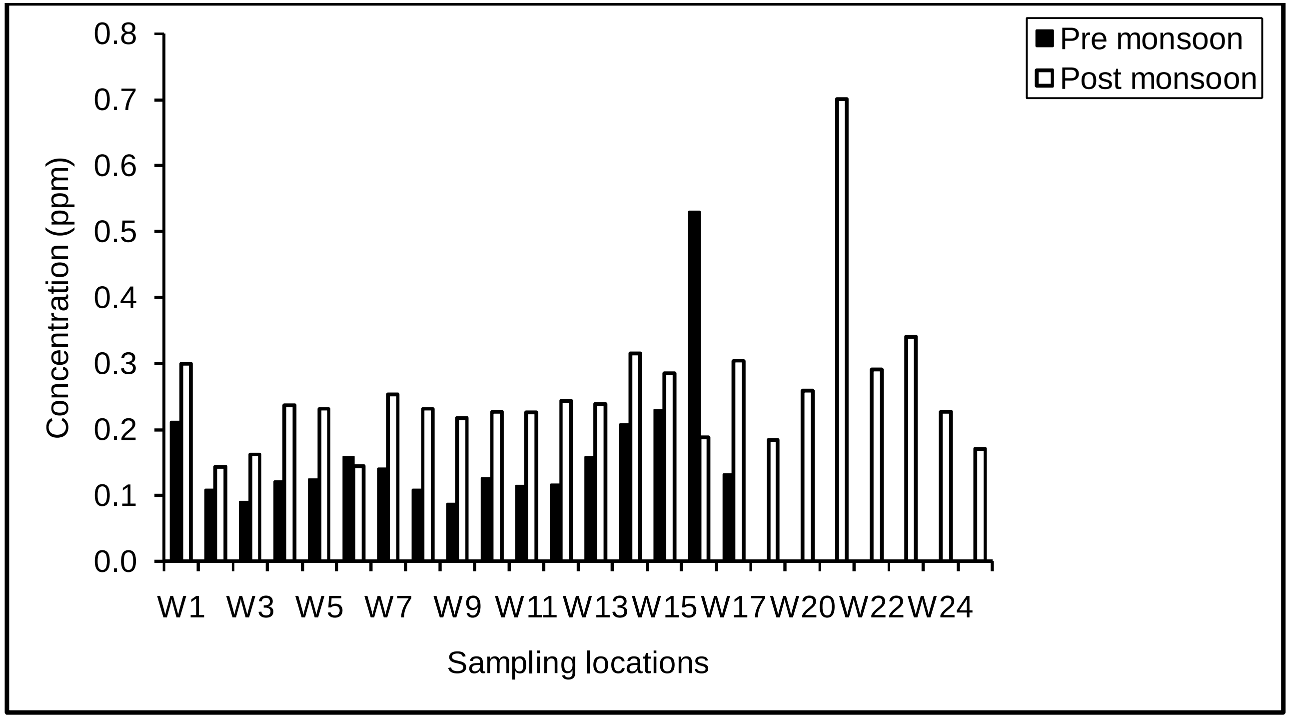


Fig. 4.31 Bar diagram showing the seasonal (pre and post monsoon) variation in Mn concentration in water samples at each location

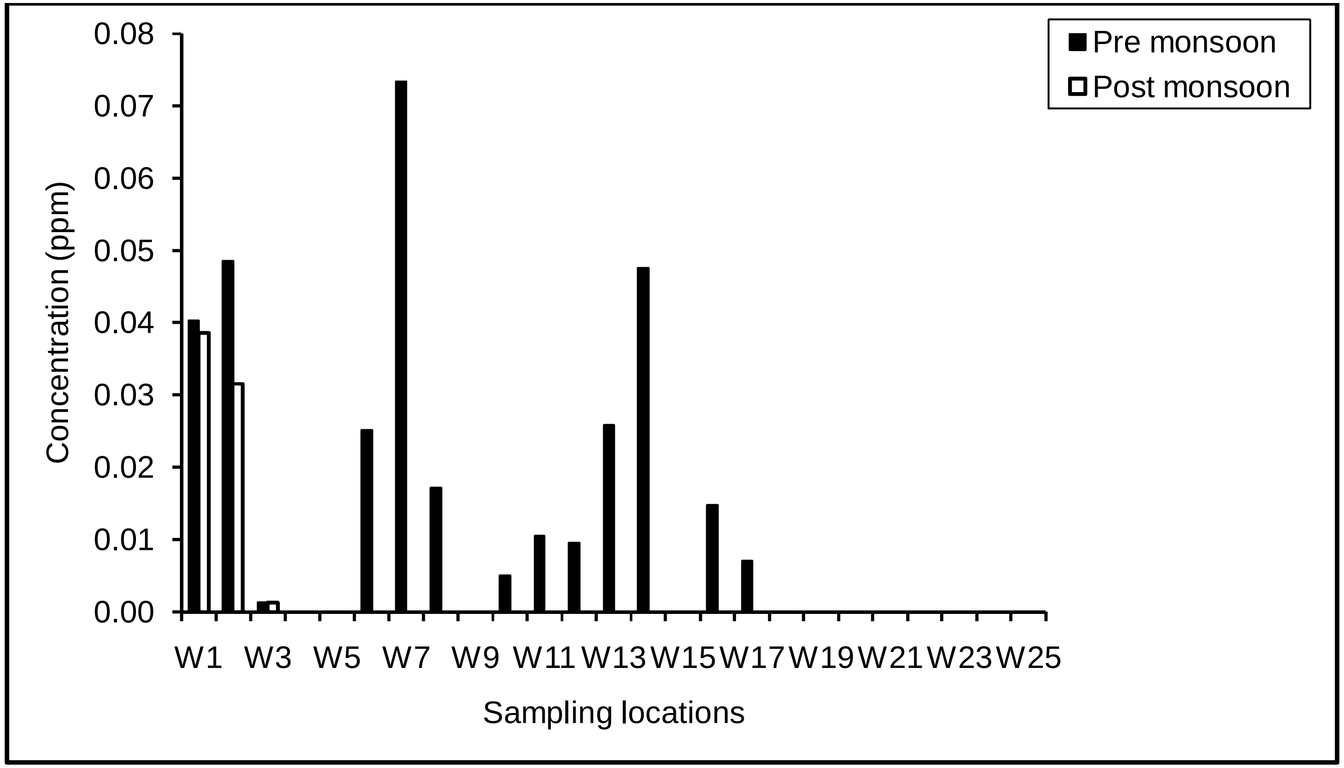


Fig. 4.32 Bar diagram showing the seasonal (pre and post monsoon) variation in Pb concentration in water samples at each location

It is observed that Fe and Zn show the variation in the concentration of AF and FA samples in both seasons. Mn, Cu, Co, Ni and Pb do not show variation in concentration of AF and FA.

Fe is the most redox sensitive element and form nodules in the groundwater with the changing environmental conditions (Thomson *et al*., 1993). Fe nodules have high heavy metal sequestration capacity (Goldberg, 1954; Filipek *et al*., 1982). On acidification, the Fe nodules gets dissolve which result in release of Fe. It is also observed that with increase in Fe concentration, the concentration of Zn also increases in AF (acidification followed by filtration). It suggests that Fe-nodules has scavenges the present Zn from water. While in FA, filtration separates the Fe nodules from water during filtration which results in low concentration of Fe.

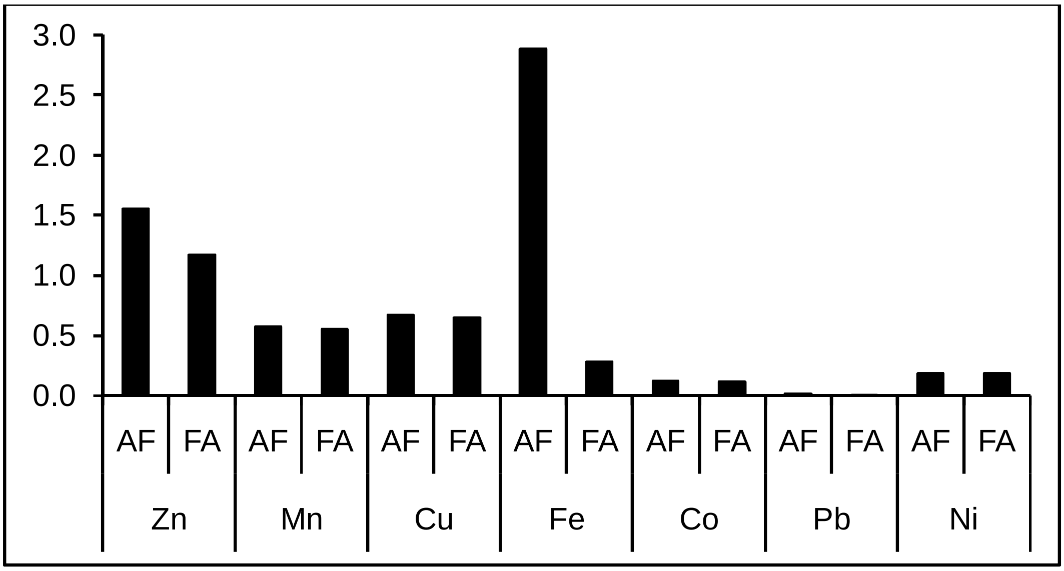


Fig. 4.33 Bar diagram showing the heavy metal concentration in water (AF and FA) samples during pre monsoon

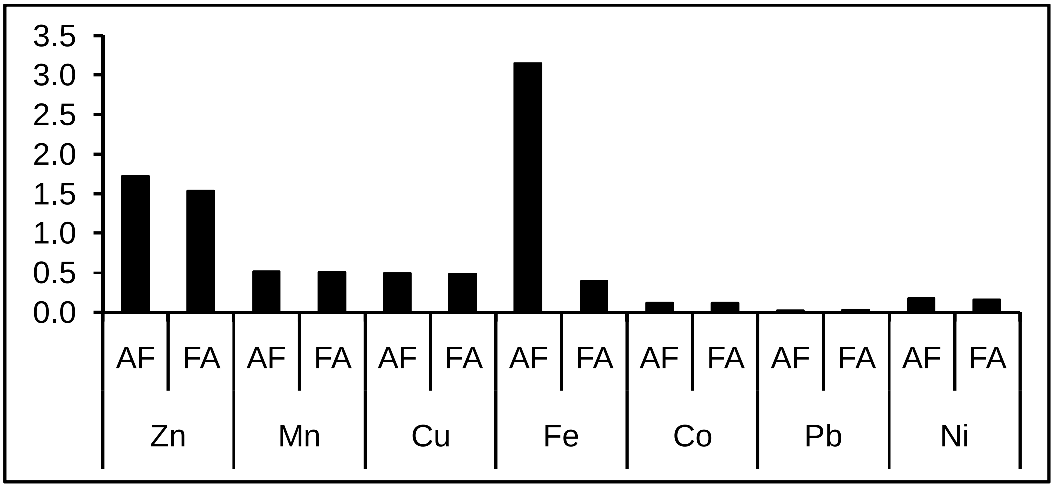


Fig. 4.34 Bar diagram showing the heavy metal concentration in water (AF and FA) samples during post monsoon

Concentration of heavy metals determined in the water (slurry) flowing over the tailings is shown in the Fig. 4.35. Concentration of Fe, Zn and Ni are found more in the AF compared FA. Hence, acidification increases the availability of heavy metals in the sludge water flowing over tailings. Concentration of Mn is comparatively higher than other analyzed heavy metals may be due to its high sensitivity to pH and redox potential.

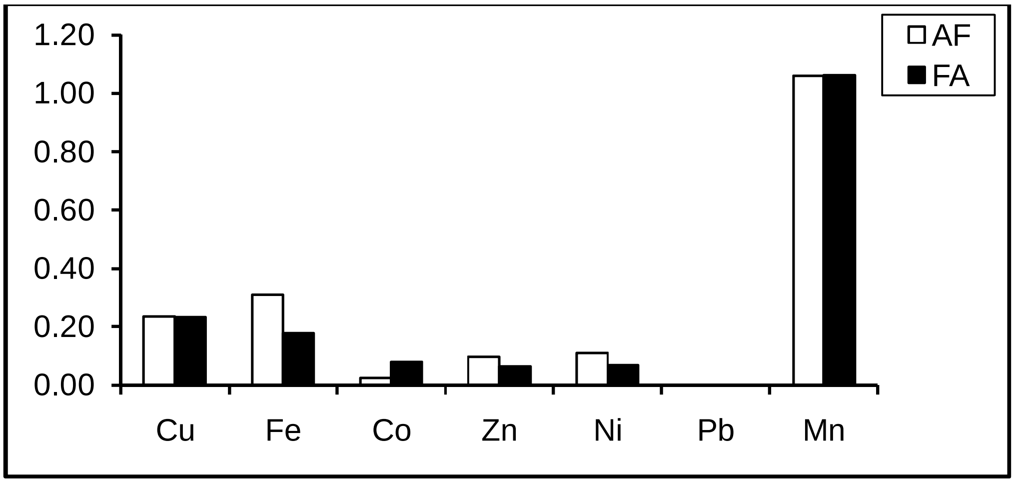


Fig. 4.35 Bar diagram showing heavy metal abundances in the sludge water flowing over the tailings

4.1.3.7 Ficklin diagram

A Ficklin diagram (Ficklin *et al*., 1992; Caboi *et al*., 1999) is used to classify the studied water samples on the basis of total metal concentration and pH (Fig. 4.36). It has been found that most of the samples lay in near neutral and high metal region except two reference samples (W24 & W25) those lies in neutral and low metal region. The sample from Chaandmari mine (W18) lies in acidic and high metal concentration region.

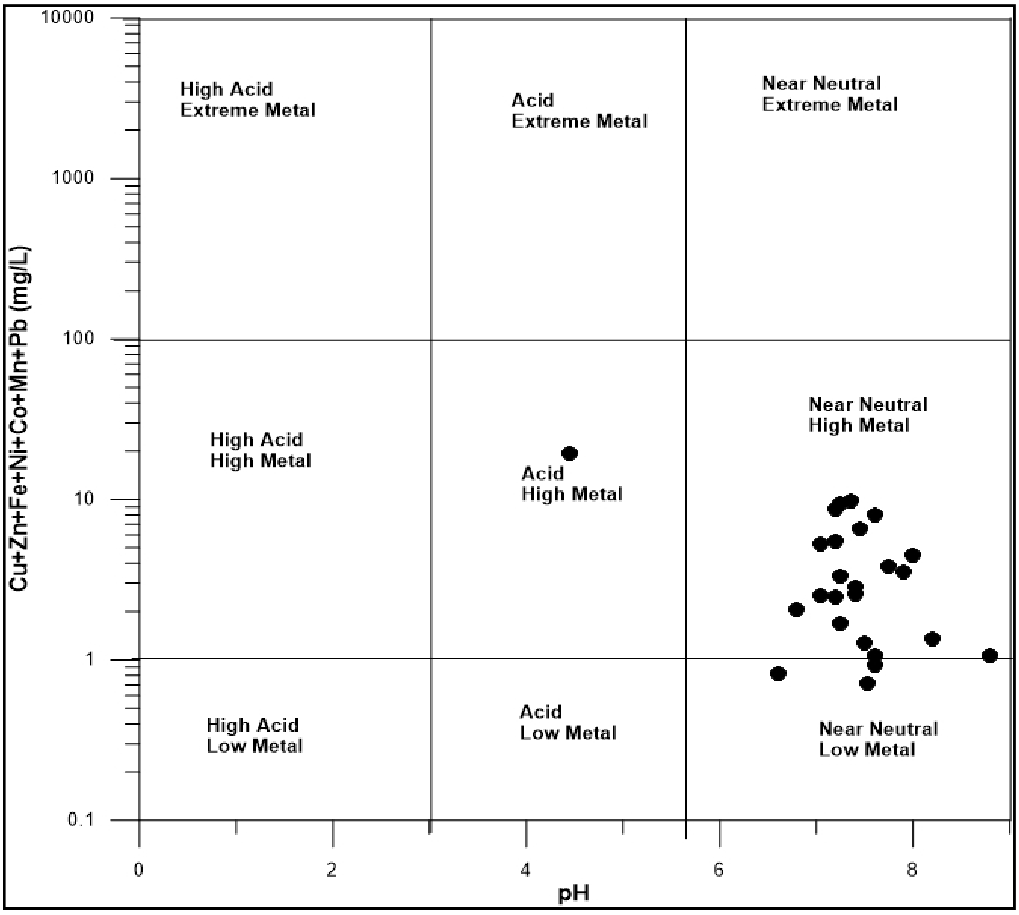


Fig. 4.36 Classification of water samples on the basis of total metal concentration vs. pH

4.1.4 Vegetables

A total of eight varieties of vegetables (Guar, Spinach, Pepper, Ridged gourd, Brinjal, Bottle gourd, Daikon and Lady's finger) were collected from gardens neighbouring the mine, tailings and overburden materials, and were analysed for seven heavy metals (Cu, Zn, Ni, Mn, Fe, Pb and Cd) to understand their distribution and variation in the vegetables. The results are discussed in the following sections.

4.1.4.1 Distribution of heavy metals in vegetables

Cu concentration varies from 53 to 131 ppm with an average of 72±25 ppm. Maximum Cu concentration is found in guar (131 ppm) followed by spinach (84 ppm) and ridged gourd (73 ppm) while lowest (53 ppm) is found in lady's finger (Fig. 4.37). Guar is a legume and legumes are used for phytoremediation (accumulator) of heavy metals (Taylor *et al.*, 1991; Piechalak *et al.*, 2002; Wong, 2003). Fe concentration varies from 47 to 373 ppm with an average of 143±118 ppm. The maximum concentration of Fe is found in guar (372 mg/kg), spinach (307 ppm) and brinjal (119 ppm) and the least is in lady's finger (46 ppm).

Zn concentration in vegetables varies from 26 to 81 ppm with an average of 43±21 ppm. The order of abundance of individual heavy metals in vegetables is Fe > Cu > Zn > Mn > Ni > Pb > Cd (Punia and SIddaiah, 2017). The detailed description of the heavy metal concentrations in the vegetables of Khetri region are given in the Table 4.15.

Table 4.15 Heavy metal concentration (in ppm) in the vegetables

Vegetables	Cu	Fe	Zn	Mn	Pb	Co	Ni	Cd	Cr
Brinjal	65.2	119.8	32.5	17.2	0.11	0.09	0.15	0.01	1.17
Bottle gourd	62.2	93.8	26.8	17.1	1.08	0.00	0.00	0.00	3.05

Lady’s finger	53.4	46.9	33.4	28.6	0.00	0.00	0.00	0.00	0.00
Ridged gourd	72.7	115.7	47.9	15.9	0.00	0.10	0.50	0.00	0.00
Daikon	53.5	74.1	25.5	19.7	0.00	0.00	6.03	0.10	0.00
Pepper	72.7	109.4	80.8	13.9	0.00	0.17	0.23	0.01	0.00
Spinach	83.6	307.2	70.6	43.9	0.00	0.00	0.58	0.00	0.00
Guar	130.8	372.9	47.0	28.3	0.00	0.00	1.91	0.00	2.26
Minimum	53.4	46.9	25.5	13.9	0.00	0.00	0.00	0.00	0.00
Maximum	130.8	372.9	80.8	43.9	1.08	0.17	6.03	0.10	3.05
Average	74.3	154.9	45.6	23.1	0.17	0.05	1.18	0.02	0.81
Median	68.9	112.5	40.2	18.4	0.00	0.00	0.37	0.00	0.00
STDEV	25.0	118.0	20.5	10.1	0.40	0.07	2.06	0.03	1.23

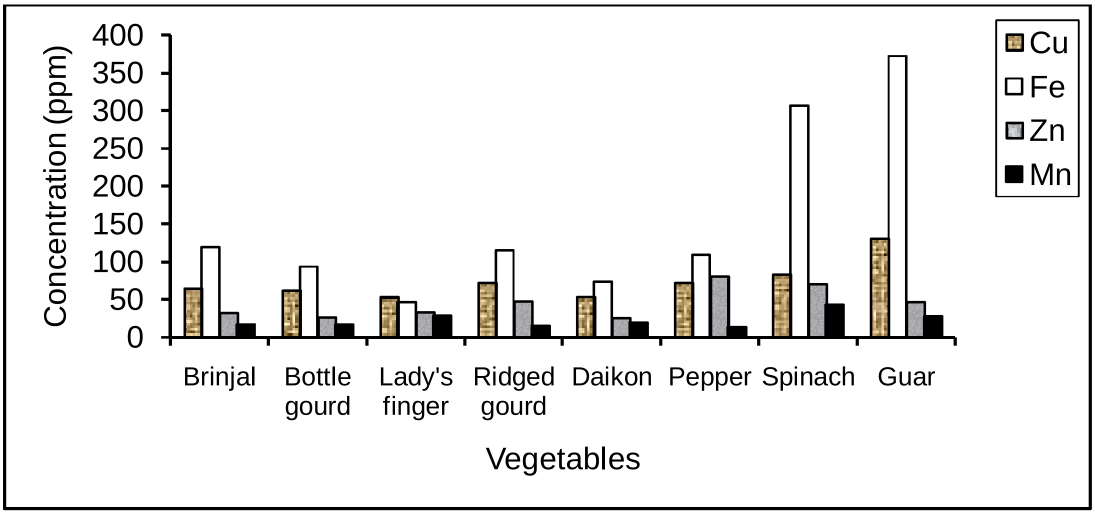


Fig. 4.37 Bar diagram showing the average heavy metal concentration (Cu, Fe, Zn and Mn) in vegetables

Different vegetables have varying heavy metal accumulation capacity. The rank order of vegetables according to their decreasing heavy metal abundances is guar > spinach > pepper > ridged gourd > brinjal > bottle gourd

> daikon > lady’s finger (Fig. 4.38). While Tewari and Pande, 2013 found the lady’s finger as best accumulator for Cu, Ni and Pb.

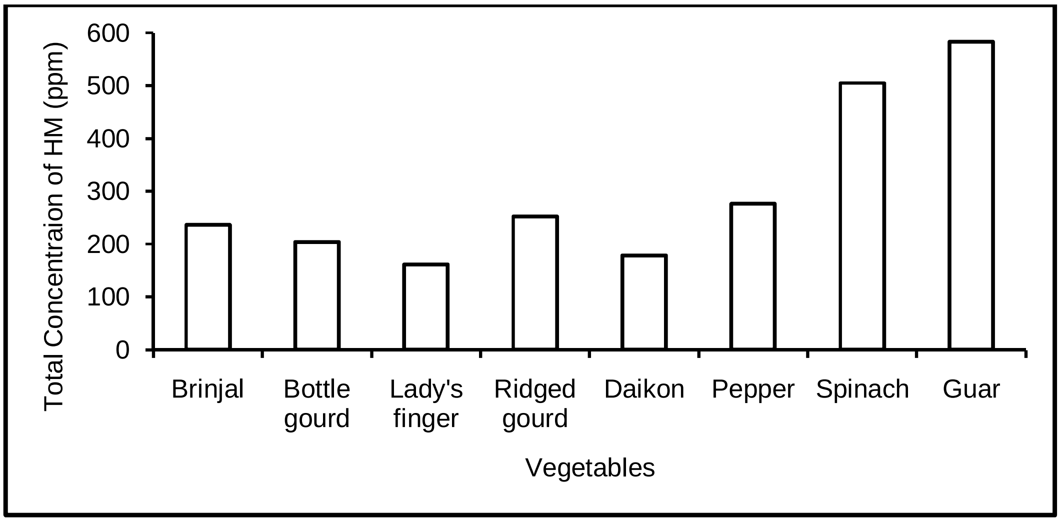


Fig 4.38 Bar diagram showing total heavy metal (Fe, Cu, Zn, Mn, Pb, Cd, Ni and Co) concentration in the vegetables

On categorising the vegetables into three types *first* leafy, *second* fruits and *third* roots. The rank order among the 3 types of vegetables in decreasing order of heavy metal contents is Leafy > fruits > roots. The heavy metal accumulation in vegetables follows two paths *first* through soil and *second* by atmospheric deposition. Leafy vegetable (spinach) have high capacity to accumulate the heavy metals from the atmosphere compared to fruit vegetables due to high surface area. While, in roots the heavy metals are only accumulated through the soil. Hence, roots have the lowest heavy metals concentration. It is observed that Fe (307 ppm) concentration is relatively high in leafy vegetables compared to fruit & root vegetables (Fig. 4.39).

The similar results are also observed by different researchers. Sinha *et al*. (2006) reported lowest concentration of Cr in the underground vegetables namely potato (11.81 µg g^{-1} dw), garlic (19.27 µg g^{-1} dw), and turmeric (20.86 µg g^{-1} dw) compared to leafy and fruit vegetables. Farooq *et al*. (2008) found high concentration of heavy metals [Cu (0.923 mg kg^{-1}), Cd (0.073 mg kg^{-1}), Cr (0.546 mg kg^{-1}), Zn (1.893 mg kg^{-1}) and Pb (2.652 mg kg^{-1})] in the leafy vegetables namely spinach, cabbage, cauliflower, radish and coriander as compared to other vegetables.

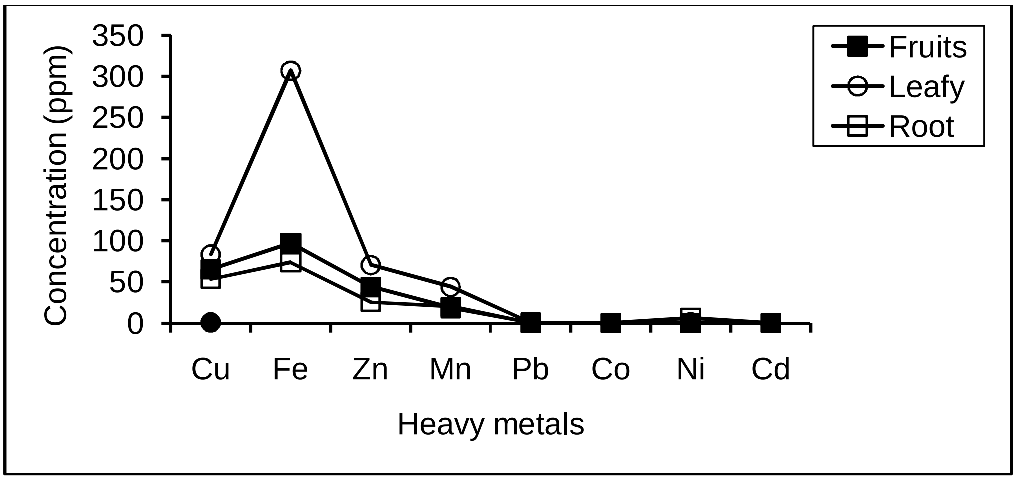


Fig. 4.39 Heavy metal contents in leafy, fruit and root vegetables

4.1.4.2 Heavy metal accumulation at different locations

Vegetables near the mines, overburden & tailings such as Khetri Nagar (near mines/extraction plant), Banwas (underground mines & overburden materials) and Maliyun Dhani (tailings dam) have high concentration of Fe, Cu, Zn and Mn (Fig. 4.40). Vegetables from Banwas and Khetri Nagar are highly contaminated with Cu & Fe compared to other locations. Compared to Khetri nagar, vegetables from Banwas have high concentration of heavy metals (Cu, Fe & Zn). This is due to the presence of both mine & overburden materials at Banwas.

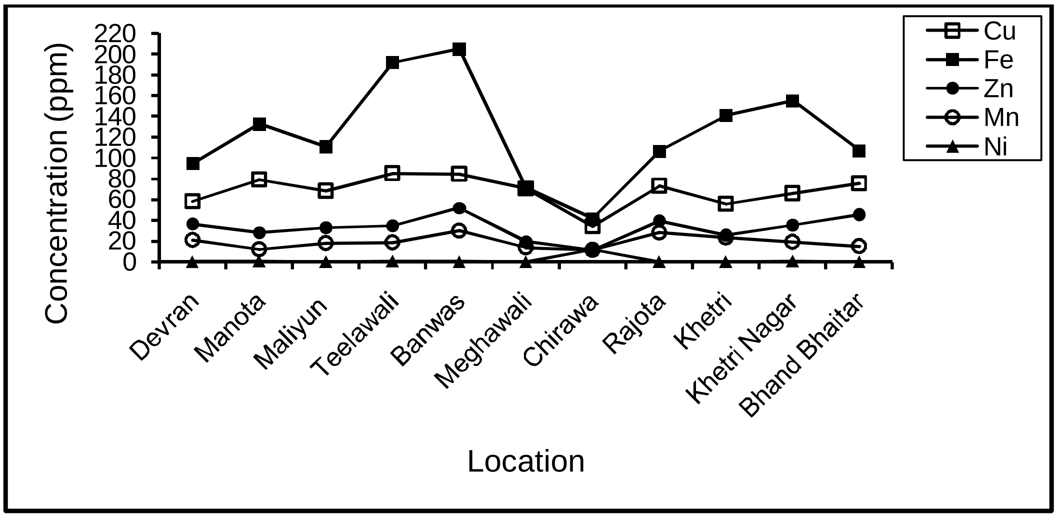


Fig. 4.40 Average heavy metal (Cu, Fe, Zn, Mn and Ni) concentration in vegetables from different locations of Khetri area

Statistically, the average heavy metal concentration in vegetables varies widely from location to location. Vegetables from Teelawali and Banwas have the highest Cu concentration i.e. 85 and 84 ppm respectively. Vegetables from Chirawa have the lowest concentration of Cu (34 ppm) as these are brought from distant locations from mining activities. Average Fe concentration in the vegetables from Banwas, Teelawali and Khetri Nagar is 204, 195 & 155 ppm respectively. At Chirawa, the average concentration of Fe in vegetables is the lowest (42 ppm). Like Cu & Fe, the average concentration of Zn in all the vegetables at Banwas is the highest (52 ppm) and lowest at Chirawa (11 ppm).

4.1.4.3 Comparison with permissible limits

Heavy metal concentrations in vegetable of Khetri are compared with the Prevention of food Adulteration (PFA) act (Awasthi, 2000) and WHO/FAO, (2007) to assess the extent of heavy metal contamination in vegetables (Fig, 4.41, 4.42 & 4.43). It is found that concentration of Cu and Zn in vegetables exceeds the PFA permissible limits. Concentration of Zn exceeds the permissible limits in pepper & spinach, while Cu exceeds in all the vegetables. Cu concentration is 2 times higher than the PFA. Hence, the vegetables grown in the Khetri region are contaminated with Cu.

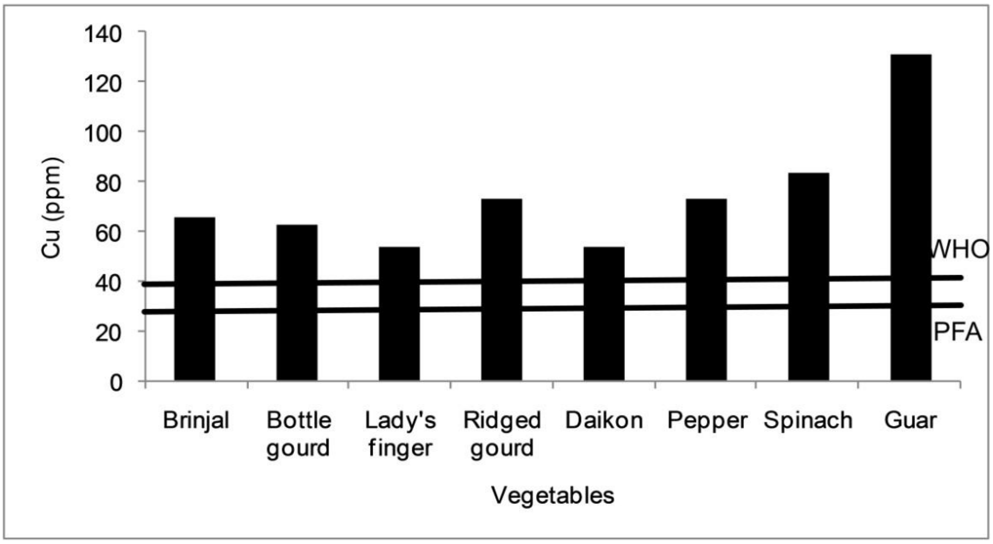


Fig. 4.41 Concentration of Cu in vegetables compared with WHO and PFA limits

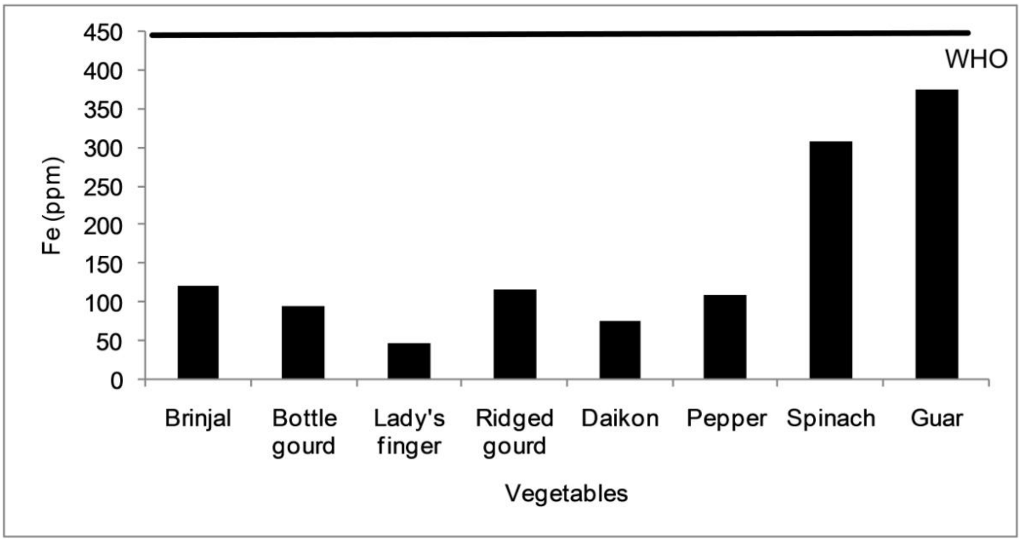


Fig. 4.42 Concentration of Fe in vegetables compared with WHO and PFA limits

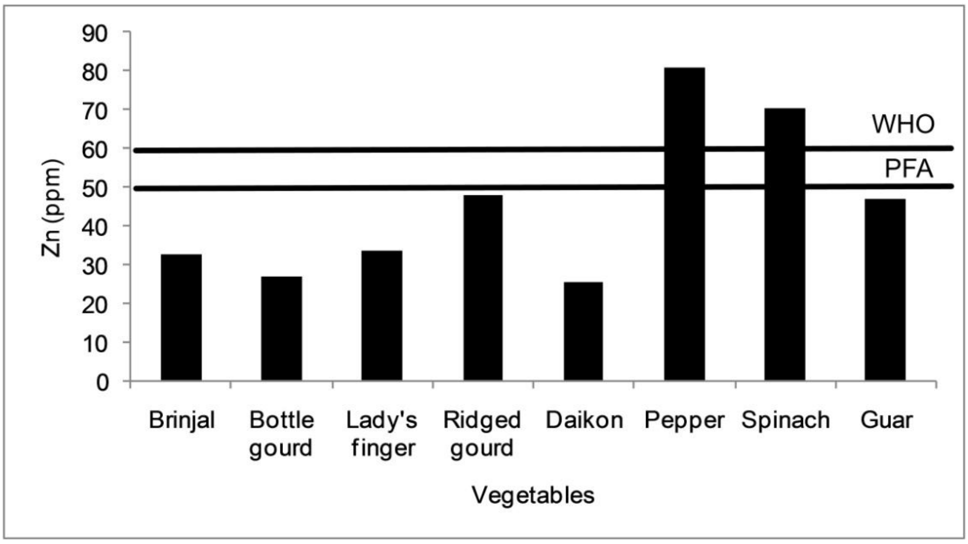


Fig. 4.43 Concentration of Zn in vegetables compared with WHO and PFA limits

On comparison with WHO/FAO permissible limits the results are similar to PFA limits. Cu concentration exceeds WHO permissible limits in all vegetables while Zn exceeds in pepper & spinach. Despite of higher concentration of Fe in vegetables it is within the Permissible limits of WHO/FAO (450 ppm).

4.1.5 Fractionation of Heavy Metal in Tailings and Soils

The reporting of abundance of heavy metals in the environment is not sufficient for the environmental studies. To understand and compare the trends in behaviour of heavy metal (Cu, Zn, Ni, Cr and Pb) mobility in tailings and soils, a method proposed by Ribet *et al*. (1995) was followed for both tailings and soils. Along with the sequential extraction method single reagents (EDTA and acetic acid) were used to assess the total available content of heavy metals in the tailings and soils. The samples were physically fractionated to assess the impact of grain size on the heavy metal accumulation.

In sequential fractionation heavy metals are extracted on the basis of their solubility with different extractants i.e. water soluble, acid leachable, reducible (available in reducing condition) and remaining are left in the residue (heavy metals bound to silicate minerals lattice and of geogenic origin). First three steps indicate the mobility of heavy metals in environment which helps in assessing the behaviour of heavy metals in short and long term along with the changing environmental conditions and discussed in detail in the latter section.

4.1.5.1 Physical fractionation of soils and tailings

In tailings, 67% of grains are of +63 mesh size and 33 % of grains are of -63 mesh size despite of crushing during beneficiation (Table 4.16). Finer the grain size of ore, the greater will be the extraction efficiency of mineral from the ore because finer fractions have high size to volume ration which results in more binding of chelates to ore. Hence, the coarser size of tailings indicates the less extraction efficiency at Khetri.

In soils, on average 73% of grains are of +63 mesh size and rest 27% are of -63 mesh size. Soil (L1) neighbouring Karkaria mountain bed is of coarser grain size having 93% of grains above the 63 mesh size. Similarly, soil neighbouring Ahiro Dhani mountain bed (L6) is having 88% of grain above the 63 mesh size. In contrast, the soils from the Ajit Sagar dam reservoir (L4) and Pana Sagar talab (L8) are have relatively finer grains i.e. 45 and 50% of grains below the 63 mesh size.

Table 4.16 Grain Size Proportion (wt. %) of tailings and soils

	Grain Size Proportion (wt. %)	
Tailings	**+63 mesh size**	**-63 mesh size**
S1-T2	63	37
S2-T1	69	31
S3-T1	77	23
S5-T3	77	24
S7-T1	62	38
S9-T1	56	44
Average	67	33
Soil		
L1	93	7
L4	45	55
L6	88	12
L8	50	50
L10	79	21
L13	89	11
L19	53	47
L26	90	10
Average	73	27

4.1.5.2 Single reagent extraction

To assess the mobility and behaviour of heavy metals (Cu, Zn, Ni, Cr and Pb) in tailings and soils of Khetri copper region, the extraction of heavy metals with single reagents (EDTA and acetic acid) methods were adopted (Table 4.17

and 4.18). The EDTA and acetic acid (AA) extracts the easily available heavy metals bound to exchangeable, organic and carbonates sites (McLaren *et al*., 1986; Ure, 1996).

Heavy metal extraction is more in finer fraction compared to bulk. In tailings, average concentration of Cu extracted with EDTA is 75 and 93 ppm in bulk and finer fraction respectively. Extraction of Cu with AA is 116 and 130 ppm in bulk and finer fraction respectively. In soils, ETDA extracts 98 and 117 ppm of Cu in bulk and finer fraction respectively and with AA it is 218 and 253 ppm. Cu extraction with EDTA and AA in soils is more compared to tailings despite its high concentration in tailings as shown in Fig. 4.44 & 4.45 it indicates the anthropogenic origin (mining activities) of Cu in the soils (binds to exchangeable sites i.e. free ions, soluble carbonates and organic matter) while in tailings Cu is present in the unrecovered sulphides. It also shows the negligible effect of total concentration on the extraction efficiency with EDTA and AA as it extracts only the available fraction.

On comparing the extraction efficiencies of EDTA and AA, the extraction of heavy metals with AA was more may be because EDTA extracts heavy metals bound to carbonates and organic matter while AA attacks the sites those are bound to water soluble, exchangeable, carbonates, and organic matter (McLaren *et al*., 1986; McGrath 1996; Ure 1996). In addition, AA generates slight acidic condition which results in dissolution of heavy metals into solution. Extraction of Pb is more with EDTA than AA as EDTA forms the stable, soluble and phytoavailable Pb chealtes due to its high Pb affinity (Shahid *et al*., 2012).

Extraction of Zn with EDTA and AA in tailings and soils is approximately equal (Fig. 4.46 & 4.47) and may be because of high mobility of Zn in the environment. Concentration of Cr and Ni is approximately equal in both soils and tailings. But the extraction of Ni with EDTA and AA is more compared to Cr indicating the high mobility of Ni compared to Cr. Tyler and McBride, 1982 found highest mobility of Ni in the soils compared to Cu, Zn and Cd.

It is found that Ni and Zn are extracted more with AA while Pb is extracted more with EDTA suggesting the high mobility of Ni and Zn in acetic condition. The similar results were also reported by Salomons (1993), McGrath (1996) and Kennedy (1997). In addition, the extraction of Ni with EDTA and AA is more in tailings than that of soils indicating its high mobility in tailings compared to soils.

Table 4.17 Heavy metal (Cu, Zn, Cr, Pb and Ni) concentration (in ppm) extracted with EDTA and acetic acid from tailings

	EDTA									
	Cu		**Zn**		**Cr**		**Pb**		**Ni**	
	B	**C**	**B**	**C**	**B**	**C**	**B**	**C**	**B**	**C**
S1-T2	77.8	49.9	3.5	14.0	0	0	0.2	0.3	1.9	5.6
S2-T1	66.3	80.2	1.2	7.5	0.0	0.4	0.0	0.0	2.2	4.0
S5-T3	106.2	104.8	1.8	24.2	0.6	0.6	0.1	0.2	3.3	6.6
S7-T1	31.7	133.1	15.7	10.9	0.3	0.3	0.0	0.0	5.9	14.5
S9-T1	95.2	96.7	3.1	7.3	0.4	0.2	2.6	0.2	14.6	16.8
Average	75.4	92.9	5.1	12.8	0.2	0.3	0.6	0.1	5.6	9.5
STDEV	28.9	30.8	6.0	7.0	0.2	0.2	1.1	0.1	5.3	5.7
	Acetic Acid (A.A.)									
S1-T2	78.7	35.8	5.1	15.9	0	0	0	0	10.2	12.2
S2-T1	154.6	180.3	7.5	14.6	0.0	1.1	0	0	10.3	16.1
S5-T3	177.5	182.3	10.3	27.7	0.6	0.0	0	0	9.7	18.9
S7-T1	60.2	127.6	28.9	19.9	1.5	1.2	0	0	11.7	17.3

S9-T1	107.4	121.6	10.3	13.3	6.2	5.4	0	0	40.4	43.9
Average	115.7	129.5	12.4	18.3	1.7	1.5	0	0	16.4	21.7
STDEV	49.6	59.6	9.5	5.8	2.6	2.2	0	0	13.4	12.7

^{B}Bulk

^{C}Finer fraction

Table 4.18 Heavy metal (Cu, Zn, Cr, Pb and Ni) concentration (ppm) extracted with EDTA and acetic acid from soils

	EDTA									
	Cu		**Zn**		**Cr**		**Pb**		**Ni**	
	B	**C**	**B**	**C**	**B**	**C**	**B**	**C**	**B**	**C**
L4	36.8	41.8	3.5	13.0	1.6	1.4	2.60	1.87	3.07	2.45
L6	43.7	62.6	3.0	17.2	0.4	0.9	0.71	0.64	2.03	1.67
L10	167.3	242.2	2.2	15.1	0.0	0.7	2.04	3.14	4.04	8.66
L13	3.3	18.9	1.0	5.3	0.0	0.4	0.15	0.58	1.25	1.18
L19	240.5	222.9	15.9	10.2	0.8	0.9	5.56	4.29	1.57	1.46
Average	98.3	117.7	5.1	12.2	0.6	0.9	2.2	2.1	2.4	3.1
STDEV	101.0	106.2	6.1	4.6	0.7	0.3	2.1	1.6	1.1	3.2
	Acetic Acid (A.A.)									
L4	319.8	315.5	9.4	12.9	0.5	0.3	0.00	0.00	8.21	7.18
L6	55.1	90.0	8.6	50.0	0.0	0.0	0.00	0.00	8.45	5.84
L10	383.1	498.9	10.9	19.9	0.0	0.0	0.00	0.00	12.04	15.78
L13	7.5	30.3	3.1	10.4	0.4	2.4	0.00	0.67	5.95	5.49
L19	323.6	331.6	30.9	26.7	1.4	0.0	0.07	0.00	4.72	5.20

Average	217.8	253.3	12.6	24.0	0.5	0.5	0.0	0.1	7.9	7.9
STDEV	172.9	191.5	10.7	15.9	0.6	1.0	0.0	0.3	2.8	4.5

[B] Bulk

[C] Finer fraction

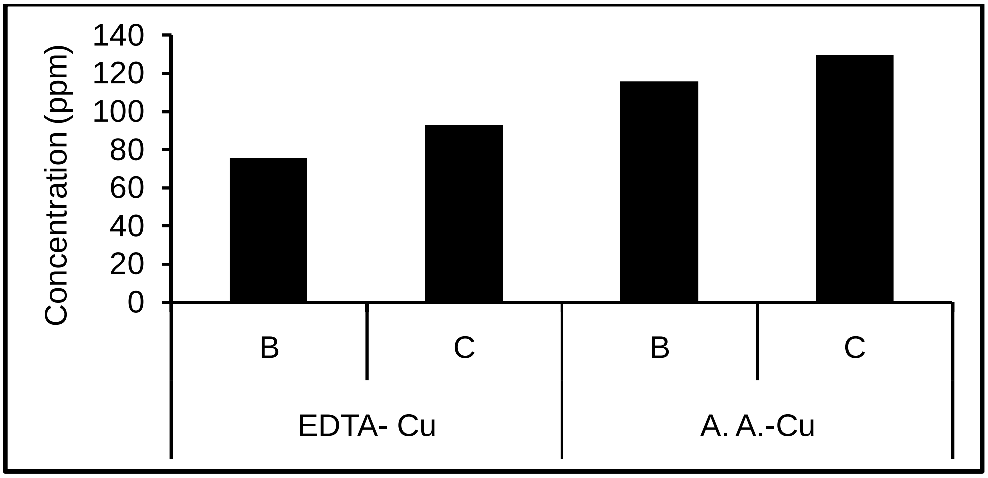


Fig. 4.44 Average concentration of Cu extracted with EDTA and Acetic Acid from tailings

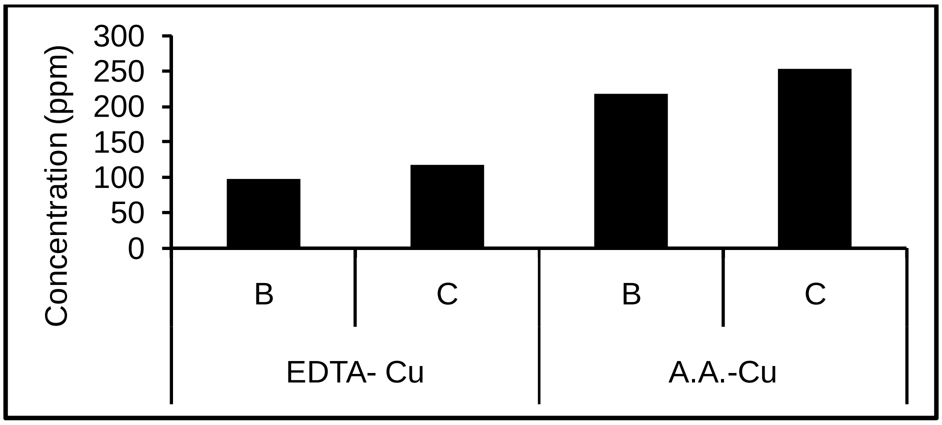


Fig. 4.45 Average concentration of Cu extracted with EDTA and Acetic Acid from soils

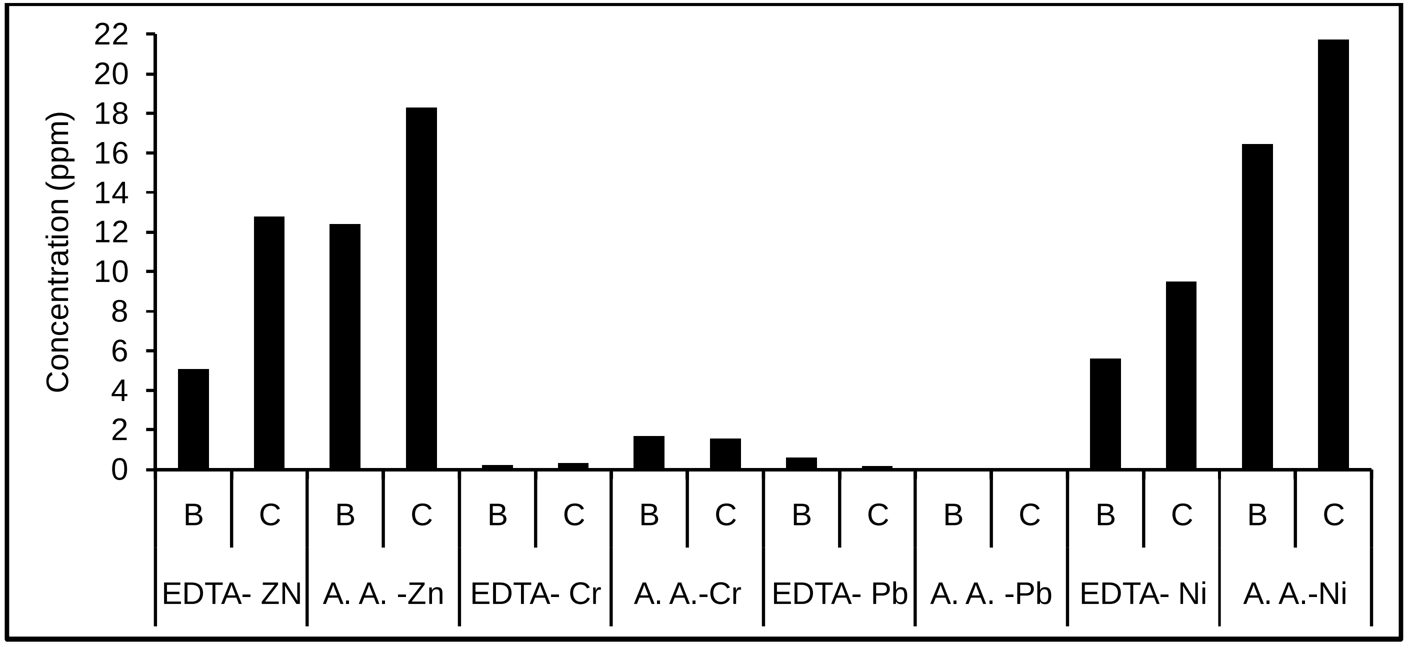


Fig. 4.46 Average concentration of heavy metals extracted with EDTA and Acetic Acid from tailings

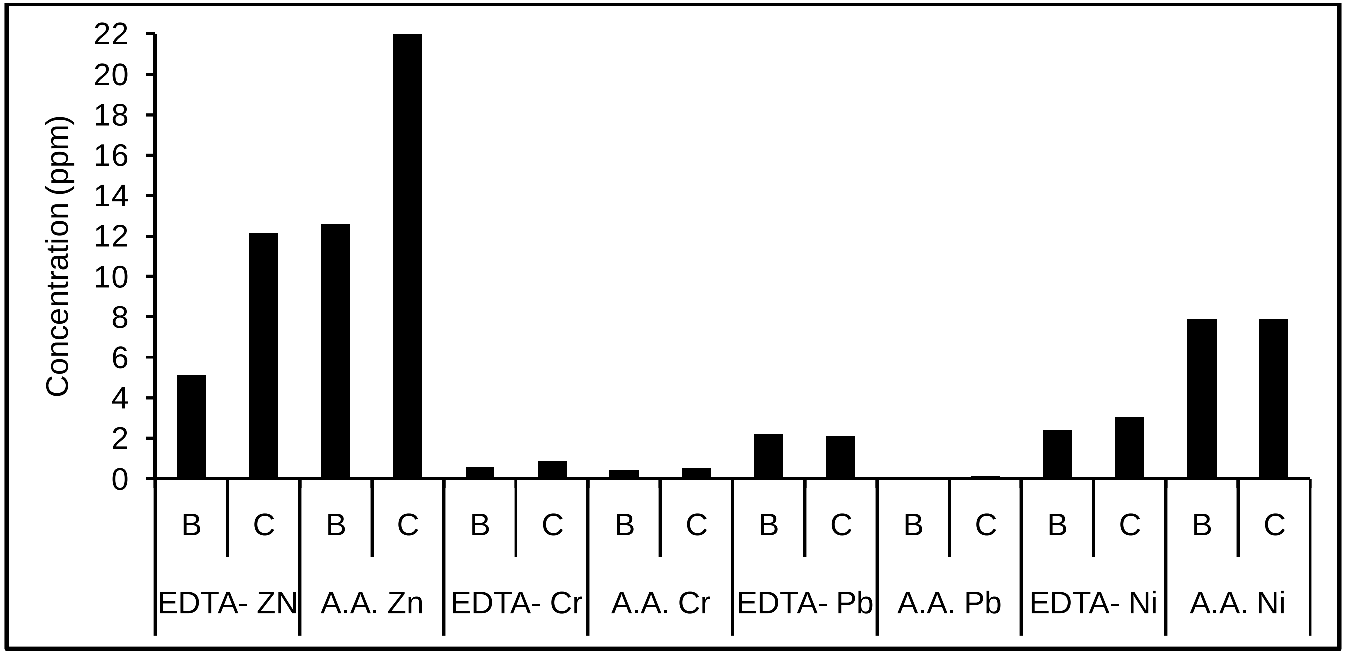


Fig. 4.47 Average concentration of heavy metals extracted with EDTA and Acetic Acid from soils

4.1.5.3 Sequential extraction

In both tailings and soils, finer fraction of bulk sample is heavy metal enriched compared to bulk sample for all fractions (water soluble, acid leachable, reducible and residual) as the finer fraction have more size to volume ratio and have more exchangeable sites. The details of concentration of each fraction in the tailings and soils are given in Table 4.19 & 4.20.

In tailings, 4, 214, 64 and 1714 ppm of average Cu concentration is extracted in water soluble, acid leachable, reducible and residue fraction respectively in bulk and it is 19, 230, 63 and 351 ppm respectively in finer fraction (Fig. 4.48 & 4.49). The presence of high concentration of Cu in residue of bulk indicates the presence of unrecovered Cu. In soils, water soluble, acid leachable, reducible and residue fractions contains 12, 256, 259 and 423 ppm of average concentration of Cu in bulk sample. In finer fraction the content of Cu in water soluble, acid leachable, reducible and residue fractions is higher compared to bulk and it is 43, 279, 309 and 405 ppm respectively.

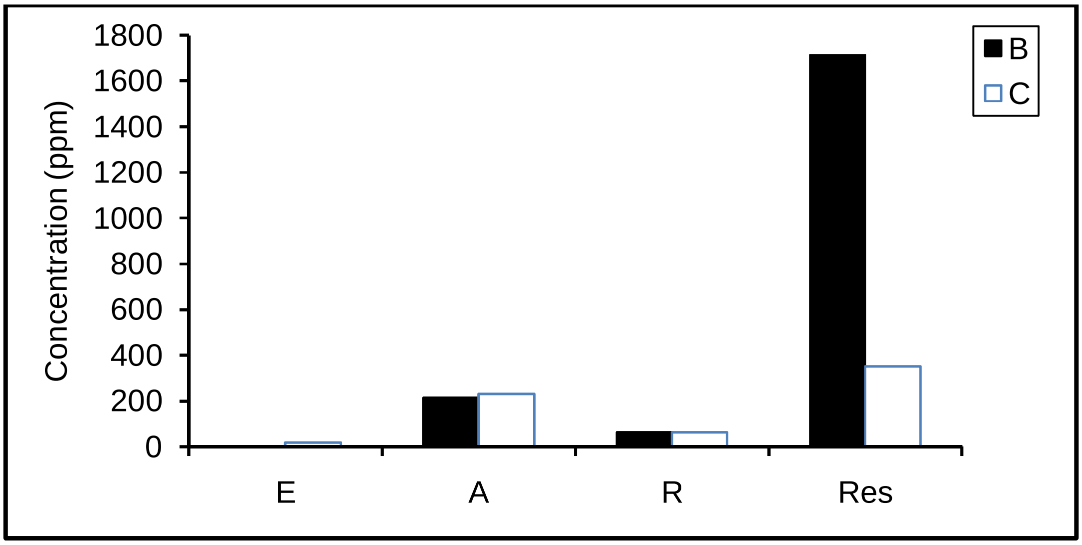


Fig. 4.48 Cu concentration in different fractions, E (exchangeable), A (acid leachable), R (reducible fraction) and Res (residue) in tailings

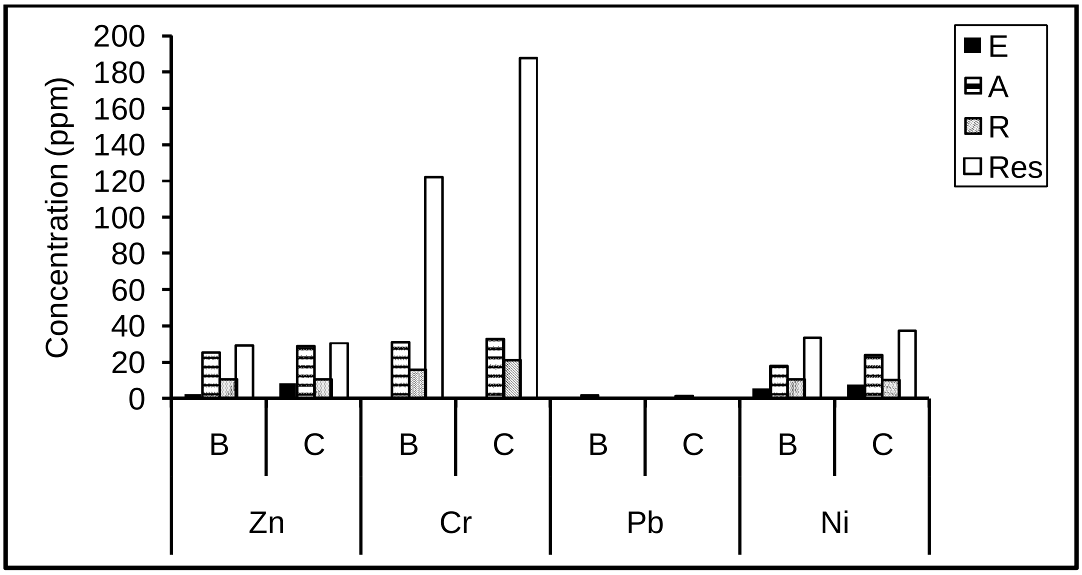


Fig. 4.49 Heavy metal concentrations in different fractions, E (exchangeable), A (acid leachable), R (reducible fraction) and Res (residue) in tailings

The rank order for different fraction in tailings is residue > acid leachable > reducible > water soluble for both bulk & finer fraction and in soil it is residue > reducible > acid leachable > water soluble (4.50 & 4.51).

In tailings, heavy metals are bound more to acid leachable than in soils due to abundance of crushed unrecovered sulphide minerals in tailings. As the acidic environment develops the Cu leaches out into the solution and also shows high abundance of potentially available heavy metals in tailings. Thus the generation of AMD could enhance leaching of Cu from tailings dam in the Khetri environment. Strong acid such as HCl that does not dissolve silicate matrix, on digestion gives an estimate of the maximum amount of heavy metals those are mobile with the changing environment (Ure, 1996; Rao *et al.*, 2008). This fraction do not mobilise heavy metals from geological, silicate parent materials but dissolve metal pollutants entered the soil environment in non-silicate bound forms.

Water soluble fraction includes weakly adsorbed heavy metals present in soil solution and sediment pore water. The heavy metals present in water soluble fraction are the most available and could easily be uptaken by the plants. The acid leachable and reducible fraction (bound to Fe and Mn oxides) are also potentially available fraction in long term. Presence of high concentration of Cu in available fraction (water soluble, acid leachable and reducible fractions) of soils compared to that of in tailings indicates that in tailings most of heavy metals are present in the lattice of silicate or unrecovered sulphides. The high extraction of Cu in the water soluble, acid leachable and reducible fractions confirms their presence as a pollutant pool in the soils. The anthropogenic originated heavy metals are extracted in the initial steps and heavy metals present in the silicate lattices are extracted in the last step (Rubio *et al*., 1991).

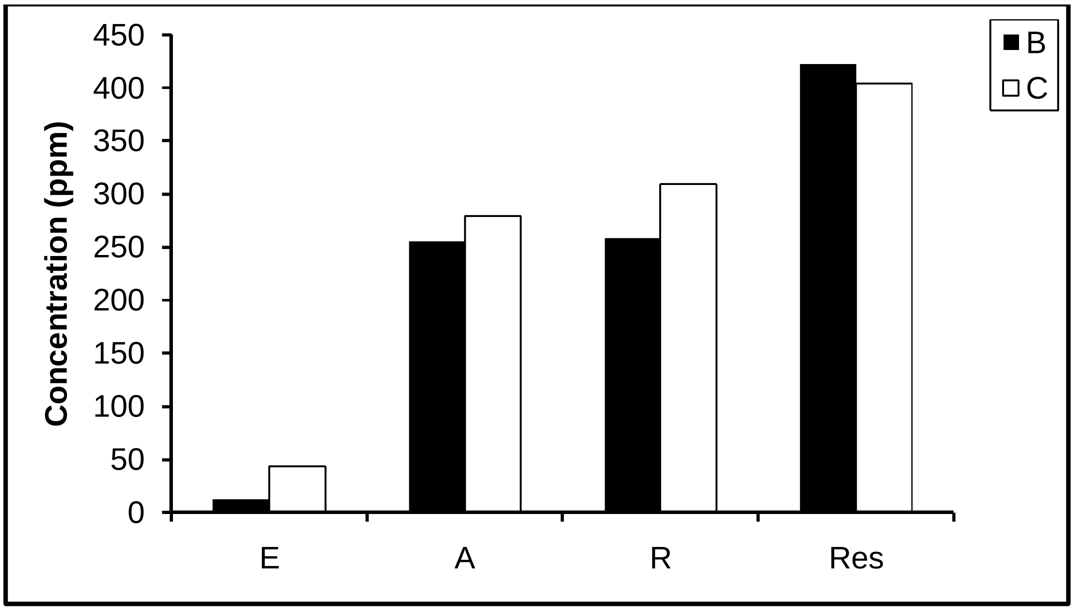


Fig. 4.50 Cu concentration in different fractions, E (exchangeable), A (acid leachable), R (reducible fraction) and Res (residue) in soils

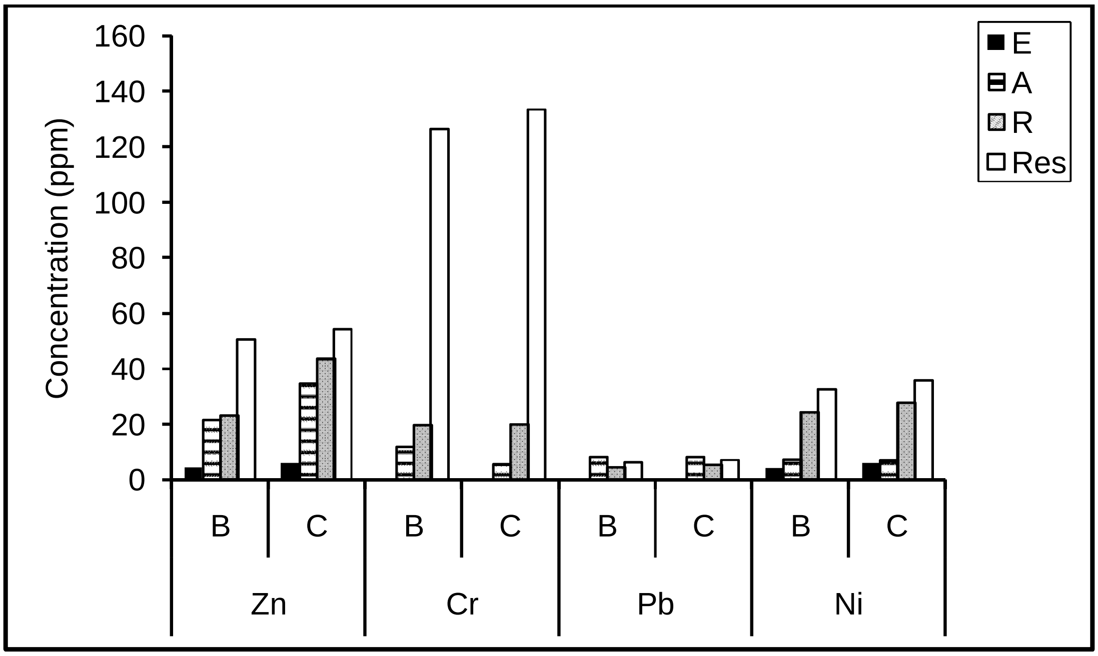


Fig. 4.51 Heavy metal concentrations in different fractions, E (exchangeable), A (acid leachable), R (reducible fraction) and Res (residue) in soils

In bulk fraction of tailings, 86% of Cu is present in residue, 10% in acid leachable and 3% in reducible and very low 0.18% in water soluble fraction. In finer fraction, 53% in residue, 35% in acid leachable, 10% reducible and 3% in water soluble fraction (Fig. 4.53). The high abundance of Cu in residue fraction in bulk compared to finer fraction. It also indicates that Cu is remains high in the coarser fraction (bulk) as the Cu extraction is less in this fraction. During froth flotation process extraction efficiency of Cu is depends upon the grain size as the chelating agent bound more on the finer fraction. So in finer fraction Cu is already extracted during froth flotation process. It is also observed that for other elements there is no significant difference in the extracted concentration among bulk and finer fraction.

Similarly, Leppinen *et al*. (1997) and Hansen (2005) found more extraction of Cu in smaller fraction compared to larger fraction suggesting that in smaller fraction Cu is associated with oxides while in larger fraction it is present in sulphides. Wadsworth (1979) also found increase in copper leaching on decreasing particle size.

Pb is present in trace quantity and 100% of Pb is bound to acid leachable fraction for both bulk and finer fractions. The extraction of Cr in the water soluble fraction is zero for both bulk and finer fraction. Its 72 and 78% of fraction is bound with residue for bulk and finer fraction respectively shows that Cr is strongly bound to silicate minerals and immobile in environment. As the mobility of Zn and Ni is high, they are easily extracted in the earlier step and are bound to non residual fraction more compared to Cr.

The concentration of Cu, Zn and Ni bound with non residual fractions are more in soils compared to tailings (Fig. 4.52). 45 and 39 % of Cu is associated with residue and 27 and 30 % with reducible fraction in bulk and finer fraction respectively and 27 % of Cu is bound to acid leachable fraction in both grain size fractions (Fig. 4.52). In finer fraction water soluble fraction (4%) is more compared to bulk (1%) hence Cu is adsorbed more on the finer fraction.

Both Cr and Pb are absent in the water soluble fraction in both bulk and finer fraction. In bulk fraction, 80 % of Cr is bound to residue fraction, 13 % to reducible and 8% to acid leachable while in finer fraction 84 % of Cr is bound to residue fraction, 12 % to reducible, 3% to acid leachable. The abundance of Cr in the residue fraction indicates it presence in silicate matrix and its geogenic origin. In soils, Pb is approximately equal distributed in different fraction 37 and 35% is bound with residue, 22 and 25% with reducible and 40 and 41% with acid leachable fraction in bulk and finer fraction respectively.

Table 4.19 Heavy metal concentration (ppm) in different fractions, E-exchangeable, A-Acid leachable, R-Reducible fraction and Res-Residue in tailings

Exchangeable										
	Cu		**Zn**		**Cr**		**Pb**		**Ni**	
	B	C	B	C	B	C	B	C	B	C
S1-T2	3.2	3.2	1.5	3.6	0.0	0.0	0.0	0.0	4.7	4.9
S2-T1	2.9	3.0	1.1	1.2	0.0	0.0	0.0	0.0	4.5	4.2
S5-T3	3.0	2.9	1.1	1.2	0.0	0.0	0.0	0.0	3.9	4.8
S7-T1	4.9	80.3	2.7	30.9	0.0	0.0	0.0	0.0	7.7	16.8
S9-T1	3.5	3.5	4.6	3.7	0.0	0.0	0.0	0.0	6.0	6.8
Average	3.5	18.6	2.2	8.1	0.0	0.0	0.0	0.0	5.3	7.5
STDEV	0.8	34.5	1.5	12.8	0.0	0.0	0.0	0.0	1.5	5.3
Acid leachable										
S1-T2	152.2	137.0	17.6	31.4	18.7	26.1	0.3	1.6	13.3	14.0
S2-T1	315.1	367.5	21.8	39.4	62.4	51.9	1.3	3.2	5.7	24.0
S5-T3	268.6	290.5	19.2	24.9	20.9	32.0	1.8	1.3	12.9	21.7

S7-T1	140.6	145.4	23.3	17.1	16.4	13.6	1.3	0.0	9.3	7.3
S9-T1	193.4	212.2	45.1	31.9	36.8	39.5	4.0	1.0	47.7	53.5
Average	214.0	230.5	25.4	28.9	31.1	32.6	1.7	1.4	17.8	24.1
STDEV	75.5	98.3	11.2	8.4	19.3	14.4	1.4	1.2	17.0	17.7
Reducible										
S1-T2	53.1	47.9	13.4	15.8	18.9	27.6	0.0	0.0	14.2	18.6
S2-T1	39.8	36.0	8.1	8.8	8.3	15.9	0.0	0.0	4.4	5.7
S5-T3	49.4	51.2	8.2	11.9	8.1	17.7	0.0	0.0	5.5	8.9
S7-T1	110.2	141.2	9.0	9.0	20.7	25.0	0.0	0.0	10.2	6.1
S9-T1	65.6	40.9	14.8	6.9	23.7	20.0	0.0	0.0	18.9	11.0
Average	63.6	63.4	10.7	10.5	15.9	21.2	0.0	0.0	10.6	10.0
STDEV	27.7	43.9	3.2	3.5	7.3	4.9	0.0	0.0	6.1	5.3
Residue										
S1-T2	2786.0	409.0	32.0	30.9	159.2	254.2	0.0	0.0	35.6	40.0
S2-T1	1288.4	410.6	28.8	27.2	115.0	200.1	0.0	0.0	41.0	45.7

S5-T3	3837.2	534.8	30.7	27.8	103.4	190.8	0.0	0.0	41.9	47.4
S7-T1	257.0	115.1	25.1	28.9	106.2	153.4	0.0	0.0	21.6	23.5
S9-T1	404.0	284.9	28.1	36.3	127.7	141.9	0.0	0.0	26.4	28.8
Average	1714.5	350.9	28.9	30.2	122.3	188.1	0.0	0.0	33.3	37.1
STDEV	1555.4	158.7	2.6	3.7	22.7	44.3	0.0	0.0	9.0	10.5

Table 4.20 Heavy metal concentration (ppm) in different fractions, E-exchangeable, A-Acid leachable, R-Reducible fraction and Res-Residue in soils

	Exchangeable									
	Cu		Zn		Cr		Pb		Ni	
	B	C	B	C	B	C	B	C	B	C
L4	4.2	4.6	1.3	1.5	0.5	0.9	0.0	0.2	4.3	4.3
L6	16.7	17.5	6.1	6.3	0.0	0.7	0.2	0.0	4.2	4.1
L10	5.7	169.9	4.1	17.5	0.0	0.0	0.0	0.0	4.1	12.8
L13	8.9	4.1	4.2	1.4	0.0	0.0	0.0	0.0	4.3	4.0

L19	25.2	19.5	5.3	2.2	0.6	0.4	0.3	0.0	3.7	4.7
Average	12.1	43.1	4.2	5.8	0.2	0.4	0.1	0.0	4.1	6.0
STDEV	8.8	71.2	1.8	6.9	0.3	0.4	0.1	0.1	0.3	3.8
Acid leachable										
L4	94.8	83.5	20.5	37.4	11.8	4.2	17.5	17.1	3.4	7.6
L6	75.0	155.1	9.6	56.9	6.3	1.7	9.3	7.2	7.6	5.7
L10	428.5	474.8	13.1	14.8	13.7	3.5	4.7	7.2	12.1	9.4
L13	77.4	120.1	18.3	30.8	10.8	12.8	3.9	3.0	7.0	7.3
L19	601.7	563.6	46.0	33.4	16.9	5.6	5.5	6.8	6.1	4.8
Average	255.5	279.4	21.5	34.7	11.9	5.6	8.2	8.3	7.3	7.0
STDEV	244.9	222.5	14.4	15.1	3.9	4.3	5.6	5.2	3.1	1.8
Reducible										
L4	51.7	65.3	33.2	44.2	22.6	20.9	5.2	3.9	30.2	28.9
L6	248.5	250.8	16.7	69.8	14.3	14.1	4.5	4.3	29.9	28.8
L10	658.6	731.2	23.8	28.8	37.0	31.1	3.7	5.1	36.1	34.7

L13	23.9	66.4	12.8	29.2	15.3	22.6	1.9	3.4	13.5	29.2
L19	309.9	433.3	28.9	46.0	9.9	11.6	7.2	10.1	12.7	17.0
Average	258.5	309.4	23.1	43.6	19.8	20.1	4.5	5.4	24.5	27.7
STDEV	255.3	280.8	8.4	16.7	10.6	7.7	1.9	2.7	10.7	6.5
Residue										
L13	62.3	59.6	51.2	51.0	158.6	152.0	5.4	5.9	25.9	26.2
L10	1271.5	1030.4	50.5	56.3	138.9	123.9	4.3	3.9	40.2	49.2
L6	392.4	296.6	49.1	53.5	133.2	139.3	10.9	7.9	42.0	39.1
L4	68.2	76.0	55.8	77.49	100.1	116.6	5.8	7.9	34.4	35.1
L19	321.0	560.0	45.8	55.6	101.8	135.7	3.9	9.3	20.0	28.6
Average	423.1	404.5	50.5	54.1	126.5	133.5	6.1	7.0	32.5	35.7
STDEV	496.8	404.5	3.6	2.4	25.2	13.8	2.8	2.1	9.4	9.2

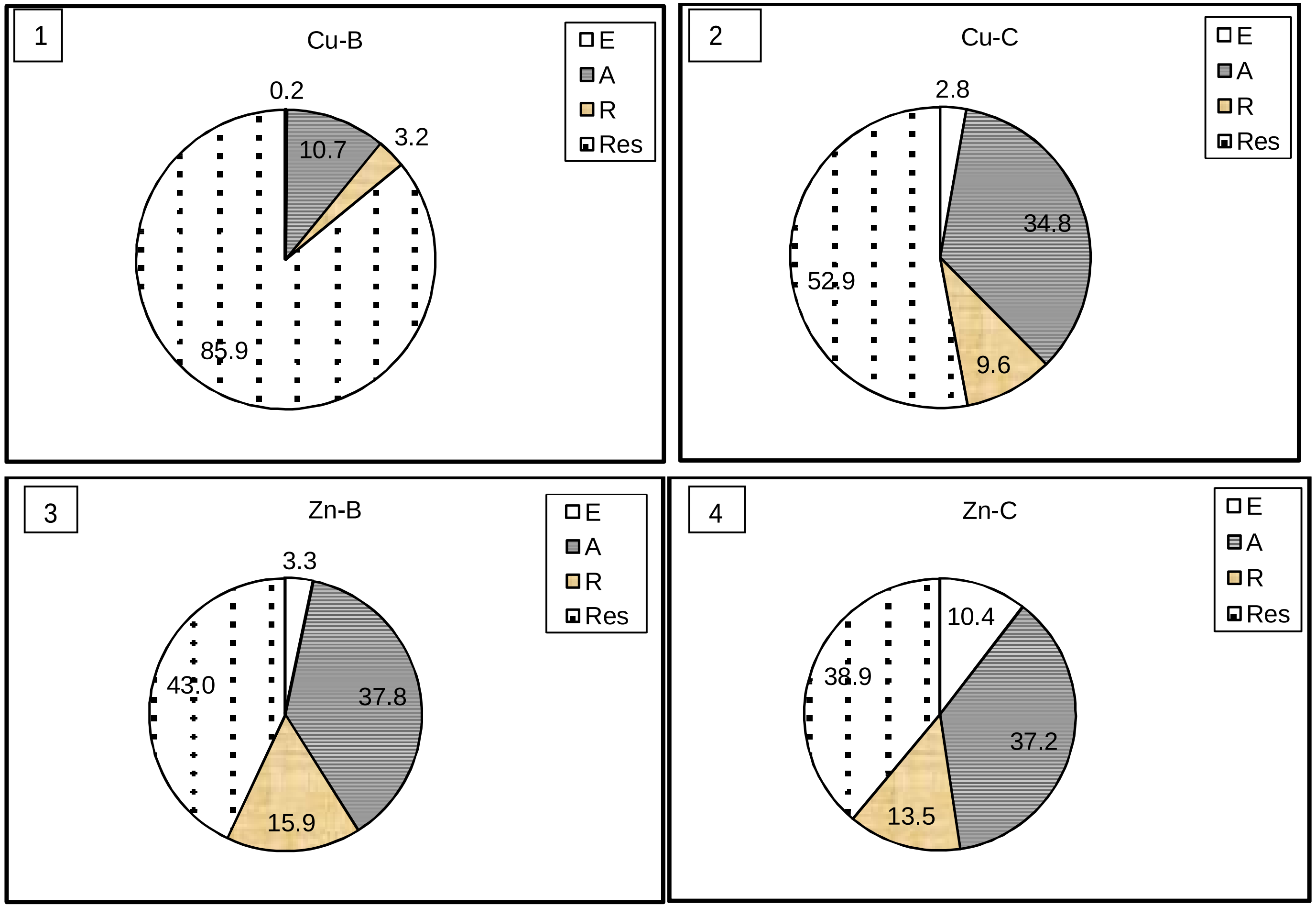
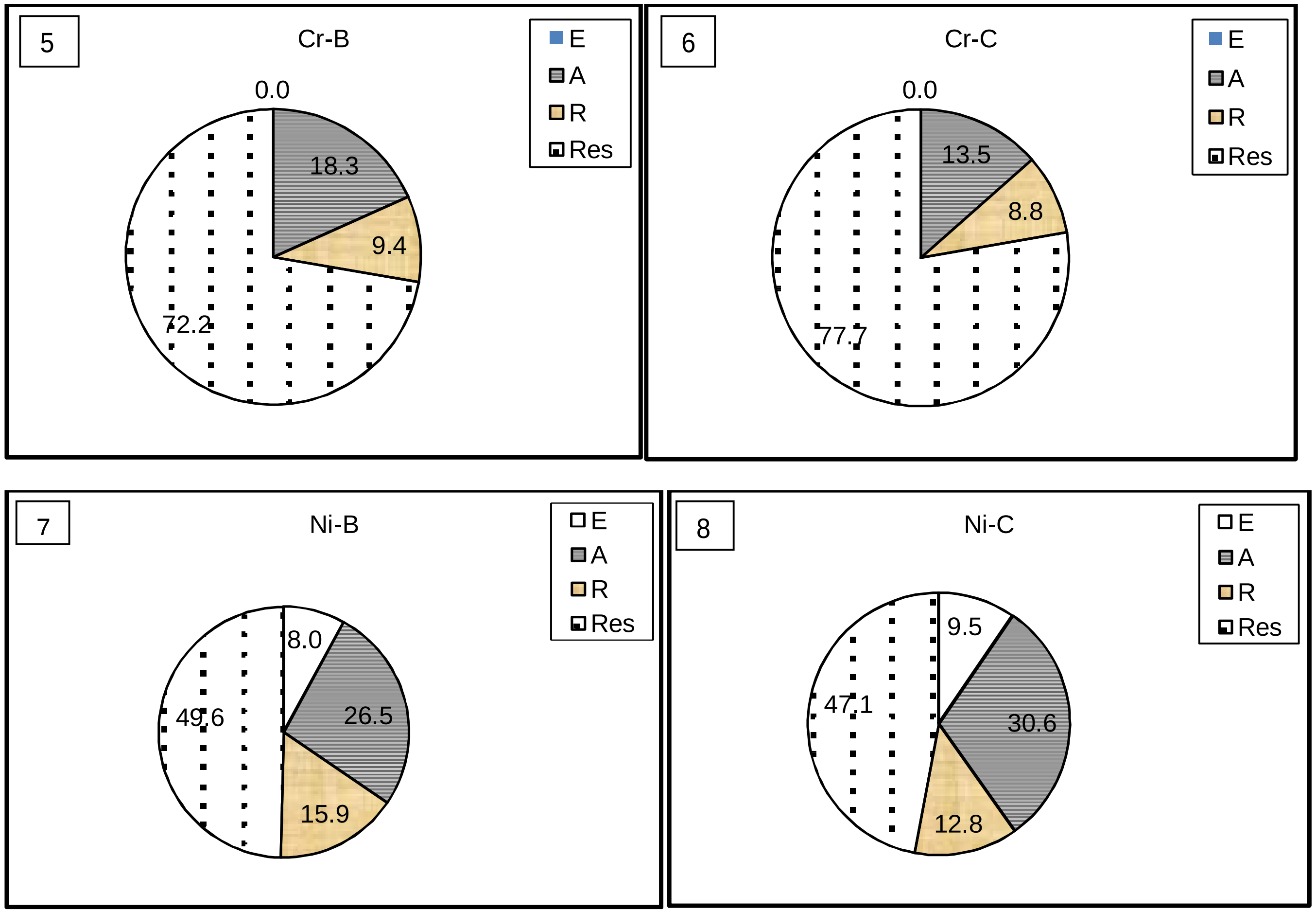


Fig. 4.52 Percentage of Cu (1 & 2), Zn (3 & 4), Cr (5 & 6) and Ni (7 & 8) concentration in different physical fractions (B-bulk and C- minus 63 micron) in tailings



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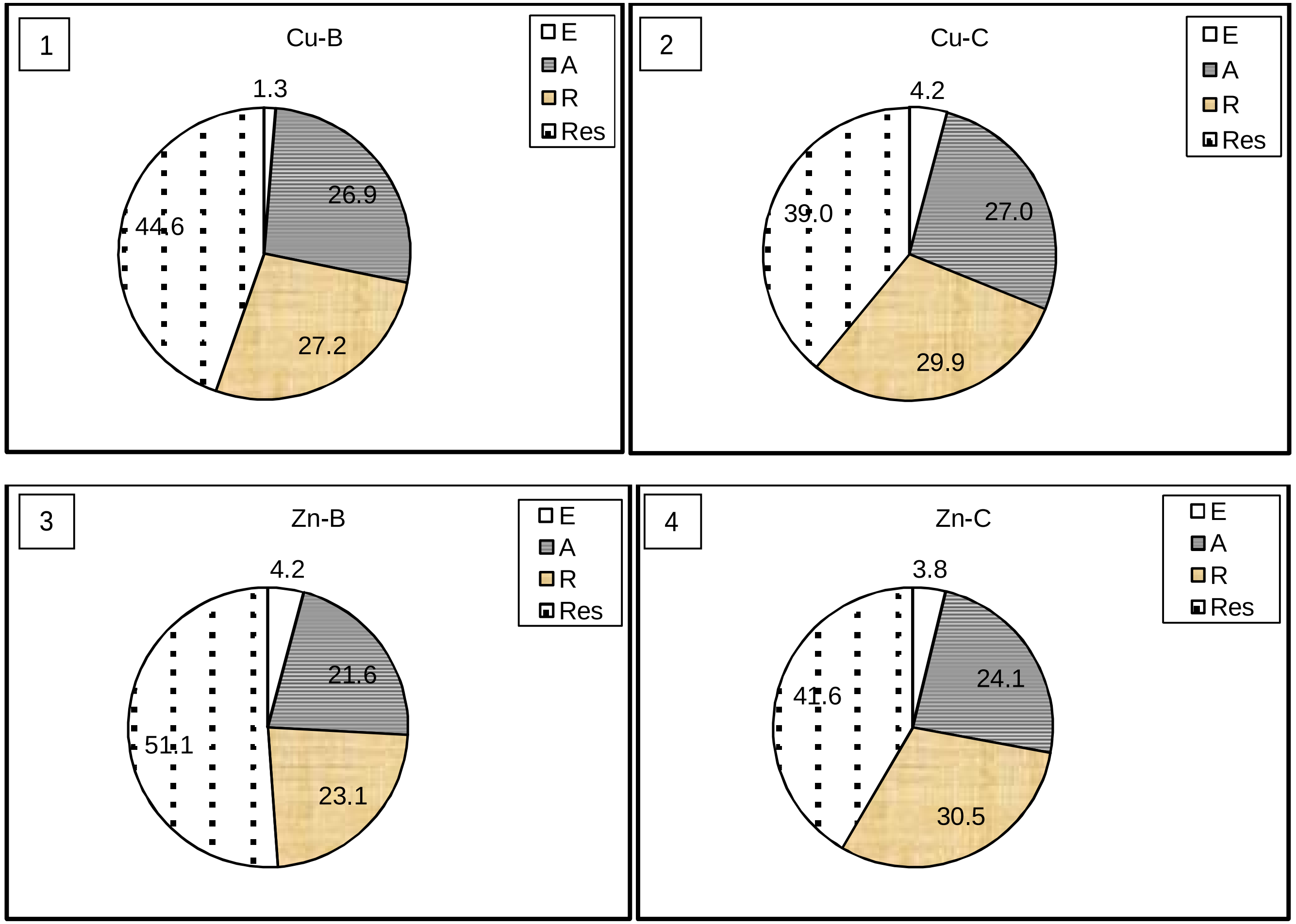


Fig. 4.53 Percentage of Cu (1 & 2), Zn (3 & 4), Cr (5 & 6), Pb (7 & 8) and Ni (9 & 10) concentration in different physical fractions (B-bulk and C- minus 63 mesh size) in soils of Khetri region

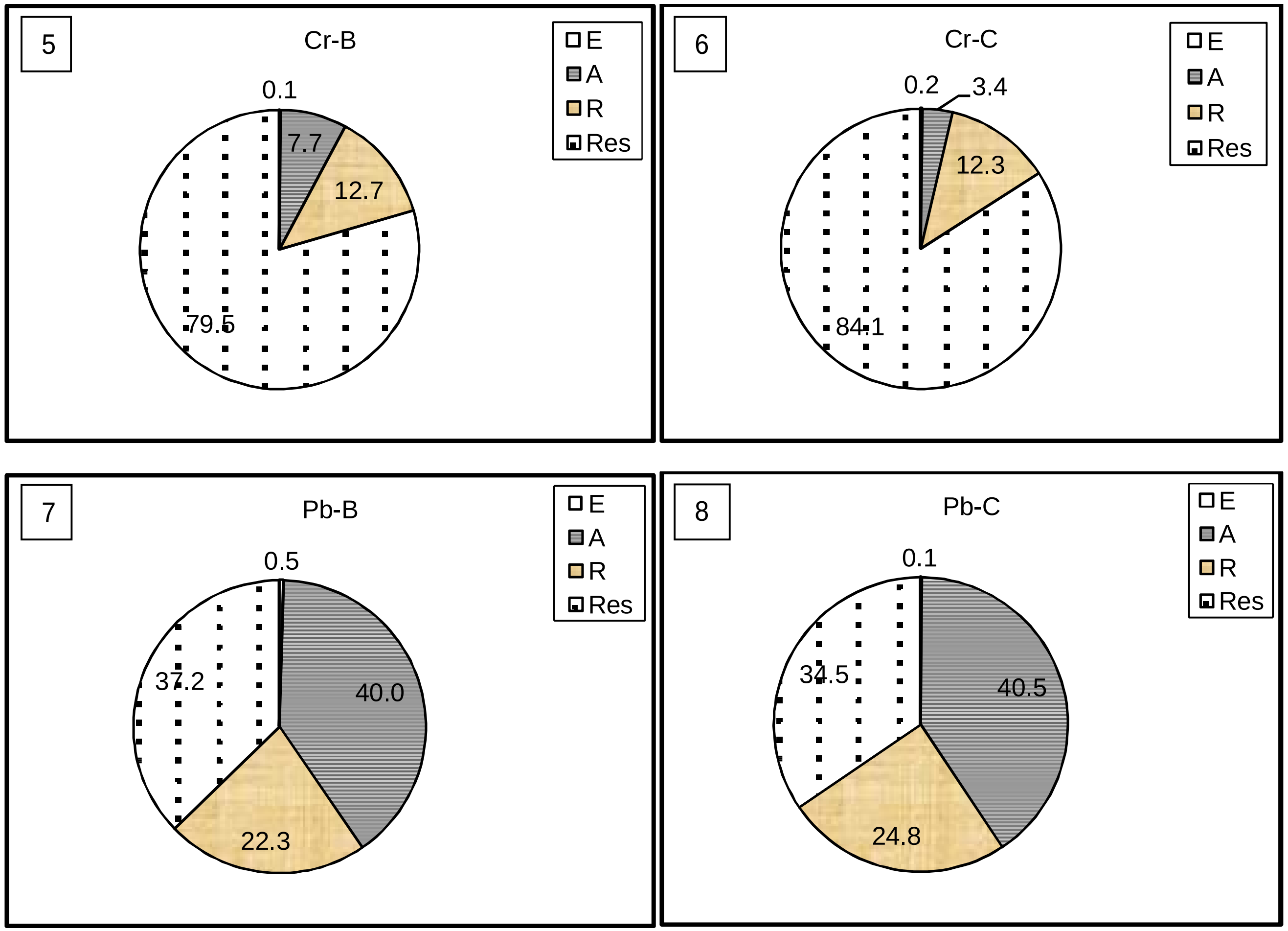


Fig. 4.53 Continued…

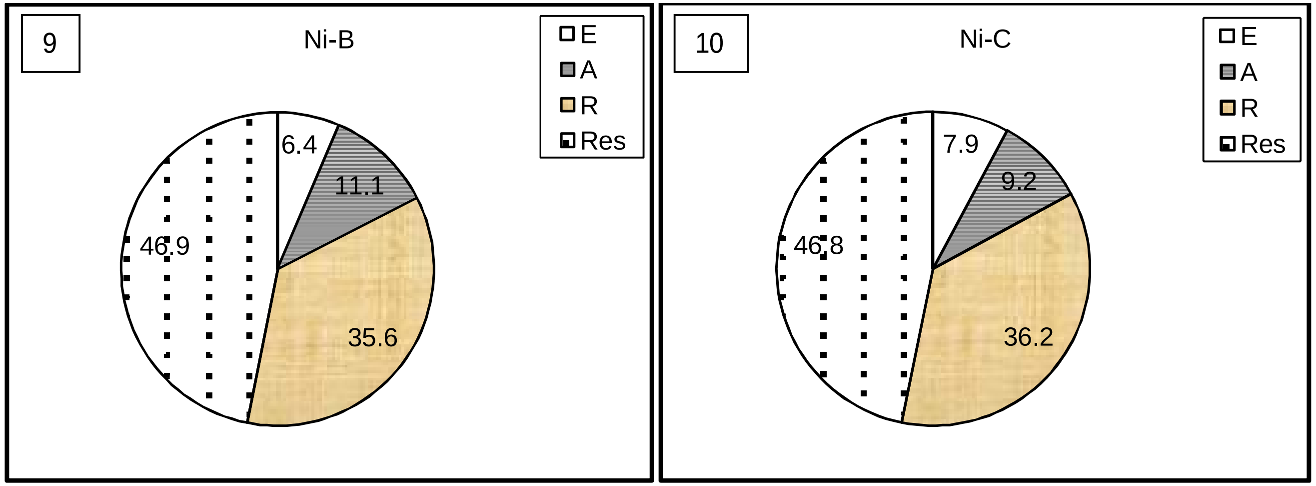


Fig. 4.53 Continued…

Cu, Zn and Ni are bound more with water soluble fraction at all location except soil (L4) from the dried Ajit Sagar reservoir located at the distant location from the mines it has high concentration in the residue fraction indicating the geogenic origin of these elements (Fig. 4.54, 4.55 & 4.56). Heavy metals present in crystal lattices (residue) are mainly not available or mobilized (Ma and Rao 1997). GSI, 1977 also reported the presence of Cu ore and its associated minerals at the Ajit Sagar.

Cu concentration in acid leachable fraction is high in the soils near the overburden materials of Chaandmari (L10) and Banwas (L19). Both the sites are sulphide rich due to presence of nearby overburden materials. Hence, the presence of sulphides enhances the leaching of HM in acidic environment. In contrary to this, soil from Ahrio Dhani (L6) despite of having high concentration of Cu the Cu does not leach out in acid leachable fraction in higher quantity. The Ahrio Dhani is located approximately 10 km away from the mines but in very close proximity of Ajit Sagar dam. The abundance of heavy metals at this site may be due to oxidation and precipitation of minerals present in the region because of once reservoir water. But the low availability in the acid leachable and water soluble confirm their low potential availability.

4.1.5.4 Metal mobility or risk assessment for soil and tailings

The water soluble fraction of heavy metals is considered as a most toxic because it becomes easily available to plants. In the present study, the water soluble concentration of heavy metals is determined to assess the available concentration of heavy metals in the soils and tailings of Khetri region.

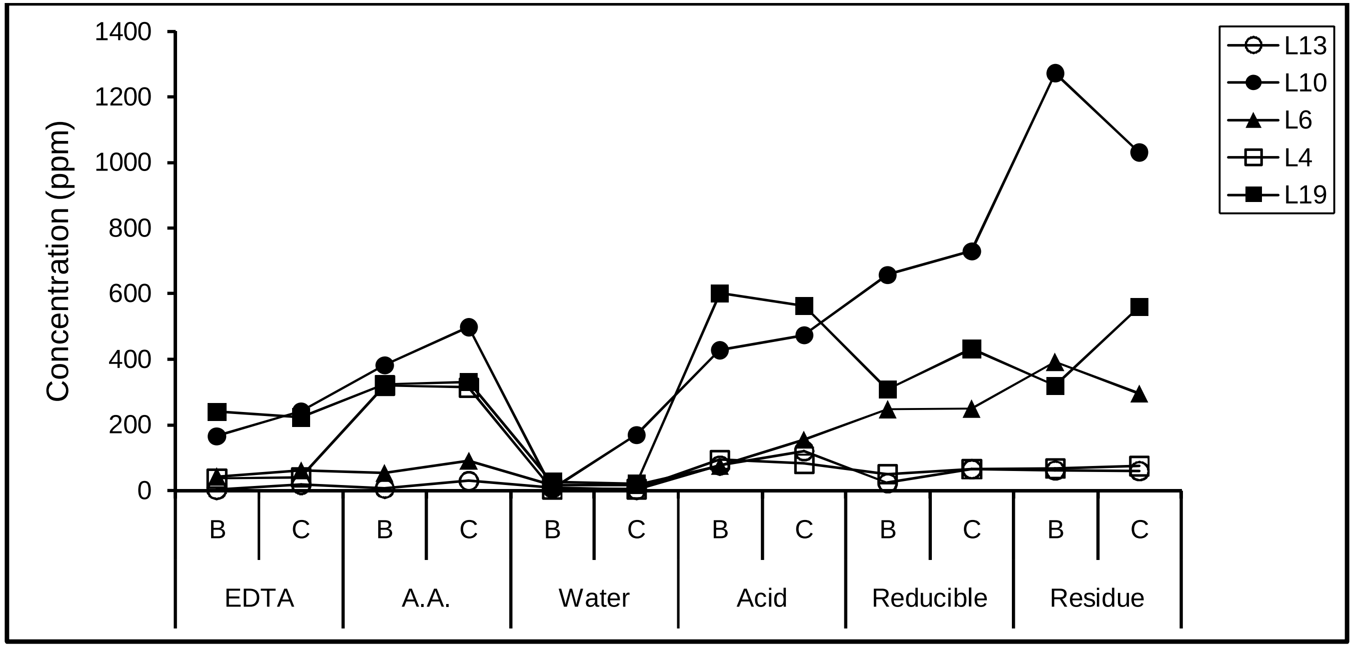


Fig. 4.54 Cu concentration in soils at different locations

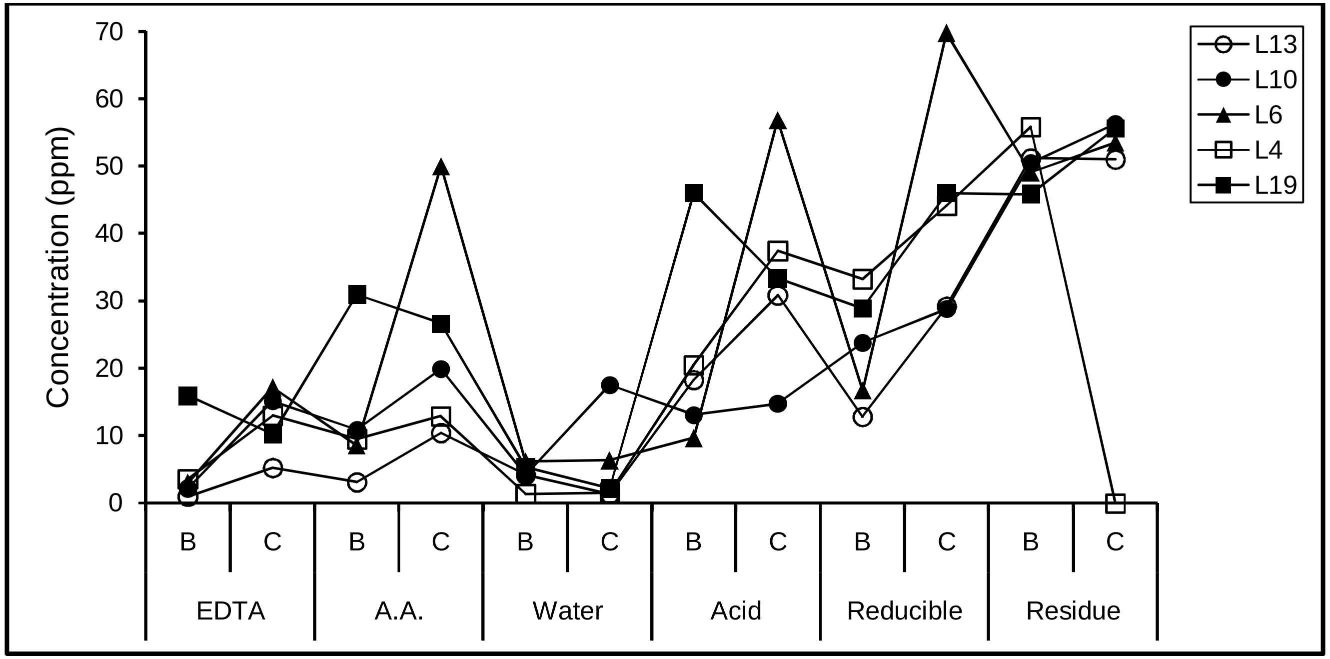


Fig. 4.55 Zn concentration in soils at different locations

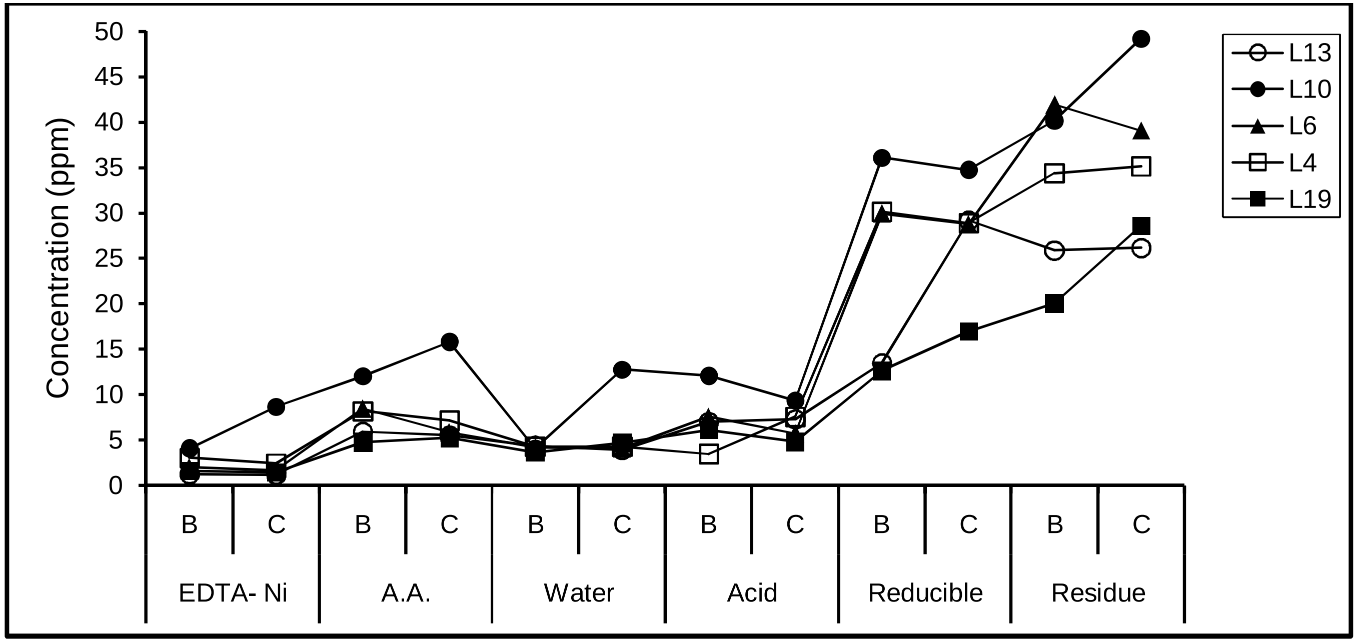


Fig. 4.56 Ni concentration in soils at different locations

The heavy metals extracted in the first step of the speciation are anthropogenic metals while those extracted in the last step i.e. residual fraction are lithogenic originated (Rauret *et al*., 1989). The analysis of water soluble fraction in the soils is important for the environmental point of view. Ni is found most mobile element in water soluble fraction followed by Zn > Cu > Pb > Cr in soils of Khetri copper mine region. Tailings also follows the same trend except Cr and Pb both are completely absent in the water soluble fraction.

Perin *et al*. (1985) proposed risk assessment code (RAC) which shows that the release of <1% of metal concentration in water soluble, exchangeable and carbonate fraction by sediments will be considered safe for the environment. The water soluble fraction for Cu, Zn and Ni in both soils and tailings of Khetri is <1% of the total metal concentration indicates the high mobility of Cu, Zn and Ni in the environment (Fig. 4.57). It is found that Zn is extracted more in water soluble fraction in soils compared to tailings. Zn is easily absorbed by the clay minerals, hydrous oxides or carbonates so Zn is more bio-available metal and get easily available into the environment (McLean and Bledose, 1992).

In soils, the exchangeable sites such as cation sites, carbonates and organic matter are present more compared to tailings. Hence, it has more exchangeable sites on which heavy metals can easily adsorbed and become available in favourable conditions. While in tailings, presence of carbonates and organic matter is supposed to be in low quantity due to absence of vegetation and dissolution of carbonates by sulphides.

Cr and Pb both are found in trace quantity in water soluble fraction of the soils compared to Cu, Zn and Ni. These three heavy metals are more mobile in soils of the Khetri copper mine region compared to Cr and Pb. Approximately 80% of the Cr fraction is bound to residual fraction in the soil.

Hence, the anthropogenic originated heavy metals are more mobile compared to geogenic originated heavy metals.

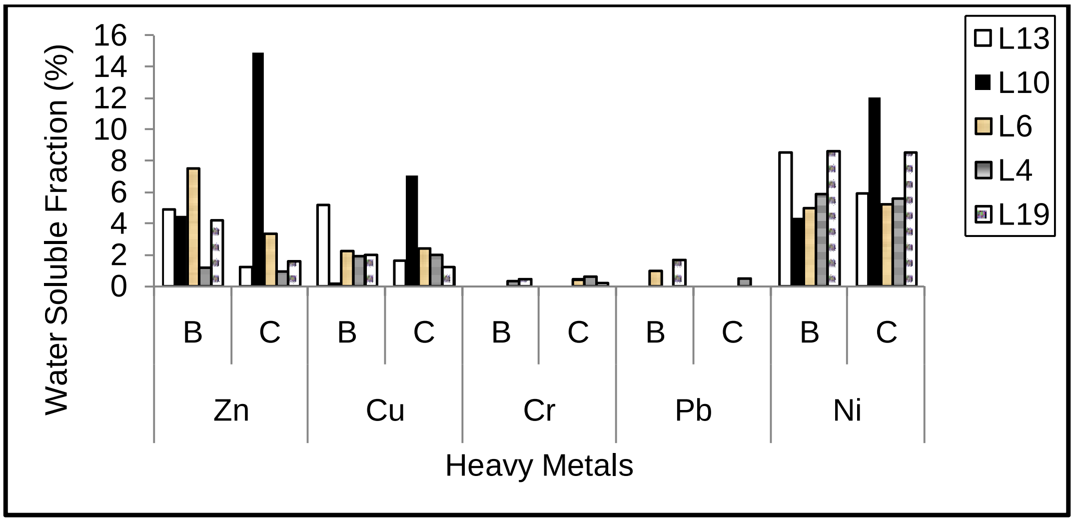


Fig. 4.57 Water soluble fraction (%) of heavy metals in soils of different locations

Section II

Source Identification, Pollution Indices and Risk Assessment

4.2 Source Identification, Pollution Indices and Risk Assessment

Information on abundance and distribution of heavy metals in the environment (tailings, soils and groundwater/surface water) alone is not sufficient to assess the pollution load in the environment. Source identification of pollutants is an important parameter in the assessment of causes of pollution. Pollution indices (Index of Geo-accumulation, Pollution index load and enrichment factor) were calculated for tailings and soils to assess the enrichment of heavy metals and pollution load in the tailings and soils. For water quality assessment, the indices namely water quality index, heavy metal pollution index, contamination index, and index of environmental risk were calculated to assess the heavy metal contamination in the groundwater and surface water of the region. In vegetables, the metal pollution index along with the average daily dose was calculated. In addition to pollution indices, the probable health risk assessment due to consumption contaminated water and vegetables were also calculated.

4.2.1 Tailings and Soils

Identification of source of heavy metals in the soils is important as these metals could have been derived from either weathering of parent or anthropogenic activities or from both. The enrichment factor (EF), index of geo-accumulation (I_{geo}) and pollution load index (PLI) were used to assess the heavy metal pollution in the soils. The results of the present study will provide the degree of heavy metal pollution in the region due to copper mines.

4.2.1.1 Source identification

The results show that the tailings and soils surrounding the mine area are contaminated with heavy metals namely Cu, Zn, Cr, Co, Ni, Mn and Fe. To identify the source of heavy metals in the soil samples the correlation matrix and PCA were used.

pH does not show any strong correlation with heavy metal concentration in tailings as shown in Table 4.21. This may be due to rapid reactions (oxidation) of sulphides with surrounding environment (Ribet *et al*., 1995). Cu shows strong positive correlation with Zn (0.98, p>0.01), Co (0.41, p>0.05) and Fe (0.57, p>0.01), and Zn is correlated with Co (0.45, p>0.05) and Fe (0.62, p>0.01). Thus, the observed lack of association among heavy metals in tailings can be attributed to selection of ore minerals, and diverse geology of Khetri region (Kaur *et al*., 2007). Hence, the composition of tailings depends upon the ratio of sulphide to gangue (silicates) during mining and milling. In addition, the extraction efficiency may not be uniform for a long time and this might affect the composition of the tailings. The observed high concentration of Cr in tailings and with no correlation with other heavy metals (Cu, Zn, Co, Mn and Fe) suggests that its source may not be same as for other elements and it could be derived from granite and amphibolites.

pH is one of the important parameters in controlling the mobility and toxicity of the heavy metals (Chuan *et al*., 1996). The correlation matrix shows a significant negative correlation of pH with Cu (-0.79, p>0.01), Zn (-0.67, p>0.01) and Fe (-0.47, p>0.05), which suggests decrease in pH of soils with contamination of soils with tailings and overburden materials. The decrease in pH is attributed to oxidation of sulphides which generates acid on reacting with oxygen and water (Akcil and Koldas, 2006).

In soils, Cu shows strong positive correlation with Zn (0.96, p>0.01), Cr (0.45, p>0.05), Co (0.68, p>0.01), Ni (0.51, p>0.01) and Fe (0.76, p>0.01), suggesting the mining source for these elements. All elements (Cu, Zn, Cr, Co, Ni, Mn and Fe) show strong correlation with each other except Pb and Cd. As already discussed both Pb and Cd are present in very low concentration in tailings compared to soils, this indicates weathering of parent rock and other anthropogenic activities as the potential sources for these elements.

Table 4.21 Correlation matrix for heavy metals in soils and tailings

	pH	**Cu**	**Zn**	**Cr**	**Cd**	**Co**	**Ni**	**Pb**	**Mn**	**Fe**
Soil										
pH	1	-0.79**	-0.67**	-0.20	0.11	-0.38	-0.25	-0.06	-0.08	-0.47*
Cu		1	0.96**	0.45*	-0.12	0.68**	0.51**	0.00	0.21	0.76**
Zn			1	0.58**	-0.04	0.74**	0.65**	0.19	0.28	0.87**
Cr				1	0.13	0.72**	0.83**	0.06	0.60**	0.81**
Cd					1	0.00	0.10	0.28	0.08	0.06
Co						1	0.87**	-0.01	0.46*	0.81**
Ni							1	0.11	0.52**	0.83**
Pb								1	0.03	0.18
Mn									1	0.45*
Fe										1
Tailings										
pH	1	0.32	0.25	0.04	-	0.10	0.31	-0.18	-0.18	-0.19

Cu	1	0.98**	-0.23	-	0.41*	0.32	-0.09	-0.04	0.57**
Zn		1	-0.18	-	0.45*	0.38	-0.04	0.00	0.62**
Cr			1	-	0.13	0.43*	-0.22	-0.23	-0.01
Cd				-	-	-	-	-	-
Co					1	0.56**	0.12	0.14	0.55**
Ni						1	-0.44*	-0.41*	0.38
Pb							1	0.99**	0.20
Mn								1	0.24
Fe									1

*Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

The PCA divides the variables into groups on the basis of their correlation with each other. Three principal components (PCs) with Eigen values >1 were extracted. The PCA lead to a reduction of the initial dimension of the dataset to three components, which explain 86.04% and 82.80% of the data variation in tailings and soils respectively. The graphical representation of three PCs for tailings and soils are shown in Fig. 4.58 & 4.59.

The first component (PC1) for soils shows the strong association of Cu, Zn, Cr, Co, Ni, Mn and Fe which explain the 55.435% of variance (Table 4.22) and these elements are found in abundant quantity in association with sulphide ores, hence their source is of mining activities. Principal ore minerals at Khetri mines are chalcopyrite, pyrrhotite and pyrite along with minor quantities of magnetite, cubanite, sphalerite, ilmenite, arsenopyrite, mackinawite, molybdenite, cobaltite and pentlandite (Sarkar and Dasgupta, 1980). For Cu chalcopyrite and cubanite, and for Fe pyrrhotite and pyrite may be the source. The sphalerite is the source for Zn, pentlandite and mackinawite for Fe and Ni, and cobaltite for Co.

In the second component (PC2), the association of Cd and Pb was identified with 15.43% of variance. The presence of Cd and Pb in the soils explains their source is weathering of parent rock, as the Cd and Pb are not found in the tailings. Hence, the PC2 explains the lithogenic source (weathering). The third component (PC3) contains only Pb with variance of 12.27%, which may be anthropogenic source other than mining activities (automobile/vehicular). The common sources of Pb in soils are lead-arsenate pesticides, manure, industrial fumes and vehicle exhausts (Kober *et al*., 1999).

For tailings, the PC1 shows the association of Cu, Zn, Co, Ni and Fe, which explains 39.11% of variance (Table 4.22). The source of these elements is sulphides such as chalcopyrite, cubanite, pyrite, pyrrhotite, cobaltite, pentlandite and mackinawite. While the PC2 contains Mn and Pb with 30.28% of variance, gangue minerals along with sulfides may be the source. The PC3 contains only Cr with a 16.65% of variance, thus the source for Cr may be granite (Carr and Turekian, 1962) and amphibolites present in the Khetri region. Hence, the source of Cu, Zn, Cr, Co, Ni, Mn and Fe in Khetri soil is mining activities while Cd and Pb are from lithogenic and other anthropogenic sources.

Table 4.22 Principle component analysis (PCA) for soils and tailings

	Soils			**Tailings**		
Parameter	**PCA 1**	**PCA 2**	**PCA 3**	**PCA 1**	**PCA 2**	**PCA 3**
Cu	0.79	-0.38	0.37	0.86	0.10	-0.42
Zn	0.88	-0.20	0.39	0.90	0.13	-0.33
Cr	0.85	0.19	-0.30	0.02	-0.48	0.73
Cd	0.05	0.81	0.08	0.00	0.00	0.00
Co	0.91	-0.09	-0.09	0.73	0.11	0.44
Ni	0.90	0.13	-0.18	0.66	-0.53	0.37
Pb	0.13	0.63	0.59	-0.10	0.94	0.29
Mn	0.56	0.26	-0.56	-0.06	0.95	0.28
Fe	0.96	0.01	0.11	0.78	0.30	0.16
Eigen value	4.99	1.36	1.10	3.13	2.42	1.33
% of variance	55.44	15.10	12.27	39.11	30.28	16.65
Cumulative %	55.44	70.53	82.80	39.11	69.39	86.04

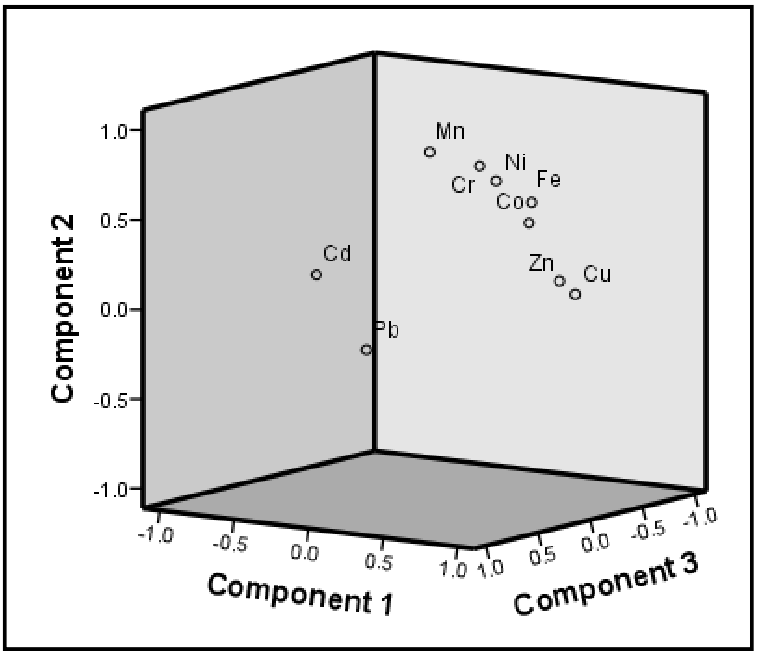


Fig. 4.58 Loading plot of PC1, PC2 and PC3 for soils

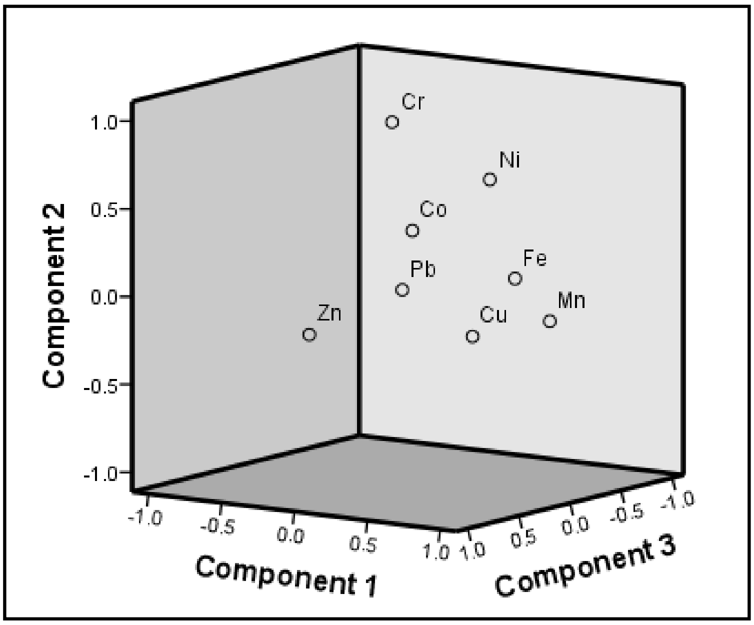


Fig. 4.59 Loading plot of PC1, PC2 and PC3 for tailings

4.2.1.2 Pollution indices

The geochemical parameters were used to calculate the pollution indices (EF, I_{geo} and PLI) for soils and tailings using the world average shale (WAS) along with the average of two regional background soils (LS).

Enrichment factor

The enrichment factor (EF) is calculated to assess the origin of heavy metals i.e. natural or anthropogenic. Al is used as normalizing element to compensate the variability in metal concentration as it is most conservative element (Summers *et al.*, 1996). EF is calculated using formula (Eq. 1) given by Buat-Ménard and Chesselet (1979).

$$EF = \frac{(M_n / Al)_{Sample}}{(M_n / Al)_{Background}} \quad \text{--(1)}$$

Where, $(M_n/Al)_{Sample}$ is the metal and Al concentration in the sample, $(M_n/Al)_{Backround}$ is the metal and Al concentration in the background. The LS and WAS (Turekian and Wedepohl, 1961) were used as background.

The level of enrichment is divided into five grades namely, <2 (depletion to minimal enrichment), 2-5 (moderate enrichment), 5-20 (significant enrichment), 20-40 (very highly enriched) and >40 (extremely enriched) (Sutherland, 2000).

The soils and tailings are highly contaminated in terms of EF calculated using WAS as a background (Table 4.23). The average EF for Cu in soils is 6.53 ± 15.05 which shows significant enrichment, and for other heavy metals it is depletion to minimal enrichment (<2) i.e. 1.08 ± 0.94 for Zn, 1.12 ± 0.35 for Cr, 0.85 ± 1.03 for Co, 0.55 ± 0.34 for Ni, 1.26 ± 0.54 for Pb, 0.65 ± 0.54 for Mn, 0.99 ± 0.49 for Fe and 0.41 ± 0.81 for Cd (Fig. 4.60). The maximum EF for Cu is 67.4 (extremely enriched) is observed in the soils near overburden materials at L10 and 35.0 (very highly enriched) at L19.

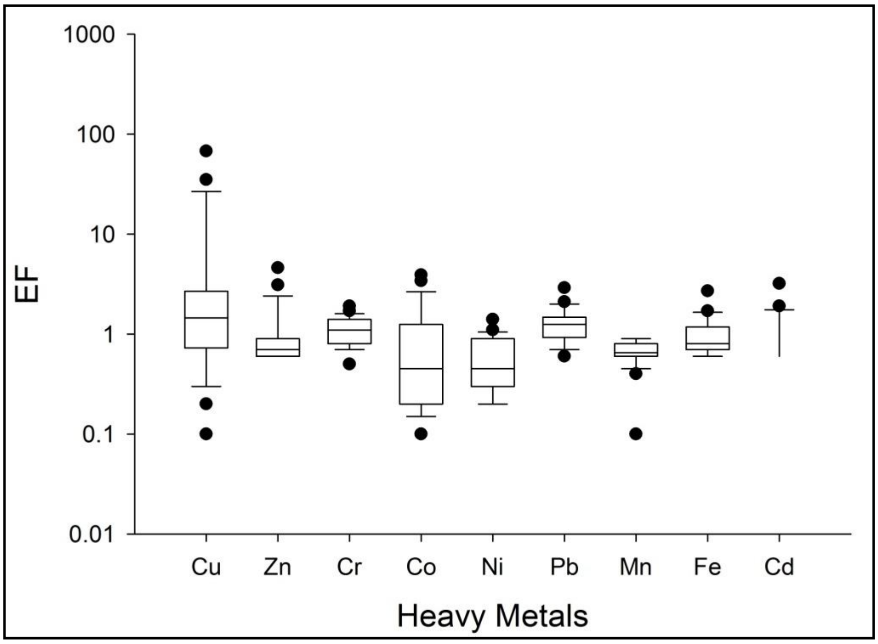


Fig. 4.60 Box plot showing the average values of EF in soils of Khetri region

Table 4.23 EF for soils using WAS as a background

Sample location	Cu	Zn	Cr	Co	Ni	Pb	Mn	Fe	Cd
L1	0.9	0.6	1.7	0.6	0.5	0.9	0.8	0.9	0.7
L2	0.4	0.6	1.0	0.2	0.5	1.4	0.6	0.7	1.9
L3	0.9	0.6	1.0	0.0	0.5	0.0	0.5	0.6	0.0
L4	1.9	0.9	1.5	1.4	1.0	1.0	0.7	1.2	0.0
L5	2.3	0.9	1.5	1.6	1.1	1.2	0.8	1.3	0.3
L6	18.4	1.5	1.2	3.4	1.0	0.8	0.6	1.1	0.0
L7	0.6	0.6	0.5	0.1	0.3	0.9	0.4	0.9	0.0
L8	6.3	1.6	1.4	1.8	1.0	1.9	0.7	1.6	0.9
L9	6.6	1.7	1.5	1.9	1.0	2.1	0.7	1.5	1.3
L10	67.4	4.6	1.9	3.9	1.4	0.6	0.9	2.7	0.0

L11	0.7	0.6	0.8	0.2	0.3	1.4	0.6	0.6	3.2
L12	2.8	0.9	1.0	0.8	0.6	1.4	0.6	0.9	1.6
L13	1.2	0.7	1.4	0.5	0.5	1.2	0.8	0.8	0.0
L14	1.0	0.6	0.8	0.2	0.2	1.5	0.7	0.6	0.0
L15	1.6	0.7	1.1	0.3	0.3	1.2	0.8	0.7	0.0
L16	1.5	0.8	1.2	0.7	0.3	0.9	0.9	1.0	0.0
L17	0.7	0.7	0.8	0.4	0.4	1.6	0.7	0.8	0.0
L18	0.8	0.6	0.7	0.2	0.3	1.2	0.6	0.7	0.0
L19	35.0	3.1	1.2	0.4	0.5	2.9	0.6	1.7	0.0
L20	2.0	0.7	0.7	0.2	0.3	1.0	0.6	0.7	0.0
L21	0.1	0.6	0.8	0.3	0.2	1.5	0.5	0.6	0.0
L22	0.2	0.6	0.9	0.2	0.2	1.4	0.6	0.6	0.0
L23	1.4	0.8	1.1	0.5	0.4	1.3	0.1	0.8	0.0
L24	1.9	0.9	1.2	0.6	0.4	1.3	0.9	0.8	0.0
Minimum	0.1	0.6	0.5	0.0	0.2	0.0	0.1	0.6	0.0
Maximum	67.4	4.6	1.9	3.9	1.4	2.9	0.9	2.7	3.2
Average	6.5	1.1	1.1	0.8	0.5	1.3	0.7	1.0	0.4
STDEV	15.1	0.9	0.3	1.0	0.3	0.5	0.2	0.5	0.8
Median	1.5	0.7	1.1	0.4	0.4	1.2	0.7	0.8	0.0

The average EF for Cu in tailings is much higher compared to soils. For Cu, it is 65 ± 39.8 which falls in the extremely enrichment, and for other heavy metals it is in the moderate enrichment (2-5) zone i.e. 4.5 ± 2.7 for Zn, 3.9 ± 1.2 for Co, 3.5 ± 17.6 for Ni, 3.3 ± 4.0 for Mn and 3.9 ± 0.5 for Fe (Table 4.24 & Fig. 4.61).

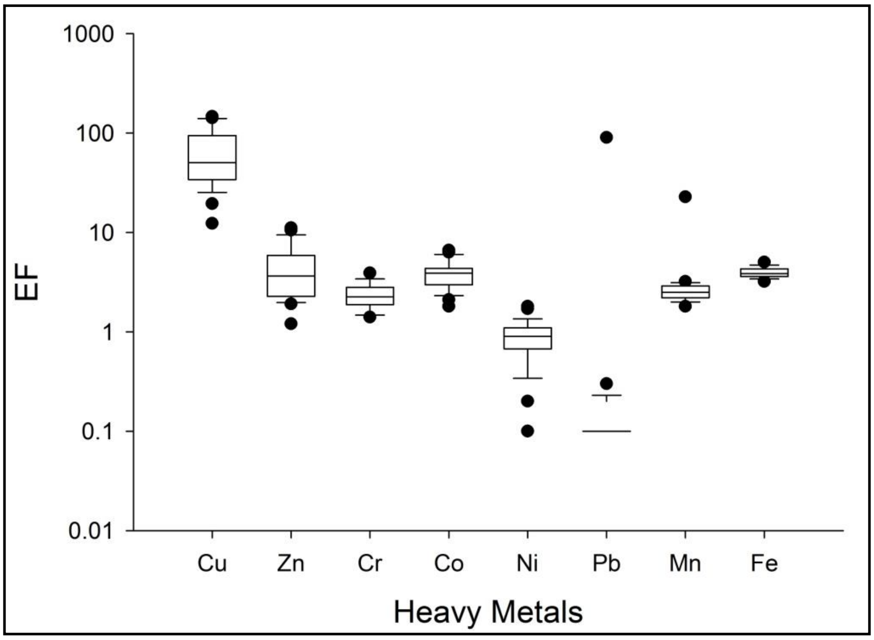


Fig. 4.61 Box plot showing the average values of EF in tailings of Khetri region

Table 4.24 EF for tailings using WAS as a background

Sample location	Depth wise sampling points	Cu	Zn	Cr	Co	Ni	Pb	Mn	Fe
S1	T1	102.1	6.1	2.2	3.6	0.7	0.0	2.9	4.7
	T2	91.8	5.7	2.5	4.6	1.2	0.3	2.9	4.5
	T3	80.7	5.5	1.4	3.9	0.8	0.0	2.7	3.9
S2	T1	103.6	6.6	1.9	4.0	1.0	0.0	2.2	3.6
S3	T1	139.7	11.1	2.3	6.3	1.8	0.0	3.1	5.0
	T2	146.1	10.5	2.5	3.0	1.0	0.0	3.2	4.7
	T3	69.8	4.3	3.1	4.2	1.0	0.0	3.0	4.0
	T4	31.1	2.1	1.6	2.1	0.2	0.1	2.6	3.5
	T5	29.2	2.0	3.4	3.5	0.7	0.0	2.2	3.4

S4	T1	33.9	2.3	2.1	2.9	0.7	0.2	1.8	3.2
	T2	27.8	2.0	2.0	1.8	0.4	0.1	2.4	3.4
	T3	141.4	9.0	1.8	6.6	0.6	0.0	2.5	4.2
S5	T1	33.9	2.2	2.2	3.0	0.8	0.0	2.4	3.6
	T2	65.8	4.1	2.3	2.7	1.1	0.0	2.4	3.7
	T3	118.3	8.2	2.3	3.9	1.1	0.0	2.6	3.9
	T4	87.4	5.8	2.1	3.7	1.0	0.1	2.5	3.7
S6	T1	51.6	3.6	3.3	4.7	1.1	0.0	2.7	3.8
	T2	48.3	3.4	1.4	4.5	1.0	0.2	2.4	3.9
S7	T1	12.3	1.2	3.2	2.4	0.6	0.1	2.1	3.5
	T2	55.3	4.4	3.9	4.2	1.1	0.1	2.0	3.8
	T3	34.1	2.6	2.7	2.4	0.6	0.1	2.0	3.8
S8	T1	49.1	3.2	1.8	4.3	0.8	0.2	3.0	4.3
	T2	36.7	2.6	2.0	3.9	0.9	0.2	2.6	4.3
	T3	35.1	2.8	2.4	4.2	0.9	0.2	2.2	4.3
S9	T1	19.4	1.9	3.4	5.9	1.7	0.2	2.3	3.7
	T2	45.9	3.7	1.5	4.3	0.1	89.8	22.7	4.1
	Minimum	12.3	1.2	1.4	1.8	0.1	0.0	1.8	3.2
	Maximum	146.1	11.1	3.9	6.6	1.8	89.8	22.7	5.0
	Average	65.0	4.5	2.4	3.9	0.9	3.5	3.3	3.9
	STDEV	39.8	2.7	0.7	1.2	0.4	17.6	4.0	0.5
	Median	50.3	3.7	2.2	3.9	0.9	0.1	2.5	3.9

Index of geo-accumulation

Index of geo-accumulation (I_{geo}) for heavy metals given by Muller (1969) is used to assess accumulation of heavy metals in the soils and tailings (Eq. 2).

$$I_{geo} = Log_2\left(\frac{C_n}{1.5 \times B_n}\right) \qquad \text{--(2)}$$

Where C_n is the metal concentration in the sample and B_n is the metal concentration in the background (WAS and LS) and 1.5 is used as a correction factor for possible lithological variations.

Using I_{geo} the sites are classified into six categories namely, uncontaminated (I_{geo}<0), uncontaminated to moderately contaminated (I_{geo}= 0-1), moderately contaminated (I_{geo}= 1-2), moderately to strongly contaminated (I_{geo}= 2-3), strongly contaminated (I_{geo}= 3-4), strongly to extremely contaminated (I_{geo}= 4-5) and extremely contaminated with I_{geo} value ≥5. The elemental concentrations having I_{geo} value ≥5 may be hundred fold greater than the geochemical background value.

In soils, average I_{geo} (Fig. 4.62 & 4.63) using LS as a background for Cu falls in moderately to strongly contaminated zone (2.58±2.22) and for Co it is in moderately contaminated zone (1.39±1.50). While using WAS as a background, average I_{geo} for all heavy metals falls in the uncontaminated to moderately contaminated zone. Hence, on using LS as a background average I_{geo} is higher compared to WAS suggesting high contamination in the region with respect to LS. Many studies (Rastmanesh *et al*., 2011; Li *et al*., 2014; Mileusnić *et al*., 2014) reported high values of I_{geo} for Cu in the copper mining area in different parts of the world but in the present study along with Cu, Co also have high values of I_{geo}.

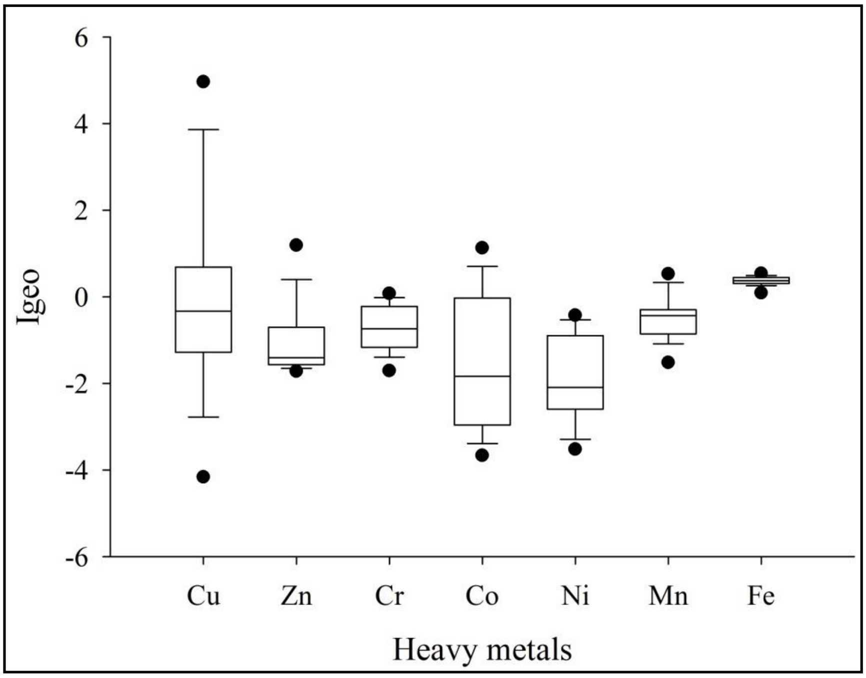


Fig. 4.62 Box plot showing average I_{geo} values for soils using WAS as a background

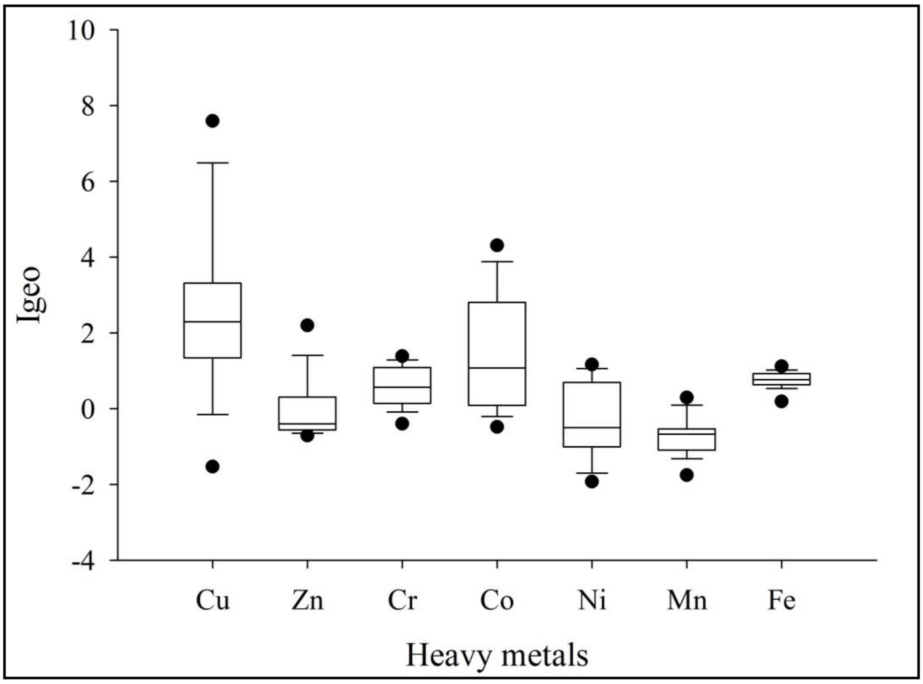


Fig. 4.63 Box plot showing average I_{geo} values for soils using LS as a background

In the study area I_{geo} values for Cu falls in strong to extremely contaminated zone at sites (L10, L19, L8, L9 & L12) located in the windward direction and at close vicinity of overburden material and tailings (Fig. 4.66 & 4.67). While sites (L20, L23 & L24) located in the windward (during summer season) direction of mines are found in moderate to strongly contaminated zone for Cu. The average I_{geo} rank order for heavy metals in the soils is Cu > Co > Mn > Cr > Zn > Fe > Ni > Pb. The GSI, 1977 reported the presence of Co mineralisation associated with Cu and Fe pyrites present in the region.

The average values of I_{geo} (Fig. 4.64 & 4.65) for tailings are much higher than those of soils. In tailings, average I_{geo} using LS for Cu falls in extremely contaminated zone (7.28±0.92) and for Co it is in strongly to extremely contaminated zone (4.0±0.50). While, using WAS as a background average I_{geo} for Cu falls in strongly to extremely contaminated zone. The rank order of average I_{geo} in tailings is Cu > Co > Zn > Fe > Cr > Mn > Ni. The I_{geo} values are in low range for tailings (S7 to S9) which are mixed with soil that diluted the effect (Fig. 4.68 & 4.69).

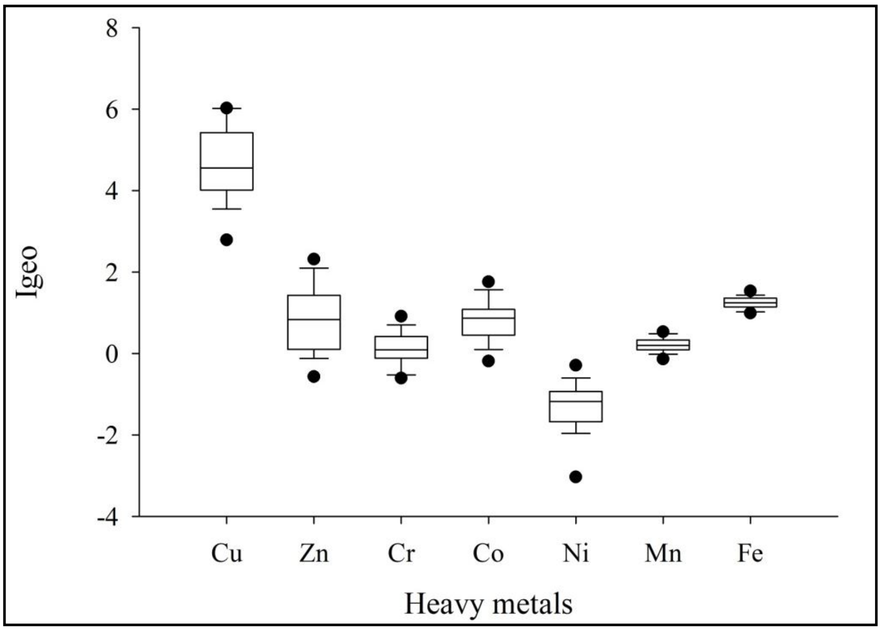


Fig. 4.64 Box plot showing average I_{geo} values for tailings using WAS as a background

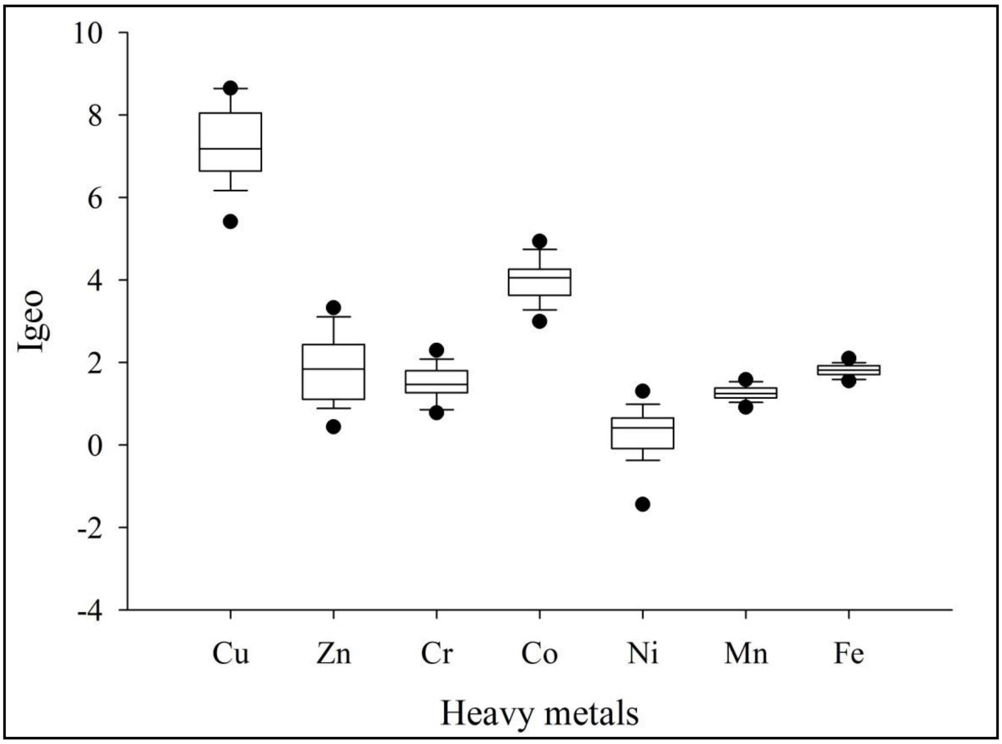


Fig. 4.65 Box plot showing average I_{geo} values for tailings using LS as a background

Cu and Co which are found in higher concentrations in tailings are also found in higher concentration in soils (average I_{geo} is high in both). Thus, the study further confirms the transport of sulpides (heavy metals) from tailings and overburden material to the neighbouring soils. Although majority of the studies (Navarro *et al*., 2008; Meza-Figueroa *et al*., 2009; Mileusnić *et al*., 2014) concerned with the dispersal of sulphides from tailings but dispersal of sulphides from overburden material cannot neglected. Hence, a further detailed study is needed to assess the dispersal of heavy metals bearing sulphides from overburden material.

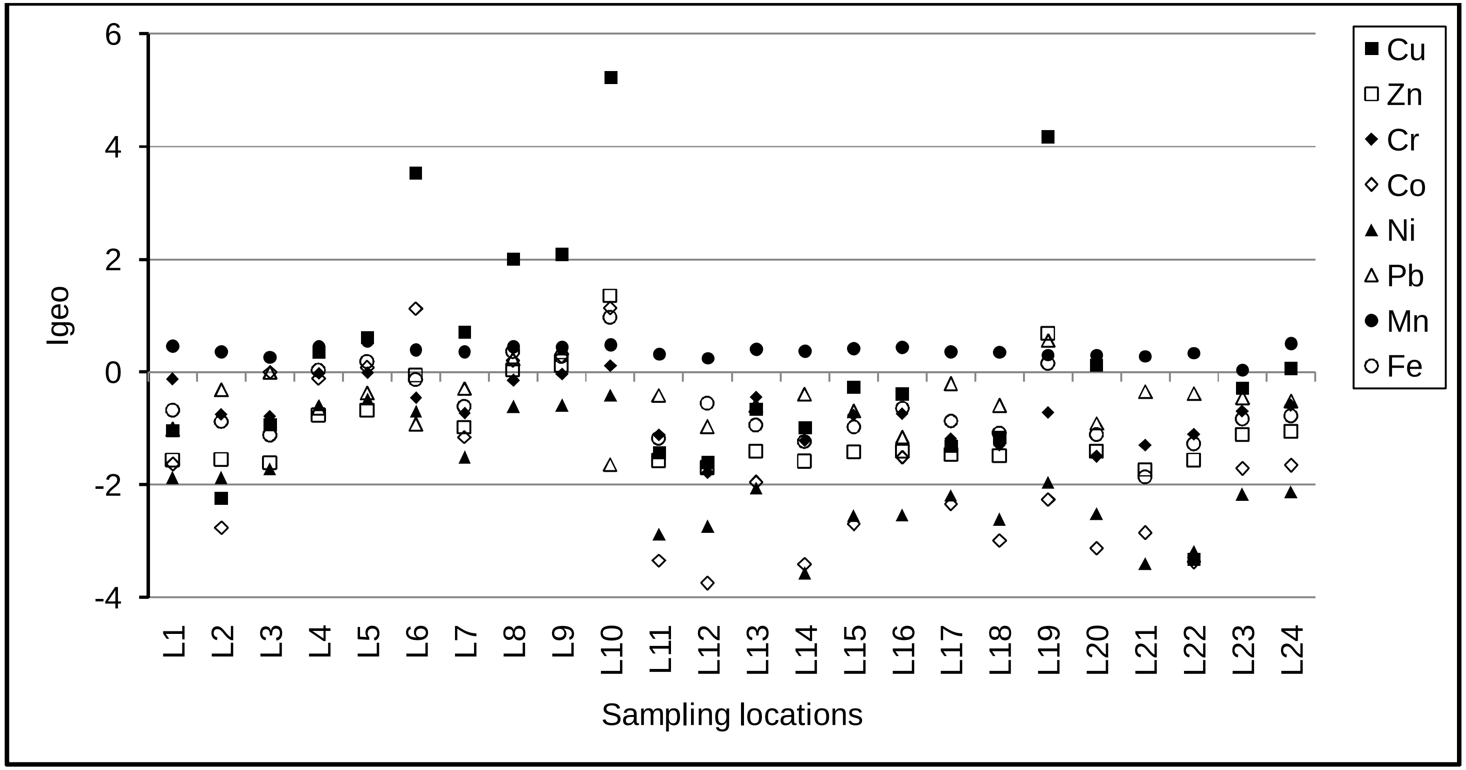


Fig. 4.66 Plot showing I_{geo} values for soils using WAS as a background.

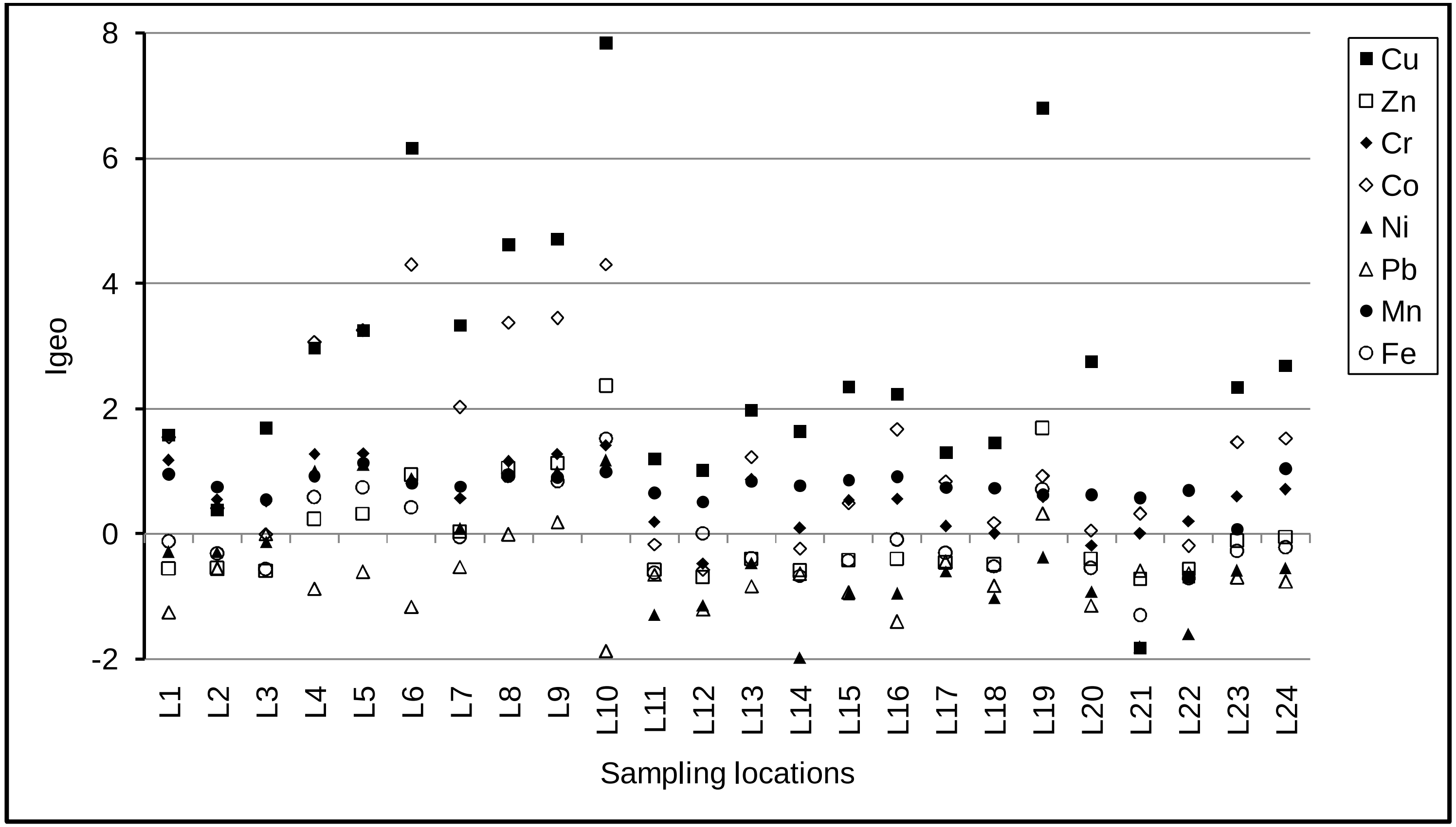


Fig. 4.67 Plot showing I_{geo} values for soils using LS as a background

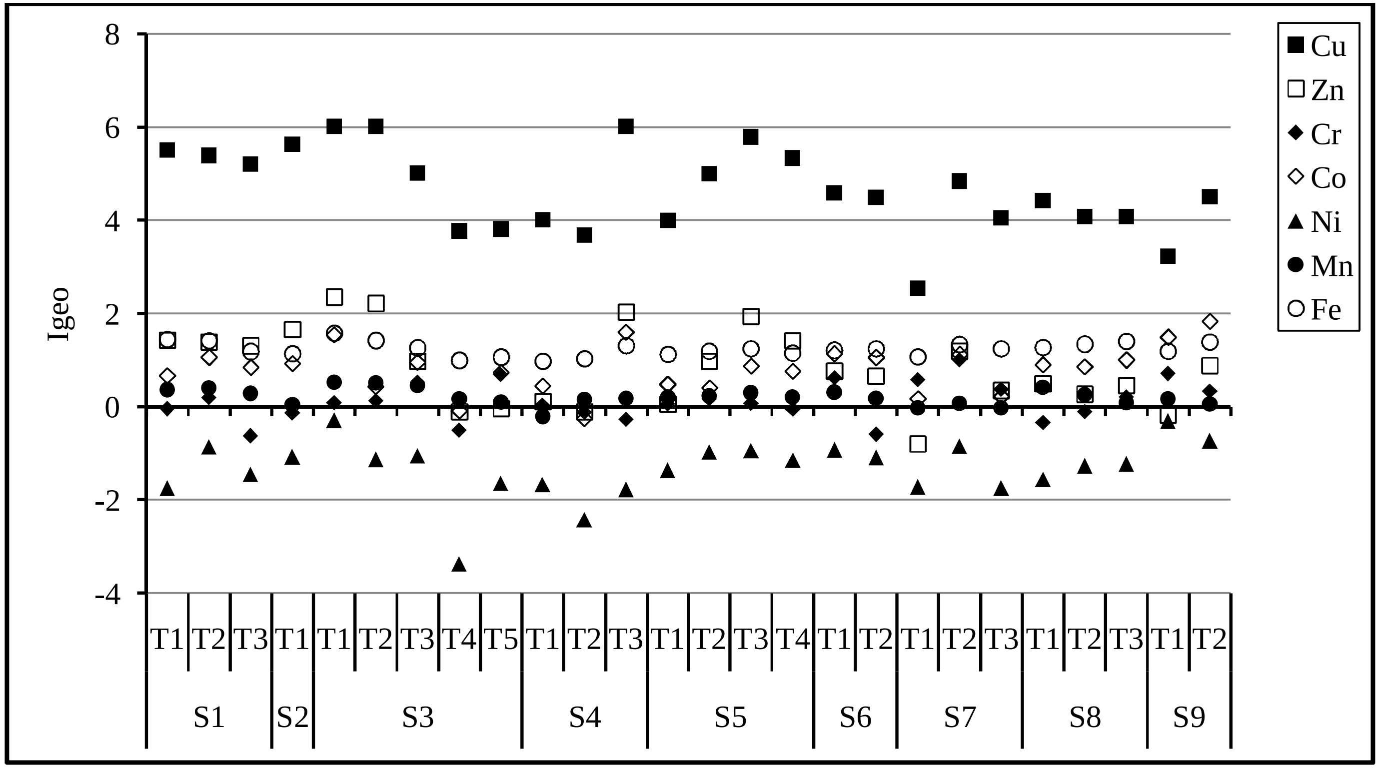


Fig. 4.68 Plot showing I_{geo} values for tailings using WAS as a background

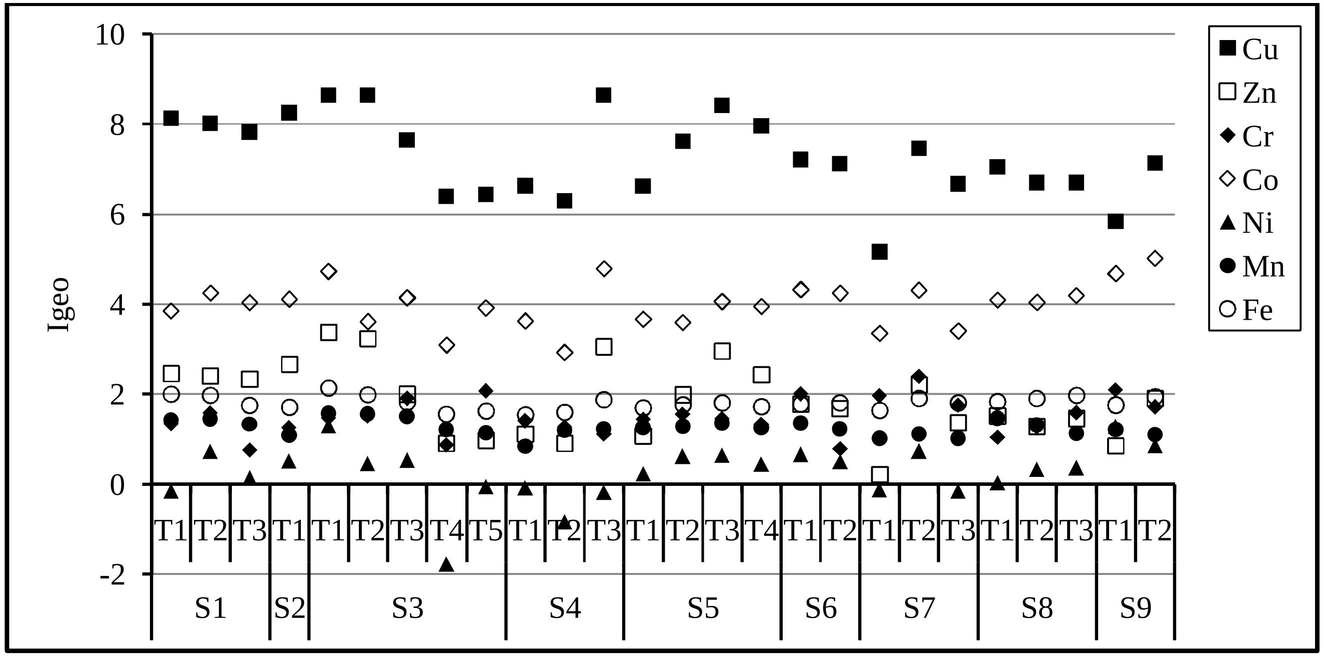


Fig. 4.69 Plot showing I_{geo} values for tailings using LS as a background

Pollution load index

The extent of pollution load in soils and tailings were evaluated using Tomlinson *et al*. (1980) method using Eq. 3

$$\mathrm{PLI} = \left(\mathrm{CF}_1 \times \mathrm{CF}_2 \ldots \mathrm{CF}_n\right)^{1/n} \qquad \text{--(3)}$$

Where, PLI is pollution load index, CF is contamination factor for each metal and n is the number of metal.

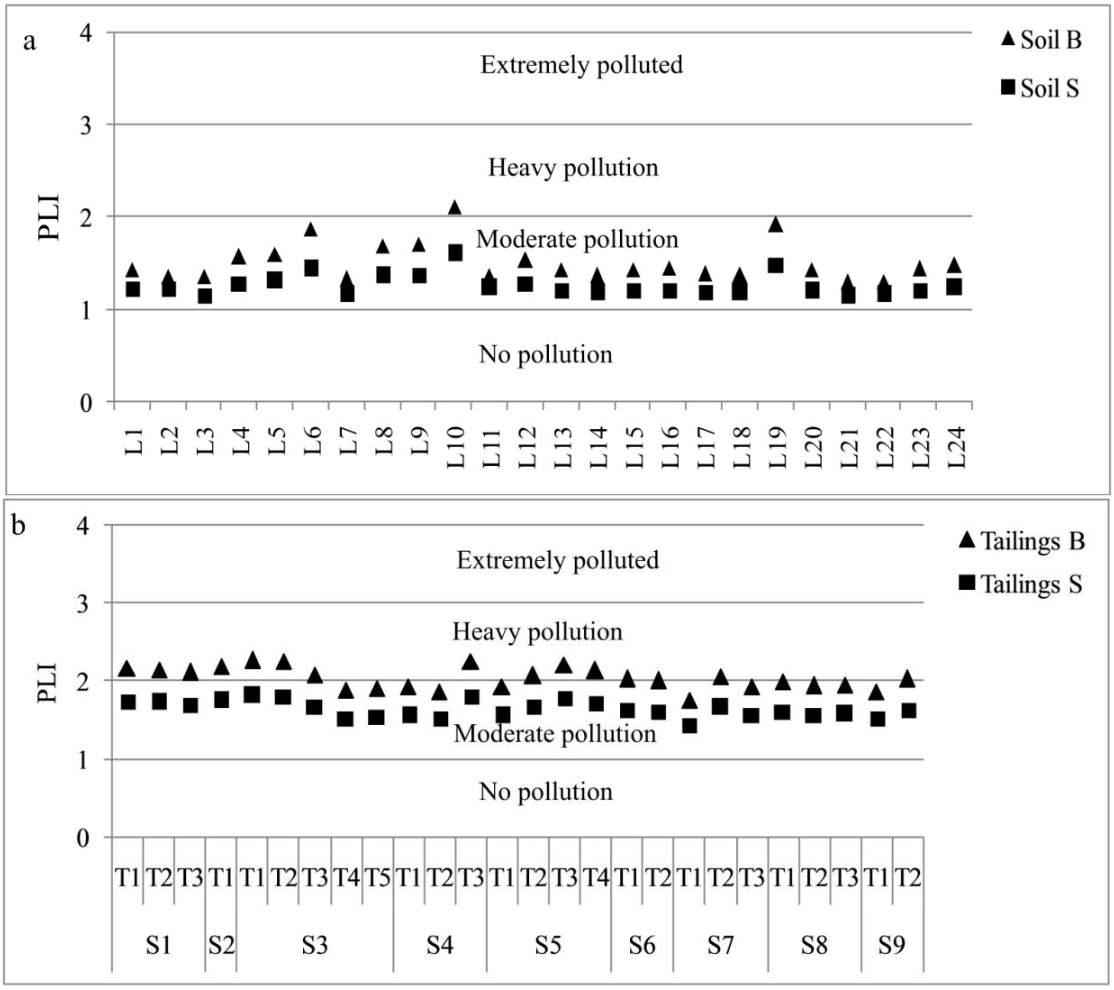
The contamination factor (CF) is calculated using Eq. 4

$$\mathrm{CF} = \frac{M_{\mathrm{sample}}}{M_{\mathrm{background}}} \qquad \text{--(4)}$$

Where, M_{sample} is the metal concentration in the sample and $M_{\mathrm{background}}$ is the metal concentration in the background i.e. WAS and LS. The pollution level have been classified into four categories depending upon the PLI values i.e. no pollution (PLI <1), moderate pollution (1<PLI<2), heavy pollution (2<PLI<3) and extreme pollution (3<PLI) (Tomlinson *et al*., 1980).

The calculated PLI shows that the soils and tailings are contaminated with heavy metals. The calculated values of CF for each site for soils and tailings are given in Table 4.25 & 4.26 respectively. The calculated values of PLI for both soils and tailings are shown in Fig. 4.70 a & b respectively. The PLI calculated using LS is higher compared to WAS. The average PLI for soils using WAS as a background is 1.26±0.12 with the highest 1.60 at L10 followed by the 1.49 at L19. The average PLI using regional soil is 1.51±0.21 with the highest 2.11 at L10 and 1.92 at L19.

The PLI is >2 in almost all of the tailings showing strong contamination using LS. The average PLI for tailings is 1.64±0.10 and 2.03±0.14 using WAS and LS respectively. According to PLI the soils of the Khetri region falls in the moderate pollution zone and tailings in the heavy pollution zone.



$^{\text{Soil B}}$PLI using WAS as a background
$^{\text{Soil S}}$PLI using LS as a background
$^{\text{Tailings B}}$PLI using WAS as a background
$^{\text{Tailings S}}$PLI using LS as a background

Fig. 4.70 Plot showing the average PLI values for soils and tailings using LS and WAS as background values

Table 4.25 CF for soils using WAS and LS as a background

Sample location	Cu		Zn		Cr		Co		Ni		Pb		Mn		Fe		Cd	
	B	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**
L1	4.5	0.7	1.0	0.5	3.6	1.4	4.4	0.5	1.2	0.4	0.6	0.7	1.4	0.7	1.4	0.9	-	0.55
L2	2.0	0.3	1.0	0.5	2.3	0.9	2.0	0.2	1.2	0.4	1.0	1.2	1.1	0.5	1.2	0.8	-	1.66
L3	4.8	0.8	1.0	0.5	2.3	0.9	0.0	0.0	1.4	0.5	0.0	0.0	0.8	0.4	1.0	0.7	-	0.00
L4	11.8	1.9	1.8	0.9	3.8	1.5	12.5	1.4	3.0	1.0	0.8	1.0	1.4	0.7	2.3	1.5	-	0.01
L5	14.2	2.3	1.9	0.9	3.9	1.5	14.3	1.6	3.2	1.1	1.0	1.2	1.7	0.8	2.5	1.7	-	0.33
L6	107.3	17.5	2.9	1.4	2.8	1.1	29.5	3.3	2.8	0.9	0.7	0.8	1.2	0.6	2.0	1.4	-	0.00
L7	3.0	0.5	0.9	0.5	1.1	0.4	1.0	0.1	0.7	0.2	0.7	0.8	0.8	0.4	1.5	1.0	-	0.00
L8	37.0	6.0	3.1	1.5	3.5	1.4	15.6	1.7	3.0	1.0	1.5	1.8	1.4	0.7	2.8	1.9	-	0.86
L9	39.1	6.4	3.3	1.6	3.8	1.5	16.4	1.8	3.0	1.0	1.7	2.0	1.4	0.7	2.7	1.8	-	1.21
L10	345.8	56.3	7.7	3.8	4.2	1.6	29.6	3.3	3.4	1.1	0.4	0.5	1.5	0.7	4.3	2.9	-	0.00
L11	3.4	0.6	1.0	0.5	1.8	0.7	1.3	0.1	0.6	0.2	1.0	1.1	1.0	0.5	1.0	0.7	-	2.58

L12	15.1	2.5	1.5	0.8	2.3	0.9	6.1	0.7	1.6	0.5	1.0	1.2	1.1	0.6	1.4	1.0	-	1.46
L13	5.9	1.0	1.1	0.6	2.9	1.1	3.5	0.4	1.1	0.4	0.8	1.0	1.3	0.6	1.1	0.8	-	0.00
L14	4.7	0.8	1.0	0.5	1.7	0.6	1.3	0.1	0.4	0.1	1.0	1.1	1.2	0.6	0.9	0.6	-	0.00
L15	7.6	1.2	1.1	0.6	2.3	0.9	2.1	0.2	0.8	0.3	0.8	0.9	1.3	0.6	1.1	0.8	-	0.00
L16	7.1	1.1	1.1	0.6	2.3	0.9	4.8	0.5	0.8	0.3	0.6	0.7	1.4	0.7	1.4	1.0	-	0.00
L17	3.7	0.6	1.1	0.5	1.7	0.7	2.7	0.3	1.0	0.3	1.1	1.3	1.1	0.5	1.2	0.8	-	0.00
L18	4.1	0.7	1.1	0.5	1.6	0.6	1.7	0.2	0.7	0.2	0.8	1.0	1.1	0.5	1.1	0.7	-	0.00
L19	167.2	27.2	4.8	2.4	2.4	0.9	2.8	0.3	1.2	0.4	1.9	2.2	0.9	0.5	2.5	1.7	-	0.00
L20	10.1	1.6	1.1	0.6	1.4	0.5	1.6	0.2	0.8	0.3	0.7	0.8	0.9	0.5	1.0	0.7	-	0.03
L21	0.4	0.1	0.9	0.5	1.6	0.6	1.9	0.2	0.4	0.1	1.0	1.2	0.9	0.4	0.6	0.4	-	0.00
L22	0.9	0.2	1.0	0.5	1.8	0.7	1.3	0.1	0.5	0.2	1.0	1.2	1.0	0.5	0.9	0.6	-	0.00
L23	7.6	1.2	1.4	0.7	2.4	0.9	4.1	0.5	1.0	0.3	0.9	1.1	0.1	0.1	1.2	0.8	-	0.00
L24	9.6	1.6	1.4	0.7	2.6	1.0	4.3	0.5	1.0	0.3	0.9	1.0	1.6	0.8	1.3	0.9	-	0.00
Mini	0.4	0.1	0.9	0.5	1.1	0.4	0.0	0.0	0.4	0.1	0.0	0.0	0.1	0.1	0.6	0.4	-	0.00

Max	345.8	56.3	7.7	3.8	4.2	1.6	29.6	3.3	3.4	1.1	1.9	2.2	1.7	0.8	4.3	2.9	-	2.58
Average	34.0	5.5	1.8	0.9	2.5	1.0	6.9	0.8	1.5	0.5	0.9	1.1	1.2	0.6	1.6	1.1	-	0.36
STDEV	76.7	12.5	1.6	0.8	0.9	0.3	8.5	0.9	1.0	0.3	0.4	0.5	0.3	0.2	0.9	0.6	-	0.00
Median	7.3	1.2	1.1	0.6	2.3	0.9	3.2	0.4	1.1	0.4	0.9	1.1	1.1	0.6	1.3	0.9	-	0.69

[B] LS as a background
[S] WAS as a background

Table 4.26 CF for tailings using WAS and LS as a background

Sample location	**Depth wise sampling points**	**Cu**		**Zn**		**Cr**		**Co**		**Ni**		**Pb**		**Mn**		**Fe**	
		B	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**	**B**	**S**
S1	T1	420.9	68.5	8.2	4.1	3.8	1.5	21.5	2.4	1.3	0.4	0.0	0.0	4.0	1.9	6.0	4.1
	T2	387.5	63.1	7.9	3.9	4.5	1.7	28.4	3.1	2.5	0.8	0.2	0.2	4.1	2.0	5.9	4.0
	T3	341.3	55.5	7.5	3.8	2.5	1.0	24.5	2.7	1.7	0.6	0.0	0.0	3.8	1.8	5.0	3.4
S2	T1	457.1	74.4	9.5	4.7	3.6	1.4	25.9	2.9	2.2	0.7	0.0	0.0	3.2	1.6	4.9	3.3

S3	T1	597.3	97.2	15.5	7.7	4.2	1.6	39.6	4.4	3.7	1.2	0.0	0.0	4.5	2.2	6.6	4.5
	T2	599.2	97.5	14.1	7.0	4.3	1.7	18.3	2.0	2.1	0.7	0.0	0.0	4.5	2.2	5.9	4.0
	T3	299.2	48.7	6.0	3.0	5.6	2.2	26.4	2.9	2.2	0.7	0.0	0.0	4.3	2.1	5.3	3.6
	T4	126.8	20.6	2.8	1.4	2.8	1.1	12.8	1.4	0.4	0.1	0.0	0.0	3.5	1.7	4.4	3.0
	T5	130.1	21.2	2.9	1.5	6.3	2.4	22.6	2.5	1.5	0.5	0.0	0.0	3.3	1.6	4.6	3.1
S4	T1	149.1	24.3	3.3	1.6	4.0	1.5	18.5	2.0	1.4	0.5	0.1	0.1	2.7	1.3	4.4	3.0
	T2	118.6	19.3	2.8	1.4	3.6	1.4	11.4	1.3	0.8	0.3	0.1	0.1	3.5	1.7	4.5	3.1
	T3	598.1	97.3	12.4	6.2	3.3	1.3	41.2	4.6	1.3	0.4	0.0	0.0	3.5	1.7	5.5	3.7
S5	T1	148.1	24.1	3.1	1.6	4.1	1.6	19.0	2.1	1.8	0.6	0.0	0.0	3.6	1.7	4.9	3.3
	T2	295.2	48.0	5.9	3.0	4.4	1.7	18.0	2.0	2.3	0.8	0.0	0.0	3.7	1.8	5.1	3.4
	T3	511.6	83.3	11.6	5.8	4.1	1.6	24.9	2.8	2.4	0.8	0.0	0.0	3.9	1.9	5.3	3.6
	T4	374.0	60.9	8.1	4.0	3.8	1.5	23.1	2.6	2.0	0.7	0.0	0.1	3.6	1.7	4.9	3.3
S6	T1	223.1	36.3	5.1	2.6	6.0	2.3	30.0	3.3	2.4	0.8	0.0	0.0	3.9	1.9	5.1	3.5
	T2	207.6	33.8	4.8	2.4	2.6	1.0	28.3	3.1	2.1	0.7	0.1	0.1	3.5	1.7	5.2	3.6

S7	T1	53.9	8.8	1.7	0.9	5.9	2.3	15.3	1.7	1.4	0.5	0.0	0.1	3.1	1.5	4.7	3.2
	T2	266.1	43.3	6.9	3.4	7.9	3.0	29.7	3.3	2.5	0.8	0.1	0.1	3.3	1.6	5.6	3.8
	T3	153.2	24.9	3.8	1.9	5.1	2.0	15.8	1.8	1.3	0.4	0.1	0.1	3.1	1.5	5.3	3.6
S8	T1	199.0	32.4	4.3	2.1	3.1	1.2	25.5	2.8	1.5	0.5	0.1	0.2	4.2	2.0	5.4	3.6
	T2	156.0	25.4	3.6	1.8	3.6	1.4	24.6	2.7	1.9	0.6	0.1	0.1	3.7	1.8	5.6	3.8
	T3	156.1	25.4	4.1	2.1	4.5	1.7	27.3	3.0	1.9	0.6	0.1	0.2	3.3	1.6	5.9	4.0
S9	T1	86.3	14.0	2.7	1.3	6.4	2.5	38.3	4.2	3.7	1.2	0.1	0.1	3.5	1.7	5.1	3.4
	T2	210.0	34.2	5.6	2.8	4.9	1.9	48.5	5.4	2.7	0.9	0.1	0.2	3.2	1.6	5.8	3.9
	Min	53.9	8.8	1.7	0.9	2.5	1.0	11.4	1.3	0.4	0.1	0.0	0.0	2.7	1.3	4.4	3.0
	Max	599.2	97.5	15.5	7.7	7.9	3.0	48.5	5.4	3.7	1.2	0.2	0.2	4.5	2.2	6.6	4.5
	Average	279.4	45.5	6.3	3.1	4.4	1.7	25.4	2.8	2.0	0.7	0.1	0.1	3.6	1.8	5.3	3.6
	STDEV	216.5	35.2	5.4	2.7	4.1	1.6	24.8	2.7	2.0	0.7	0.0	0.0	3.6	1.7	5.3	3.6
	Median	166.8	27.1	3.7	1.9	1.3	0.5	8.9	1.0	0.7	0.2	0.1	0.1	0.4	0.2	0.6	0.4

[B] LS as a background

[S] WAS as a background

Pollution indices (EF, I_{geo} and PLI) show that the soils and tailings are highly contaminated with heavy metals. The values of I_{geo} and PLI are high when LS is used as a background compared to that of WAS. Hence, the soils and tailings are highly contaminated compared to regional background soil.

4.2.2 Major Ions of Groundwater

Along with the heavy metals, the excess presence of cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) and anions (HCO_3^{-} , SO_4^{2-} , NO_3^{2-} and Cl^{-}) in the water can leads to its unsuitability for drinking and irrigation purposes. The excess of cations can increase the total hardness of water and increase in water hardness can make water unsuitable for domestic purposes such as drinking, washing and bathing. The excess of certain cations and anions can adversely affects the quality of soils which leads to decrease in production of crops. The following parameters were calculated to assess the groundwater quality for drinking and irrigation purposes along with their possible sources.

4.2.2.1 Source identification

The observed strong positive correlation between EC with Ca^{2+} (0.81. $p>0.01$), Na^{+} (0.7, $p>0.01$), Mg^{2+} (0.79, $p>0.01$), Cl^{-} (0.79, $p>0.01$) and SO_4^{2-} (0.74, $p>0.01$) during post monsoon suggest that these ions are the major contributors in enhancing the EC of groundwater. Similarly during pre monsoon season, a strong positive correlation of EC is found with Ca^{2+} (0.81, $p>0.01$), Na^{+} (0.62, $p>0.01$), Mg^{2+} (0.72, $p>0.01$), Cl^{-} (0.57, $p>0.05$) and SO_4^{2-} (0.51, $p>0.05$).

In post monsoon, the correlation coefficient of Ca^{2+} and Mg^{2+} is 0.88 and in pre monsoon it is 0.97 suggesting the silicate weathering as a source for Ca^{2+} and Mg^{2+} ions in the water (Table 4.27). The chlorite along with mica and garnets could be the source for Mg^{2+} ion in the groundwater. K^{+} is found in low concentration in groundwater compared to other cations due to its capacity to fixed in clay minerals and form secondary mineral (Gupta *et al*., 2016). K^+ could be derived from phyllite and mica in the region.

During post monsoon season, SO_4^{2-} has a positive correlation with Ca^{2+} (0.7, $p>0.01$), Mg^{2+} (0.72, $p>0.01$) and Na^+ (0.42, $p>0.05$) indicating the leaching of sulphides during rainy season which could have promoted the chemical weathering of sulphides and releasing these cations.

The correlation coefficient of Ca^{2+} and Mg^{2+} with HCO_3^- is negative or insignificant in both the seasons could be due to lack of carbonate weathering and neutralization of bicarbonates with H^+ ion released during weathering of sulphides and neutralization of bicarbonates with H^+ ion released during weathering of sulphides (Breemen *et al*., 1983) or it could be due to dominance of silicate weathering.

Na^+ shows strong positive correlation with Cl^- (post monsoon: 0.85, $p>0.01$; pre monsoon: 0.77, $p>0.01$) during both the seasons indicating the evaporites or salts as a major source. NO_3^{2-} doesn't show any significant correlation with any major ions indicating its anthropogenic sources such as fertilizers.

4.2.2.2. Evaluation of groundwater quality for drinking purposes

Total hardness

The total hardness (TH) is considered as an important parameter for assessing the suitability of water for drinking purposes and it is calculated by using Eq.5 (Todd, 1980):

$$TH(CaCO_3)mg/L = 2.497Ca^{2+} + 4.1115Mg^{2+} \qquad \text{---(5)}$$

Where, concentrations of Ca^{2+} and Mg^{2+} are represented in mg/L.

Table 4.27 Correlation matrix among measured parameters in the water samples (pre and post monsoon) from Khetri region

Post Monsoon

	pH	**EC**	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**HCO_3^{-}**	**Cl^{-}**	**SO_4^{2-}**	**NO_3^{2-}**
Ph	1	-0.47*	-0.59**	-0.67**	-0.11	-0.07	0.37	-0.12	-0.42*	-0.02
EC		1	0.81**	0.79**	0.70**	0.42*	0.06	0.79**	0.74**	0.28
Ca^{2+}			1	0.88**	0.24	0.30	-0.12	0.36	0.76**	0.25
Mg^{2+}				1	0.19	0.33	-0.06	0.32	0.72**	0.34
Na^{+}					1	0.15	0.15	0.85**	0.43*	0.06
K^{+}						1	0.64**	0.20	0.36	-0.07
HCO_3^{-}							1	-0.02	0.21	-0.03
Cl^{-}								1	0.36	0.23
SO_4^{2-}									1	0.17
NO_3^{2-}										1

Pre Monsoon

	pH	Ec	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{2-}
pH	1	-0.58*	-0.72**	-0.70**	-0.11	0.23	0.06	-0.23	-0.62**	-0.06
Ec		1	0.81**	0.72**	0.62**	0.05	-0.14	0.57*	0.52*	0.14
Ca^{2+}			1	0.97**	0.06	-0.02	-0.36	0.15	0.44	0.31
Mg^{2+}				1	-0.06	-0.07	-0.40	0.04	0.39	0.26
Na^{+}					1	0.10	0.30	0.77**	0.31	-0.24
K^{+}						1	-0.47*	0.26	0.09	-0.22
HCO_3^{-}							1	0.19	-0.25	0.22
Cl^{-}								1	0.65**	-0.11
SO_4^{2-}									1	-0.14
NO_3^{2-}										1

*. Correlation is significant at the 0.05 level (2-tailed).
**. Correlation is significant at the 0.01 level (2-tailed).

The hardness of water is primarily attributed to presence of divalent cations i.e. Ca^{2+} and Mg^{2+}. Total hardness (TH) varies from 88 to 3274 with an average of 1110 in post monsoon and from 35 to 2590 with a mean of 782 during pre monsoon (Table 4.29). Using Sawyer and Mc Carthy (1967) classification, the groundwater samples are classified into soft (0–75), moderate (75–150), high (150–300) and very hard (above 300) categories. All groundwater samples of Khetri copper mine region are in very hard category in both the seasons and needs softening prior to human consumption except surface water sample (W1). Long term consumption of hard water could lead to cardiovascular and disorders urolithiasis (Durvey *et al.*, 1991).

Water quality index

The water quality index (WQI) is widely used index for the assessment of overall water quality for drinking and other domestic purposes. It summarizes the overall effects of the chemical compound effect of individual water quality characteristic on the global quality of water for human consumption (Edet *et al.*, 2013). WQI calculation involves three step namely assigning weight, relative weight calculation and quality rating scale calculation (Horton, 1965).

First, “assigning weight” a weight (w_i) is assigned according to the importance of parameters in the water quality assessment (Table 4.28). Maximum weight is assigned to chloride and nitrate, while minimum is assigned to sulphate due to less importance in the water quality assessment.

Second, “relative weight calculation″ is calculated by using Eq. 6:

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i} \qquad \text{---(6)}$$

Where, W_i is the relative weight, w_i is the weight of each parameter and n is the number of parameters. The calculated relative weight (W_i) values of each parameter are given in Table 4.28.

Third, quality rating scale calculation is calculated by dividing concentration of parameter in each water sample by its respective permissible limit WHO 2011 (4.28) and multiplied by 100 (Eq. 7).

$$q_i = \frac{C_i}{S_i} \times 100 \qquad \text{---(7)}$$

Where, q_i is the quality rating, C_i is the concentration of each chemical parameter at each sampling location (mg/L) and S_i is the (WHO 2011) standard value for each chemical parameter. Then, WQI is calculated by the following two equations (Eq. 8 & 9):

$$SI_i = W_i \times q_i \qquad \text{---(8)}$$

$$WQI = \sum SI_i \qquad \text{---(9)}$$

Where, SI_i is the subindex of i^{th} parameter, q_i is the rating based on concentration of i^{th} parameter, n is the parameters number. The calculated WQI was categorised as: excellent (WQI: <25), good (WQI: 25–50), moderate (WQI: 51–75), poor (WQI: 76–100), and very poor (WQI: >100).

Table 4.28 Relative weight assigned to the measured parameters

Chemical parameters (mg/L)	**World Health Organization (2011)**	**Weight (W_i)**	**Relative Weight** $W_i = \frac{w_i}{\sum_{i=1}^{n} w_i}$
pH	6.5-8.5	3	0.091
TDS	600	5	0.15
TH	500	2	0.061
Ca^{2+}	75	3	0.091
Mg^{2+}	50	3	0.091

Na^+	200	2	0.061
K^+	12	2	0.061
HCO_3^-	120	2	0.061
SO_4^{2-}	250	1	0.03
NO_3^{2-}	50	5	0.15
Cl^-	250	5	0.15
		$\sum w_i$ =33	$\sum W_i$ =0.997

According to WQI classification (Table 4.29), all the samples are in the very poor category during pre and post monsoon, except surface water (W1) and groundwater away from the mines or in the upstream of groundwater flow (W4, W7, W8, W16 & W19). Hence, the groundwater in Khetri copper mine region is unsuitable for drinking purposes as per the calculated WQI for individual samples.

4.2.2.3 Evaluation of groundwater quality for irrigation purposes

For irrigation purposes, the quality of water is essential for better yield and health of crops, protection of the environment and maintenance of soil productivity (Singh *et al*., 2013). Various indices namely sodium adsorption ratio (SAR), sodium percentage (Na%), residual sodium carbonate (RSC), Kelly's ratio, magnesium hazard (MH) and permeability index (PI) are used to evaluate the suitability of groundwater for irrigation purposes.

Table 4.29 TH and water quality index values of water for drinking purposes

Sample code	**Sample Location**	**Post monsoon**		**Pre monsoon**	
		TH	**WQI**	**TH**	**WQI**
W1	Kakarai pond	88^{b}	35	35^{a}	58^{**}
W2	Kakarai school	656^{d}	$208^{\#}$	541^{d}	$212^{\#}$
W3	Maliyun dhani	1094^{d}	$199^{\#}$	304^{d}	100^{**}
W4	Ahrio ki dhani	367^{d}	78^{**}	255^{d}	93^{**}
W5	Rajota	1223^{d}	$226^{\#}$	771^{d}	$196^{\#}$
W6	Khetri	1406^{d}	$257^{\#}$	1021^{d}	$234^{\#}$
W7	Teelawali	460^{d}	99^{**}	309^{d}	$107^{\#}$
W8	Meghawali Dhani	457^{d}	88^{**}	360^{d}	$105^{\#}$
W9	Khakara Devran	773^{d}	$122^{\#}$	451^{d}	$123^{\#}$
W10	Kharkara Rajputan	456^{d}	$141^{\#}$	297^{c}	$156^{\#}$
W11	River bed	890^{d}	$156^{\#}$	479^{d}	$168^{\#}$
W12	Khetri Nagar	1796^{d}	$266^{\#}$	1406^{d}	$271^{\#}$
W13	Bhargda Dhani	1294^{d}	$209^{\#}$	1734^{d}	$264^{\#}$
W14	Near tailing	2094^{d}	$237^{\#}$	374^{d}	$115^{\#}$
W15	Kanjaniyun Dhani	1551^{d}	$224^{\#}$	1009^{d}	$182^{\#}$
W16	Gujarwas	372^{d}	95^{**}	552^{d}	$215^{\#}$
W17	Singhana	2990^{d}	$434^{\#}$	1589^{d}	$262^{\#}$
W18	Chandmari	3274^{d}	$280^{\#}$	2590^{d}	$256^{\#}$
W19	Bhand bhatiar	582^{d}	90^{**}	-	-
W20	Badheswar	927^{d}	$143^{\#}$	-	-

W21	Bawadi Dhani	1207[d]	227[#]	-	-
W22	Banwas	711[d]	109[#]	-	-
W23	Guest house	1109[d]	188[#]	-	-
W24	Bass Govind Singh	862[d]	185[#]	-	-
	Minimum	88	35	35	58
	Maximum	3274	434	2590	271
	Average	1110	179	782	173
	STDEV	789	87	664	69

Total hardness: [a]Soft, [b]moderate, [c] high, [d]very hard

WQI: [*]Good, [**] Poor, [#] Very Poor

The followings equations are used for calculations (Richards, 1954; Kelly, 1963; Szabolcs and Darab, 1964; Ramesh and Elango, 2011; Singh *et al*., 2012):

$$\mathrm{SAR} = \frac{\mathrm{Na}^{+}}{\sqrt{\frac{\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}}{2}}} \qquad \text{---(11)}$$

$$\mathrm{Na}(\%) = \frac{\left(\mathrm{Na}^{+} + \mathrm{K}^{+}\right) \times 100}{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+}\right)} \qquad \text{---(12)}$$

$$\mathrm{RSC} = \left(\mathrm{HCO_3}^{-} + \mathrm{CO_3}^{2-}\right) - \left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right) \qquad \text{---(13)}$$

$$\mathrm{KR} = \frac{\mathrm{Na}^{+}}{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)} \qquad \text{---(14)}$$

$$\mathrm{MH} = \frac{\mathrm{Mg}^{2+}}{\left(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}\right)} \times 100 \qquad \text{---(15)}$$

$$PI = \frac{\left(Na^{+} + \sqrt{HCO_3^{-}}\right)}{\left(Ca^{2+} + Mg^{2+} + Na^{+}\right)} \times 100 \qquad \text{---(16)}$$

Where, the concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+} and HCO_3^- ions are expressed in meq/L.

According to Wilcox (1955) classification for EC, the groundwater samples from Khetri copper mine region are classified into different categories such as 1 sample in excellent (<250), 2 samples in good (250-750), 11 samples in permissible (750-2250), 9 samples in doubtful category (2250-5000) and 1 sample (Singhana) in not suitable for irrigation (above 5000) during post monsoon. Singhana is located in the northern direction of mines and water table is decreasing rapidly in the area as the wells were found dried during post monsoon season sampling. Similarly, in pre monsoon, 3 samples lie in good category, 7 samples in permissible category and 8 samples in doubtful category (Table 4.30 & 4.31).

According to Richards (1954), water samples having SAR value <10 are considered as excellent for irrigation purposes. In the study area, the range of SAR varies from 0.4 to 8.38 with an average of 3.07 and 0.3 to 10.2 with a mean of 3.45 in pre monsoon and post monsoon respectively. Hence, groundwater of Khetri copper mine region is excellent for irrigation purposes in terms of SAR value.

Irrigation with water having high content of sodium reduces the soils permeability and causes infiltration problems in soils. In the Khetri copper mine region, the Na% ranges from 7.1 to 75.9 with an average of 37.08 and from 8.71 to 68.8 with an average of 33.5 in pre and post monsoon respectively. According to BIS (2003), Na% in the groundwater should be less than 60% for irrigation purposes. In terms of Na%, the water samples from Khetri copper mine region are within the safe limit of BIS (2003) and good to excellent category for irrigation purposes, except two samples (Kakarai and Kharkhara

Devran) in both seasons. The Kakarai is near the albite line (Na-rich) and Kharkara Rajputan is near the tailings. Tailing could be the major source for Na^+ as sodium ethylxanthate is being used during Cu extraction process.

The presence of excess bicarbonate and carbonate over alkaline earth elements influences the suitability of water for irrigation purposes by enhancing the adsorption of Na^+ ions on soils. The effect of HCO_3^- and CO_3^{2-} on soils can be estimated by residual sodium carbonate (RSC). On the basis of RSC irrigation water is classified into different categories i.e. >5 meq/L (harmful for plant growth), >2.5 (unsuitable for irrigation purposes), 1.25 to 2.4 (marginal quality) and <1.25 (good quality) (Singh *et al.*, 2013).

In Khetri copper mine region, the RSC ranges from -51.41 to 7.25 with an average of -9.73 and from -64.78 to 1.78 with an average of -15.71 in the pre and post monsoon respectively. Thus, all the samples lie in the safe zone except sample from Kharkhara Rajputan (W10) which is in marginal quality (RSC=1.7) in post monsoon and harmful zone (RSC=7.2) in pre monsoon. W10 consist abundance of Na^+ comparative to Ca^{2+} and Mg^{2+} as it is near to tailings which leads to increase in RSC.

According to Kelley (1946) classification, water samples with KR >1 are not suitable for irrigation purposes. In the study region, the KR is more than one in 21 and 33% of the samples in post and pre monsoon respectively. Excess presence of magnesium in groundwater reduces the agricultural yield (Szabolcs and Darab, 1964).

On the basis of Magnesium hazard (MH), 92 and 11 % of the samples are in unsafe region (i.e MH >50) for irrigation purposes during post and pre monsoon season respectively. The permeability index (PI) is an important parameter to assess the effect of irrigation on soils permeability. Water with PI >75 are considered as safe and PI < 25 as unsafe (Doneen, 1964; Domenico and Schwartz, 1990). In Khetri copper mine region, 88 and 72 % of the samples are in the marginally safe zone (PI = 25-75) in post and pre monsoon respectively.

Table 4.30 Water quality parameters for irrigation purposes during post monsoon

Sample code	**Sample Location**	**EC**	**SAR**	**Na%**	**RSC**	**MH**	**KR**	**PI**
W1	Kakarai pond	170	0.3	24	1.1	29.1	0.16	96.4
W2	Kakarai school	3534	10.2	67	-9.3	53.1	1.99	71.1
W3	Maliyun dhani	1876	3.1	32	-14.8	63.6	0.47	39.7
W4	Ahrio ki dhani	1035	4.7	55	-0.2	60.6	1.23	69.3
W5	Rajota	2207	3.0	31	-16.4	61.0	0.43	37.9
W6	Khetri	2499	2.8	29	-20.5	61.0	0.38	34.2
W7	Teelawali	590	0.6	13	-5.5	71.6	0.14	28.7
W8	Meghawali Dhani	680	1.0	20	-4.5	71.8	0.24	37.1
W9	Khakara Devran	1088	0.9	14	-9.7	65.9	0.17	26.3
W10	Kharkara Rajputan	1827	9.3	69	1.7	65.3	2.19	79.1
W11	River bed	1975	4.7	44	-14.5	60.8	0.79	49.4
W12	Khetri Nagar	2813	2.7	24	-28.8	71.7	0.32	28.8
W13	Bhargda Dhani	1969	2.0	22	-20.1	72.6	0.27	28.4
W14	Near tailing	3067	2.8	23	-38.0	47.4	0.30	26.7
W15	Kanjaniyun Dhani	2730	4.2	35	-24.4	61.3	0.53	39.8
W16	Gujarwas	1160	4.7	55	-2.0	66.3	1.23	68.3
W17	Singhana	5350	3.5	25	-53.2	57.5	0.32	27.1
W18	Chandmari	3546	1.0	9	-64.8	64.5	0.09	9.0
W19	Bhand bhatiar	929	1.1	19	-7.2	57.7	0.22	32.4

W20	Badheswar	1613	2.9	33	-10.5	64.7	0.47	41.9
W21	Bawadi Dhani	2495	2.8	32	-5.5	70.4	0.40	40.5
W22	Banwas	1285	2.3	31	-6.7	52.0	0.43	42.9
W23	Guest house	2744	5.6	46	-11.5	66.8	0.84	51.4
W24	Bass Govind Singh	2614	6.5	53	-12.1	76.4	1.11	57.9
	Minimum	170	0.3	9	-64.8	29.1	0.09	9.0
	Maximum	5350	10.2	69	1.7	76.4	2.19	96.4
	Average	2075	3.4	34	-15.7	62.2	0.61	44.4
	STDEV	1162	2.5	17	16.5	9.9	0.56	20.2

Table 4.31 Water Quality parameters for irrigation purposes during pre monsoon

Sample code	**Sample Location**	**EC**	**SAR**	**Na%**	**RSC**	**MH**	**KR**	**PI**
W1	Kakarai pond	350	2.1	76	1.3	28.8	1.81	137.2
W2	Kakarai school	2715	6.4	59	-4.7	46.8	1.38	67.6
W3	Maliyun dhani	933	2.3	40	0.0	42.8	0.65	64.1
W4	Ahrio ki dhani	1006	3.6	54	2.0	39.2	1.14	77.7
W5	Rajota	1882	1.9	27	-8.4	40.5	0.35	38.5
W6	Khetri	2394	2.1	27	-12.5	42.5	0.34	35.4
W7	Teelawali	615	0.4	11	-0.3	46.0	0.11	45.5

W8	Meghawali Dhani	715	0.7	16	-0.8	48.1	0.18	45.0
W9	Khakara Devran	1006	1.1	20	-3.2	48.7	0.25	41.4
W10	Kharkara Rajputan	1850	7.9	70	7.2	43.6	2.29	88.2
W11	River bed	1801	4.2	51	-5.8	40.8	0.96	59.3
W12	Khetri Nagar	2900	2.2	23	-21.9	52.0	0.29	29.4
W13	Bhargda Dhani	3061	1.1	12	-29.1	48.6	0.14	18.1
W14	Near tailing	1398	4.1	51	-0.7	37.0	1.05	68.2
W15	Kanjaniyun Dhani	2638	3.5	36	-14.6	49.2	0.55	43.1
W16	Gujarwas	3543	8.4	65	-6.1	25.6	1.78	71.3
W17	Singhana	3228	2.5	24	-26.1	48.0	0.31	29.6
W18	Chandmari	3501	0.7	7	-51.4	52.9	0.07	7.3
	Minimum	350	0.4	7	-51.4	25.6	0.07	7.3
	Maximum	3543	8.4	76	7.2	52.9	2.29	137.2
	Average	1974	3.1	37	-9.7	43.4	0.76	53.7
	STDEV	1057	2.4	22	14.4	7.4	0.68	29.9

4.2.3 Heavy Metals in Groundwater

Different types of pollution indices were calculated to assess the heavy metal pollution status of groundwater and surface water. The pollution level is categorized into different categories to the degree of pollution. Along with the pollution indices the possible sources of heavy metals were also assessed. The details are discussed in the following sections.

4.2.3.1 Source identification

To identify the source for heavy metals the correlation matrix was used for both pre and post monsoon. During pre monsoon, pH is negatively correlated with Cu (-0.70, $p>0.01$), Co (-0.67, $p>0.01$), Ni (-0.70, $p>0.01$) and Mn (-0.69, $p>0.01$) interfaces that with decrease in pH of water the concentration of these elements increases in the water may be due to sulphide contamination (Table 4.32). Similarly during post monsoon, pH is negatively correlated with Cu (-0.82, $p>0.01$), Co (-0.82, $p>0.01$), Ni (-0.81, $p>0.01$) and Mn (-0.80, $p>0.01$) as shown in Table 4.33. EC does not show any strong correlation with the heavy metals may be because EC of the water is majorly controlled by the major ions concentration rather the trace elements concentration.

Cu is strongly positively correlated with Co (0.94, $p>0.01$), Ni (0.99, $p>0.01$), and Mn (0.99, $p>0.01$) in pre monsoon probably due to common source for these elements in the groundwater. In post monsoon Cu shows strong correlation with Co, Ni and Mn correlation coefficient of 0.99, $p>0.01$. However, Zn and Fe show a negative correlation with these elements which may be due to precipitation or exchange of these elements with other cations. Co shows strong positive correlation with Ni (0.93, $p>0.01$) and Mn (0.96, $p>0.01$), and Ni with Mn (0.99, $p>0.01$) during pre monsoon. During post monsoon, Co shows strong correlation with Ni and Mn (0.99, $p>0.01$).

Hence, Cu, Ni, Co and Mn show strong association among themselves indicating their common source (minning activities).

Table 4.32 Correlation coefficient among heavy metals for pre monsoon season samples

	pH	**EC**	**Cu**	**Zn**	**Fe**	**Co**	**Ni**	**Mn**	**Pb**
pH	1	-0.58*	-0.70**	-0.00	0.03	-0.67**	-0.70**	-0.69**	0.37
Ec		1	0.37	0.20	0.19	0.43	0.36	0.38	-0.27
Cu			1	-0.11	-0.13	0.94**	0.99**	0.99**	-0.21
Zn				1	0.06	-0.23	-0.14	-0.13	0.38
Fe					1	-0.15	-0.13	-0.13	-0.15
Co						1	0.93**	0.96**	-0.24
Ni							1	0.99**	-0.21
Mn								1	-0.21
Pb									1

* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed)

Table 4.33 Correlation coefficient among heavy metals for post monsoon season samples

	pH	**EC**	**Cu**	**Zn**	**Fe**	**Co**	**Ni**	**Mn**	**Pb**
pH	1	-0.47*	-0.82**	0.06	0.16	-0.82**	-0.81**	-0.80**	0.02
EC		1	0.28	0.26	-0.04	0.31	0.27	0.28	-0.10
Cu			1	-0.10	-0.14	0.99**	0.99**	0.99**	-0.07
Zn				1	0.00	-0.10	-0.11	-0.10	-0.10
Fe					1	-0.12	-0.12	-0.13	-0.19
Co						1	0.99**	0.99**	-0.06
Ni							1	0.99**	-0.07
Mn								1	-0.07
Pb									1

* Correlation is significant at the 0.05 level (2-tailed)

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

The PCA lead to a reduction of the initial dimension of the dataset to three components, which explain 90.85% and 89.56% of the data variation in pre and post monsoon respectively (Table 4.34). The first component (PC1) for water during pre and post monsoon shows the strong association of Cu, Co, Ni and Mn which explains the 57.65% and 57.69% of variance respectively (Fig. 4.71 & 4.72). These elements are found in abundant quantity in association with sulphides, hence their source is of mining activities.

In the second component (PC2), the association of Zn and Pb was identified with 18.85% and 17.43% of variance during pre and post monsoon respectively. The presence of Pb in the soils explains their source is weathering of parent rock, as the Pb is not found in the tailings. Zn is found strongly associated with the sulphides in nature. Hence the PC2 explains the mixed source (weathering or anthropogenic).

The third component (PC3) contains only Fe with variance of 14.35 and 14.44 % of variance during pre and post monsoon respectively. The source of Fe is may be anthropogenic source (mining activities) but it may precipitate and shows variation depending upon the environmental conditions.

Table 4.34 The principle component analysis for water during pre and post monsoon

	Pre Monsoon			**Post Monsoon**		
Parameter	**PCA 1**	**PCA 2**	**PCA 3**	**PCA 1**	**PCA 2**	**PCA 3**
Mn	0.99	0.11	0.08	1.00	0.05	0.06
Cu	0.99	0.12	0.09	0.99	0.06	0.07
Ni	0.99	0.10	0.08	0.99	0.05	0.07

Co	0.97	0.03	0.00	0.99	0.03	0.03
Pb	-0.30	0.79	-0.05	-0.18	0.80	-0.06
Zn	-0.24	0.72	0.48	-0.17	0.64	0.58
Fe	-0.17	-0.39	0.87	-0.17	-0.41	0.81
Eigen value	4.04	1.32	1.00	4.04	1.22	1.01
% of variance	57.65	18.85	14.35	57.69	17.43	14.44
Cumulative %	57.65	76.50	90.85	57.69	75.12	89.56

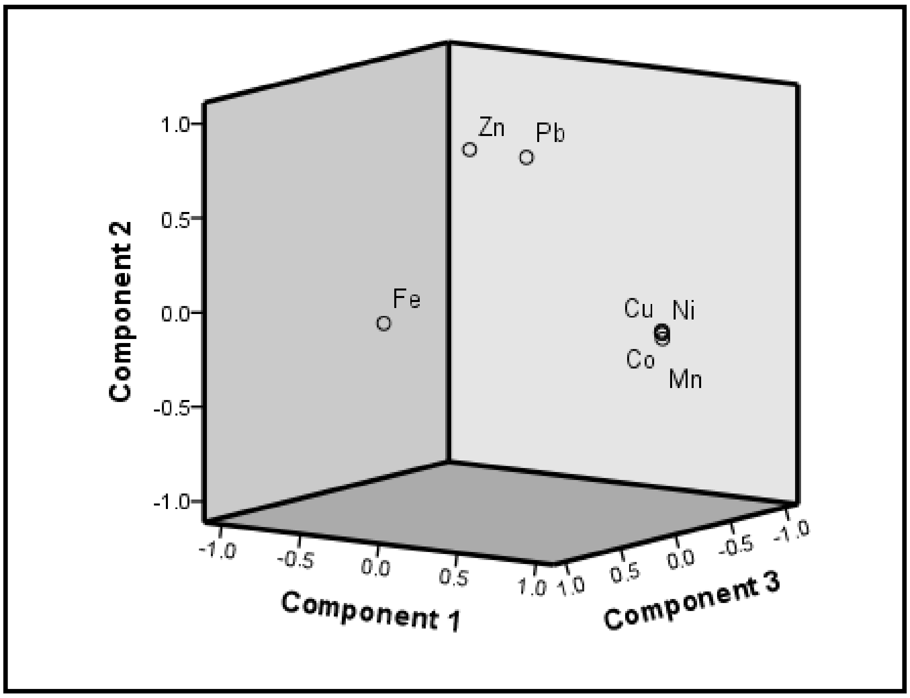


Fig. 4.71 PCA plot showing the association among heavy metals in water (post monsoon)

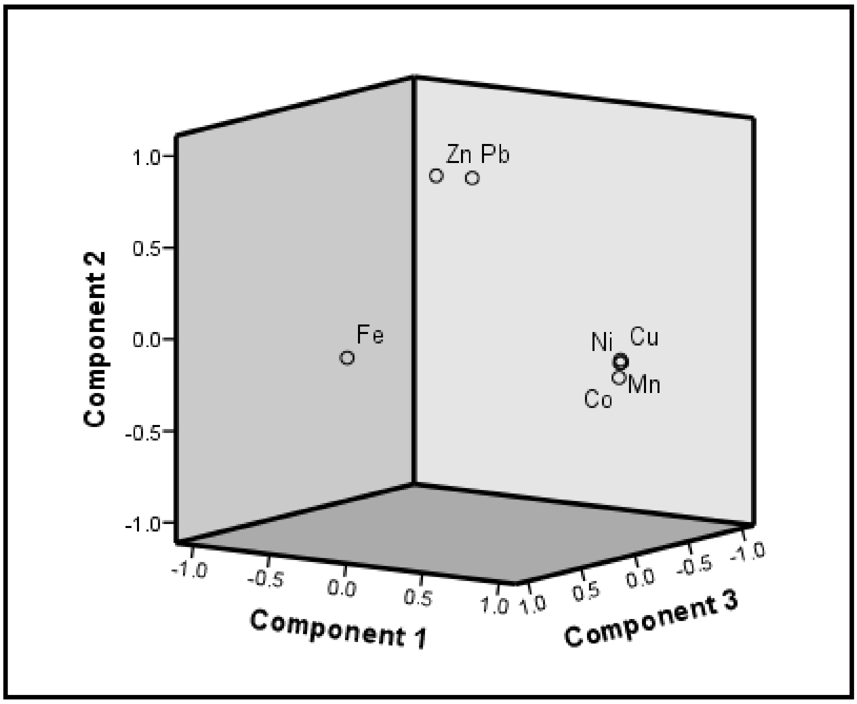


Fig. 4.72 PCA plot showing the association among heavy metals in water (pre monsoon)

4.2.3.2 Evaluation methods used for heavy metal pollution

The measured concentrations of individual elements at each sampling site were used to calculate the pollution indices (heavy metal pollution index, contamination index and index of environmental risk) and risk assessment using the maximum permissible limit of BIS, 2012.

Heavy metal pollution index (HPI)

HPI is used to represent the overall water quality on the basis of heavy metal concentration (Mohan *et al*., 1996). The index is calculated based on the weighting of the parameters and the weight values are between 0 to 1 showing the importance of the parameters. Weight of the samples can be considered as inversely proportional to the standard value for each element that have been calculated and considered for each parameter previously (Horton, 1965; Reddy, 1995).

This index is calculated by the following equation (Mohan *et al*., 1996):

$$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i} \qquad \text{---(1)}$$

Where, Q_i is sub index calculated for the i^{th} parameter, W_i is the unit weight of i^{th} parameter and n is the number of parameters considered.

The sub index (Q_i) is calculated as follows:

$$Qi = \sum_{i=1}^{n} \frac{(M_i(-)I_i)}{(S_i - I_i)} \times 100 \qquad \text{---(2)}$$

Where, M_i is measured value for the i^{th} parameter, I_i is ideal value for i^{th} parameter, S_i is standard value allowed for i^{th} parameter. The sign (-) indicating the numerical difference of two values ignoring the algebraic sign.

The calculated HPI values (Table 4.35 & Fig. 4.73) for the Khetri copper mine region samples are 4 to 9 times higher than the defined value of 100 suggesting high contamination of heavy metals in the region. The HPI varies from 463 to 8935 with the highest HPI value of 8936 is at Chaandmari (W18). The mean HPI is 1016, which is ~10 times higher than the 100. On excluding the concentration of Co and Ni from the HPI calculations, the average HPI* is 257 with a minimum of 53 is at Bass Govind Singh (W24) and a maximum of 1757 at W18. The decrease in HPI values on excluding the concentration of Co and Ni from calculation indicates high contribution of Co and Ni in enhancing the HPI values.

Table 4.35 HPI values for the ground and surface water samples for each element from Khetri mine region

Element	**Mean Concentration (ppb) of pre and post monsoon**	**Highest permissible limit (S_i)**	**Desirable Maximum Limit (I_i)**	**Unit Weightage (W_i)**	**Q_i**	**W_i x Q_i**
Cu	576.341	1500	50	0.00067	31.36	0.02
Zn	1500.346	300	0	0.00333	486.17	1.62
Fe	1680.082	15000	5000	0.00007	34.16	0.00
Co	539.289	10	0	0.10000	1209.28	120.93
Ni	7.654	20	0	0.05000	818.64	40.93
Mn	576.341	200	30	0.00500	278.73	1.39
Pb	1500.346	300	100	0.00333	46.02	0.15

$\sum W_i = 0.16240$ $\sum W_i \times Q_i = 165.051$ HPI= 1016.3

On excluding the concentration of Co and Ni from calculations $\sum W_i = 0.00248$ $\sum W_i \times Q_i = 0.64$ HPI= 257.3

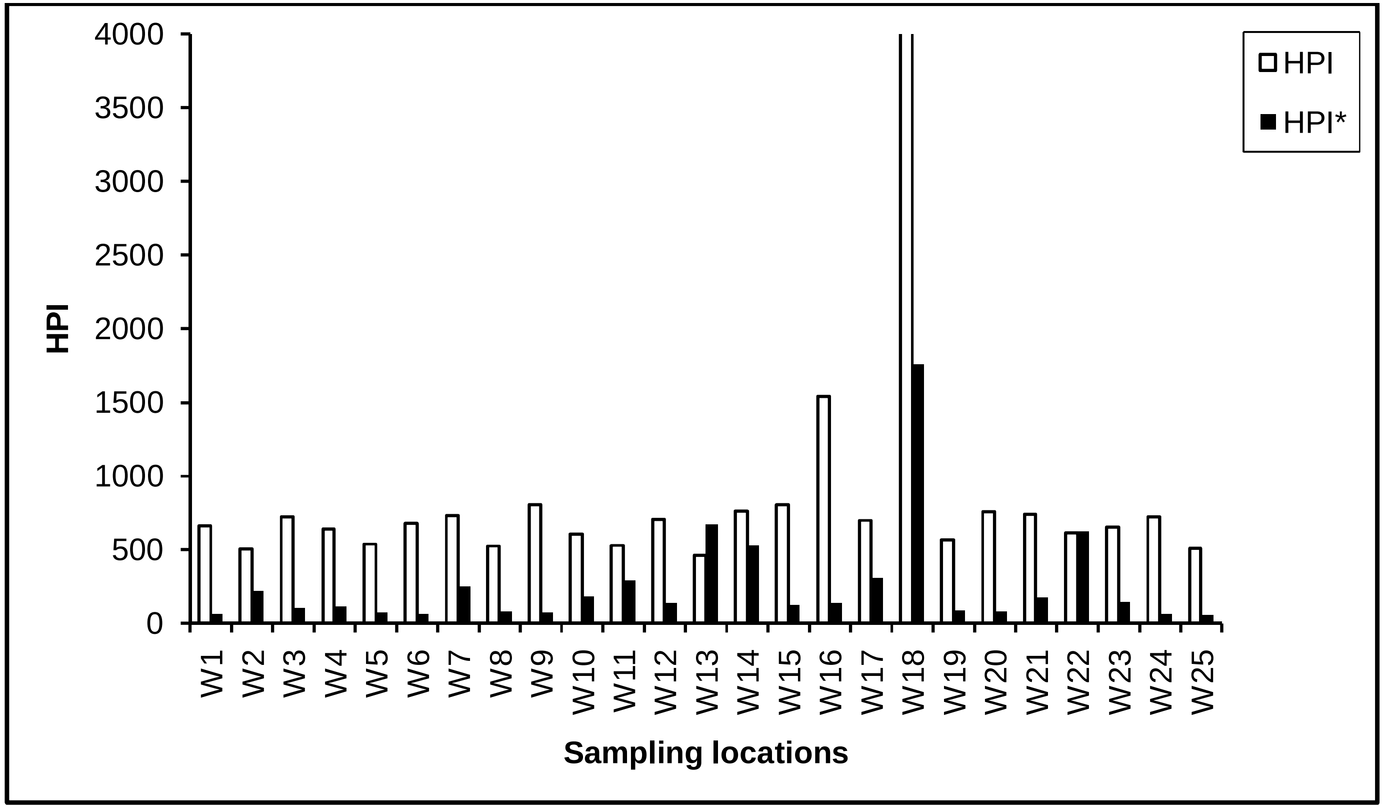


Fig. 4.73 Bar graph showing the HPI and HP* (excluding Co and Ni from calculations) values for water at each sampling location from Khetri copper mine region

Contamination index (CI)

Contamination index (CI) is calculated to evaluate the enrichment of heavy metals with respect to maximum permissible limits of BIS, 2012 by using the Eq. 3 given by Adamu (2015).

$$\mathrm{CI} = \frac{\left\{\left(\frac{\mathrm{Cu}}{1.5}\right)+\left(\frac{\mathrm{Zn}}{15}\right)+\left(\frac{\mathrm{Fe}}{0.3}\right)+\left(\frac{\mathrm{Co}}{0.2}\right)+\left(\frac{\mathrm{Ni}}{0.02}\right)+\left(\frac{\mathrm{Mn}}{0.3}\right)+\left(\frac{\mathrm{Pb}}{0.01}\right)\right\}}{7} \qquad \text{---(3)}$$

Where, CI is the contamination index and Cu, Zn, Fe, Co, Ni, Mn and Pb are the average concentration (average of pre and post monsoon) at each sampling site divided by the maximum permissible limit set by BIS, 2012 for each element. CI has been divided into three categories namely CI<1 (not contaminated); CI 1-5 (slightly contaminated); and CI>5 (contaminated).

The CI value varies from 0.89 to 17.14 with an average of 2.43. On excluding Co and Ni concentrations from calculations, the CI* values varies from 0.25 to 6.04 with an average of 1.63. The minimum values of CI i.e. 0.89 & 0.25 are observed at Pilani (W25). The highest values of CI (17 and 5) are observed at Chaandmari (W18) and Kanjaniyun Dhani (W15) respectively and both the sites are closer to overburden materials (Fig. 4.74). Both the sites are in highly contaminated category on the basis of CI values.

The value at W18 is much higher than the defined value of 5. All other samples are in the slightly contamination range except three samples (W9, W19 and W20) and the two reference samples (W24 & W25).

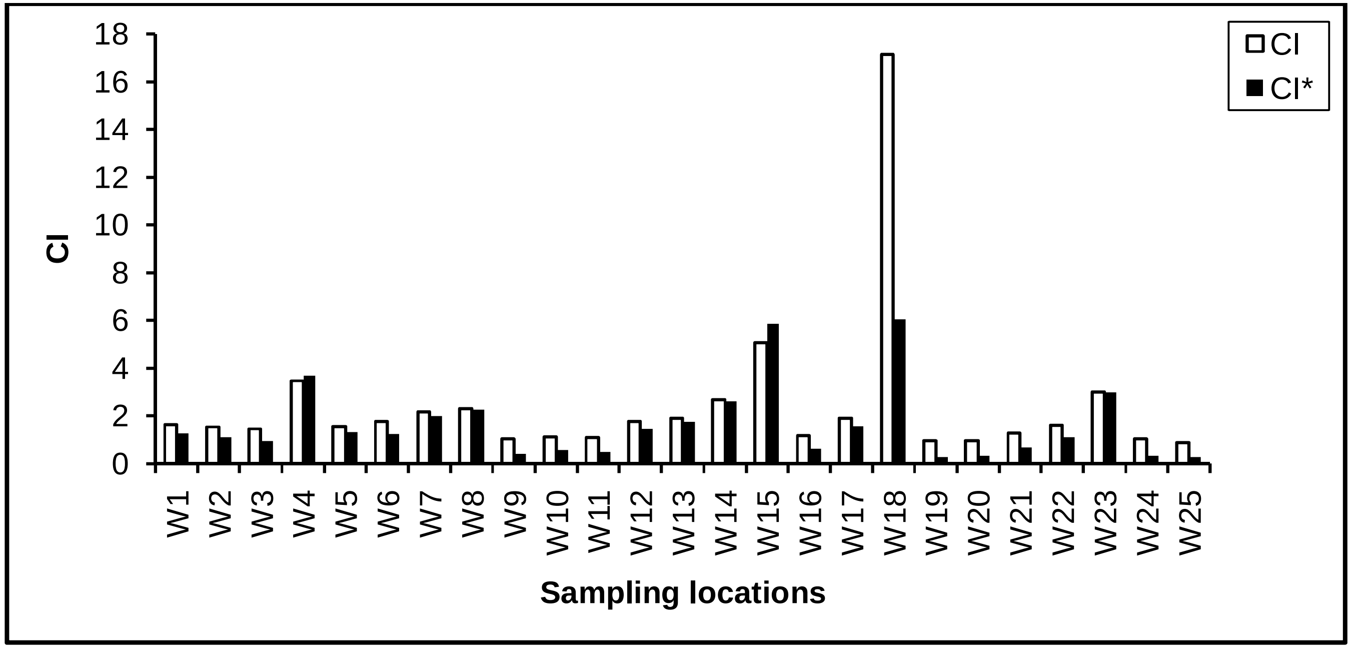


Fig. 4.74 Bar graph showing the CI and CI[*] (excluding Co and Ni from calculations) values for water at each sampling location from Khetri copper mine region

Index of environmental risk (I_{ER})

The index of environmental risk (I_{ER}) (Rapant and Kordík, 2003; Rapant *et al*., 2008, 2009; Huang *et al*., 2010) is a numerical value that predicts the probability of the occurrence of the negative impact on the environment by means of specific contaminations.

In the present study, I_{ER} is calculated to assess the magnitude of adverse impact of the concentrations of heavy metals on the environment and to characterize overall contamination state in the Khetri copper mine region. I_{ER} calculation for individual analyzed sample is based on the following equation:

$$I_{ER} = \sum_{i=1}^{n} Q_{Eri} \qquad \text{---(5)}$$

$$Q_{Eri} = \frac{AC_i}{RC_i} - 1 \qquad \text{---(6)}$$

Here, I_{ER} is the overall index of environmental risk of the sample; Q_{Eri} is the index of environmental risk quotient of the i^{th} element, which exceeds the concentration limit; AC_i is the measured concentration (average of pre and post monsoon) of the i^{th} element and RC_i is the maximum permissible concentration limit of i^{th} element. The used scale for index of environmental risk and the number of samples falls within the range are given Table 4.36.

The I_{ER} values varies from -0.8 to 113 with an average of 10 and on excluding Co and Ni concentration from calculation it (I_{ER}*) varies from -3.8 to 25.2 with an average of 3.3. Water quality is highly degraded in terms of I_{ER} values (Fig. 4.75) in all samples except groundwater from distant locations from mines (W9, W10, W11, W16, W20 & W21). The highest I_{ER} values 113 and 29 are observed at Kanjaniyun Dhani (W15) and Chaandmari (W18) respectively those falls in the extremely high risk zone. The surface and groundwater falls in different categories of I_{ER} and details are given in Table 4.36.

It is found that in the study area, the concentrations of Co and Ni contribute more in enhancing the values of HPI, I_{ER} and CI. I_{ER} which is higher in almost all the groundwater, however, the same values decreases to below 3 which is a limit for highly contamination category after excluding the concentration of Co and Ni from the I_{ER} calculation. However, in eight samples the I_{ER} values remain high.

Table 4.36 Scale for index of environmental risk (Rapant *et al*., 2009) and the number of samples falling within the range

I_{ER} vaules	**Risk magnitude**	**Samples within the range of I_{ER} values (n=25)**
0	no risk	W19, W20, W25
≤ 1	very low risk	W9, W10, W11, W24
≤ 3	low risk	W16, W21
≤ 5	medium risk	W1, W2, W3, W5, W22
≤ 10	high risk	W6, W7, W8, W12, W13, W17
≤ 15	very high risk	W14, W23
≥ 15	extremely high risk	W4, W15, W18

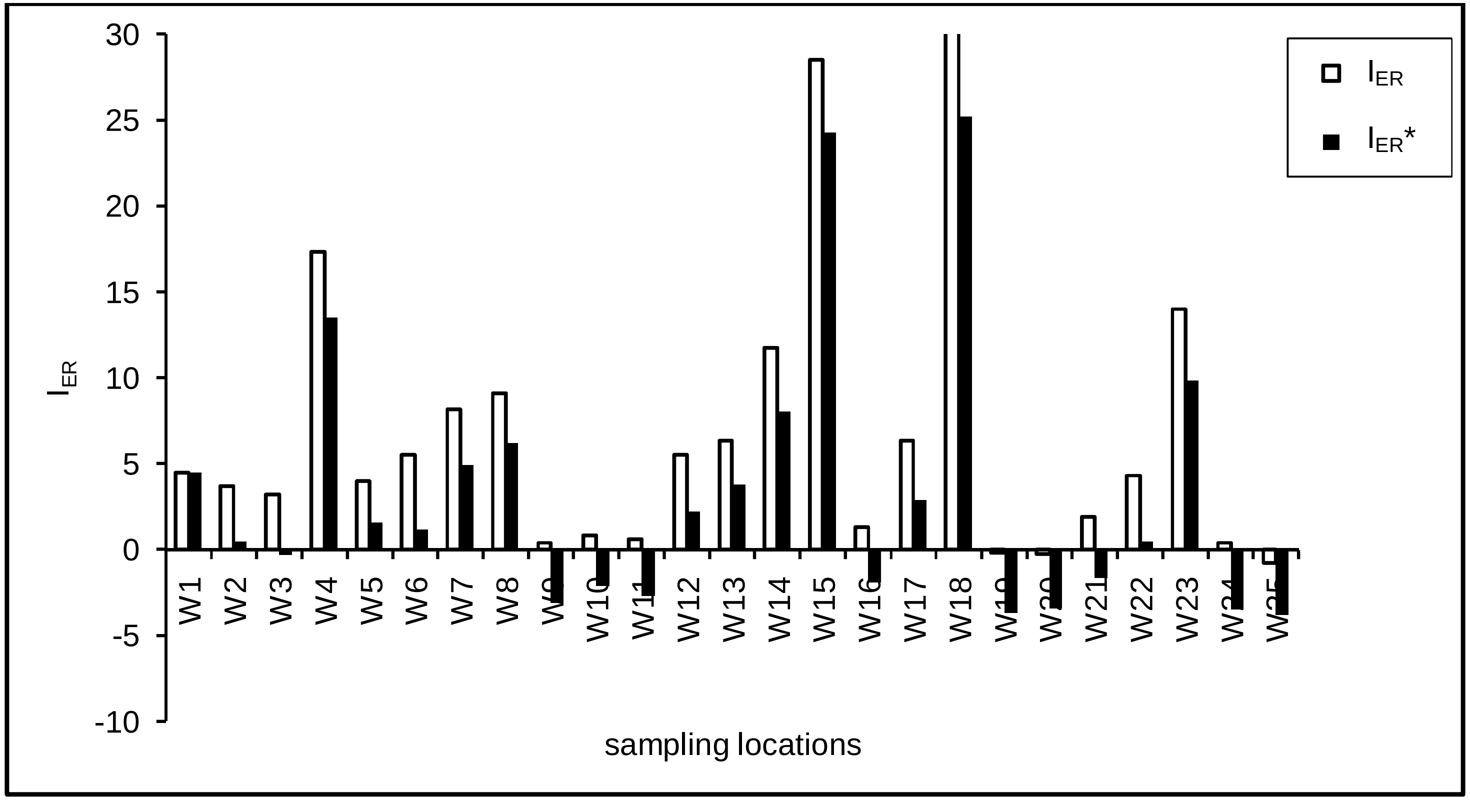


Fig. 4.75 Bar graph showing the I_{ER} and I_{ER}^{*} values (excluding Co and Ni from calculations) for water at each sampling location from Khetri copper mine region

4.2.3.3 Risk assessment

Risk assessment is a function of the hazard and exposure, and is defined as the process of estimating the probability of occurrence of any given magnitude of adverse health effects over a specified time period. The health risk assessment of each heavy metal or metalloid is usually based on quantification of the risk level and is expressed in terms of a carcinogenic or non carcinogenic health risk (USEPA, 2009). The two principal toxicity risk factors evaluated are the slope factor (SF) for carcinogen risk characterization, and the reference dose (RfD) for non carcinogen risk characterization (USEPA, 1997; 1999). The toxicity indices of some heavy metals and metalloid are shown in Table 4.37.

The estimations of the magnitude, frequency, and duration of human exposure to each heavy metal or metalloid in the environment are typically reported as average daily dose (ADD) (USEPA, 1992), as shown in the equation below

$$\mathrm{ADD} = \frac{(\mathrm{C} \times \mathrm{IR} \times \mathrm{EF} \times \mathrm{ED})}{(\mathrm{BW} \times \mathrm{AT})} \qquad \text{---(7)}$$

Where, ADD is the average daily dose (mg/kg/day), C is the mean concentration (mg/L) of heavy metal, IR is the water intake rate (3.45 L/day for adults) (Apambire *et al*., 1997; Roychowdhury *et al*., 2003), EF is the exposure frequency (365 days/year), ED is the exposure duration (70 years), BW is the average body weight (60 kg), and AT is the average time (25,550 days, i.e., 70 years × 365 days/year) (Roychowdhury *et al*., 2003; Wongsasuluk *et al*., 2014).

The non carcinogenic risk was calculated as the hazard quotient (HQ) and shown as follows;

$$\mathrm{HQ} = \frac{\mathrm{ADD}}{\mathrm{RfD}} \qquad \text{---(8)}$$

Where, ADD (exposure intake) and RfD (reference dose) (Table 4.38) are in mg/kg/day. For the risk assessment, the individual HQs are combined to form the hazard index (HI). If the value of HQ and/or HI exceeds 1, there could be potential non carcinogenic effects on health, while HQ and/or HI<1 means residents are not likely to experience any health risks as a result of exposure (USEPA, 2001; Lim *et al.*, 2008) (Table 4.38).

$$HI = \sum HQ \qquad \text{---(8)}$$

The hazard quotient for all the elements is found in acceptable range, except at W18 sample. The health index (HI) is in the range of 1 to 4 for all the samples which is in unacceptable range for non-carcinogenic health risk, except samples from W1, W6, W9, W19 & W20 and two reference samples (W24 & W25). The calculated human health risk assessment values (HI & HQ) for Cu, Zn, Fe, Ni, Co, Mn and Pb with respect to locations are given in the Table 4.39.

Table 4.37 The toxicity responses to heavy metals and metalloid as the oral reference dose (RfD) and oral slope factor (SF) (USEPA IRIS http://www.epa.gov/iris/)

Heavy Metals	**Oral RFD (mg/kg/day)**	**Oral SF $(mg/kg/day)^{-1}$**
Cu	$4x10^{-2}$	n.a.
Zn	0.3	n.a.
Fe	0.7	n.a.
Co	$2x10^{-2}$	n.a.

Ni	2×10^{-2}	n.a.
Mn	1.4×10^{-1}	n.a.
Pb	3.5×10^{-3}	n.a.

*n.a. not applicable

Table 4.38 Scales for chronic and carcinogenic risk assessment (USEPA 1999)

Risk Level	**HQ/HI**	**Chronic Risk**	**Calculated cases of cancer occurrence**	**Cancer Risk**
1	< 0.1	Negligible	< 1 per 1000,000 inhabitants	Very low
2	≥ 0.1 <1	Low	> 1 per 1000,000 inhabitants	Low
			< 1 per 100,000 inhabitants	
3	≥ 1 <4	Medium	> 1 per 100,000 inhabitants	Medium
			< 1 per 10,000 inhabitants	
4	≥4	High	> 1 per 10,000 inhabitants	High
			< 1 per 1000 inhabitants	
			> 1 per 1000 inhabitants	Very High

Table 4.39 HQ and HI values for water (all concentrations are average of pre and post monsoon season)

Sample code	**Sample Location**	**HQ**							**HI**
		Cu	**Zn**	**Fe**	**Co**	**Ni**	**Mn**	**Pb**	
W1	Kakarai pond	0.11	0.01	0.03	0.24	0.01	1.05	0.00	1.45
W2	Kakarai school	0.12	0.41	0.02	0.16	0.01	0.52	0.00	1.23
W3	Maliyun Dhani	0.13	0.15	0.10	0.26	0.01	0.52	0.00	1.16
W4	Ahiro Dhani	0.12	0.15	0.44	0.22	0.01	0.74	0.00	1.66
W5	Rajota	0.14	0.05	0.14	0.19	0.00	0.73	0.00	1.26
W6	Khetri	0.13	0.05	0.11	0.23	0.01	0.62	0.00	1.15
W7	Teelawali	0.15	0.44	0.13	0.26	0.01	0.81	0.00	1.80
W8	Meghawali Dhani	0.15	0.07	0.24	0.18	0.01	0.70	0.00	1.34
W9	Khakara Devran	0.15	0.07	0.03	0.30	0.01	0.63	0.00	1.19
W10	Kharkara Rajputan	0.16	0.29	0.05	0.21	0.01	0.73	0.00	1.43
W11	River bed	0.15	0.52	0.02	0.17	0.01	0.70	0.00	1.57
W12	Khetri Nagar	0.15	0.19	0.15	0.25	0.01	0.74	0.00	1.49
W13	Bhargda Dhani	0.25	1.33	0.15	0.13	0.01	0.82	0.00	2.67

W14	Near tailing	0.16	0.98	0.23	0.26	0.01	1.07	0.00	2.71
W15	Kanjaniyun Dhani	0.17	0.12	0.70	0.29	0.01	1.06	0.00	2.34
W16	Gujarwas	0.16	0.10	0.02	0.66	0.00	1.48	0.00	2.42
W17	Singhana	0.17	0.53	0.16	0.24	0.01	0.90	0.00	2.00
W18	Chaandbari	7.43	0.10	0.02	2.89	0.10	29.00	0.00	39.54
W19	Bhand bhatiar	0.09	0.08	0.02	0.19	0.01	0.76	0.00	1.14
W20	Badheswar	0.12	0.03	0.02	0.28	0.01	1.06	0.00	1.51
W21	Bawadi Dhani	0.11	0.01	0.02	0.27	0.01	2.88	0.00	3.29
W22	Banwas	0.12	1.17	0.10	0.19	0.01	1.19	0.00	2.78
W23	Guest house	0.18	0.13	0.33	0.22	0.01	1.40	0.00	2.26
W24	Bass Govind Singh	0.14	0.01	0.02	0.26	0.01	0.93	0.00	1.36
W25	Pilani	0.14	0.01	0.01	0.17	0.01	0.70	0.00	1.04
	Minimum	0.09	0.01	0.01	0.13	0.00	0.52	0.00	1.04
	Maximum	7.43	1.33	0.70	2.89	0.10	29.00	0.00	39.54
	Average	0.44	0.28	0.13	0.35	0.01	2.07	0.00	3.27
	STDEV	1.46	0.37	0.16	0.54	0.02	5.63	0.00	7.58

4.2.4 Vegetables

Plants have the capacity to accumulate heavy metals from atmosphere, water and soils during their metabolic processes. The contaminated vegetables and part(s) of plants are consumed by humans and hence, the assessment of metal pollution index and hazard quotient is important.

4.2.4.1 Metal pollution index

To compare the total heavy metal content in vegetables from different sampling locations, the metal pollution index (MPI) is calculated (Usero *et al*., 1996) using Eq. 1.

$$MPI = (C_{f1} \times C_{f2} \ldots\ldots \times C_{fn})^{1/n} \qquad \text{--(1)}$$

Where, C_{f1} is the heavy metal concentration in the sample and n is the total number of heavy metals.

MPI is calculated to assess the metal pollution index in the vegetables of Khetri region. The calculated MPI varies from 1.76 to 2.03 with an average of 1.87±0.10 (Fig. 4.76). The calculated MPI is maximum for Guar (2.03) followed by spinach (1.99). Higher MPI in Guar and Spinach indicates the high accumulation of heavy metals in these vegetables and could result in high health risk in humans. The minimum MPI is for lady’s finger i.e. 1.76.

4.2.4.2 Daily intake of heavy metals and Risk assessment

The health risk assessment was calculated using hazard quotient (HQ) calculated using Eq. (2)

$$HQ = \frac{ADD}{RFD} \qquad \text{--(2)}$$

Where, ADD is the average daily dose (mg kg^{-1} day^{-1}) and RFD is the oral reference doses were 4×10^{-2}, 0.3 and 1×10^{-3} mg kg^{-1} day^{-1} for Cu, Zn and Cd, respectively (USEPA, 2002) and 0.004, 0.02 and 1.5 mg kg^{-1} day^{-1} for Pb, Ni and Cr, respectively (USEPA, 1997).

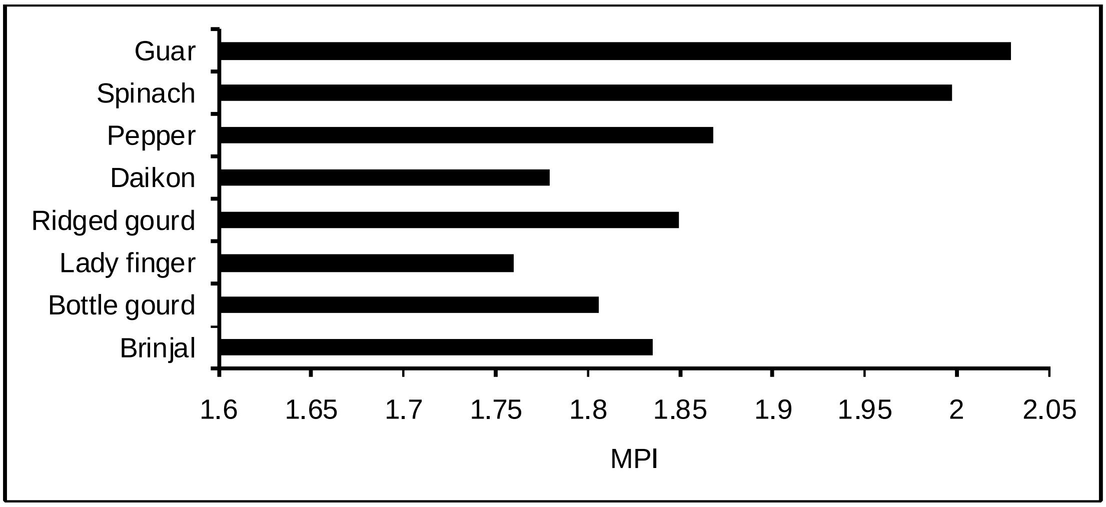


Fig. 4.76 MPI values with respect to vegetables

Estimated exposure is obtained by dividing daily intake of heavy metals by their safe limits. An index more than 1 is considered as not safe for human health (USEPA, 2002). The average daily dose of heavy metals through the consumption of the vegetables was calculated according to the given Eq. 3:

$$\mathrm{ADD}(\mathrm{mg/day}) = \frac{\mathrm{D}(\mathrm{Kg/day}) \times \mathrm{C}(\mathrm{mg/Kg})}{\mathrm{W(Kg)}} \qquad \text{--(3)}$$

Where, C is measured heavy metal concentration (mg/kg) in the fresh weight vegetables, D is the average daily dose (Kg/day) and the daily vegetable intake in rural India is 0.208 kg/day (Mittal, 2007). W, is average body weight of an adult is taken as 70 kg (Rattan *et al*., 2005).

The Gaur is oil seed and has very high concentration of heavy metals compared to other vegetables. Guar is used as vegetable when it is green. Hence, daily intake and hazard quotient were calculated for both including and excluding the heavy metal concentration in Guar.

The provisional daily intake of heavy metals Cu, Zn, Cd and Pb is 3 mg, 60 mg, 60 and 214 respectively (WHO/FAO, 2007). Average daily dose is within the limit for all the heavy metals (Table 4.40).

Table 4.40 Average daily dose and hazard quotient of heavy metals in vegetables

Elements	**Including Guar concentration**		**Excluding Guar concentration**	
	ADD (mg)	**HQ**	**ADD (mg)**	**HQ**
Cu	0.220645	5.516128	0.196651	4.916277
Fe	0.460451	-	0.367916	-
Zn	0.135398	0.451326	0.134785	0.449283
Mn	0.068581	-	0.066386	-
Pb	0.000506	0.126589	0.000591	0.147687
Co	0.000131	-	0.000149	-
Ni	0.003487	0.17435	0.003174	0.158719
Cd	4.22E-05	-	4.82E-05	-
Cr	0.002405	0.001603	0.00179	0.001194

The health risk due to consumption of vegetables is expressed as Hazard quotient for specific metal. HQ for Cu is highest among all the heavy metals and it is 4 times higher than the standard value 1 (Fig. 4.77). Cu HQ is followed by the Zn > Ni > Pb > Cr. It is same sequence followed by the water soluble fraction in the fractionation. Hence the Cu, ZN and Ni are dominantly available and get accumulated in the vegetables and can cause health risk to humans.

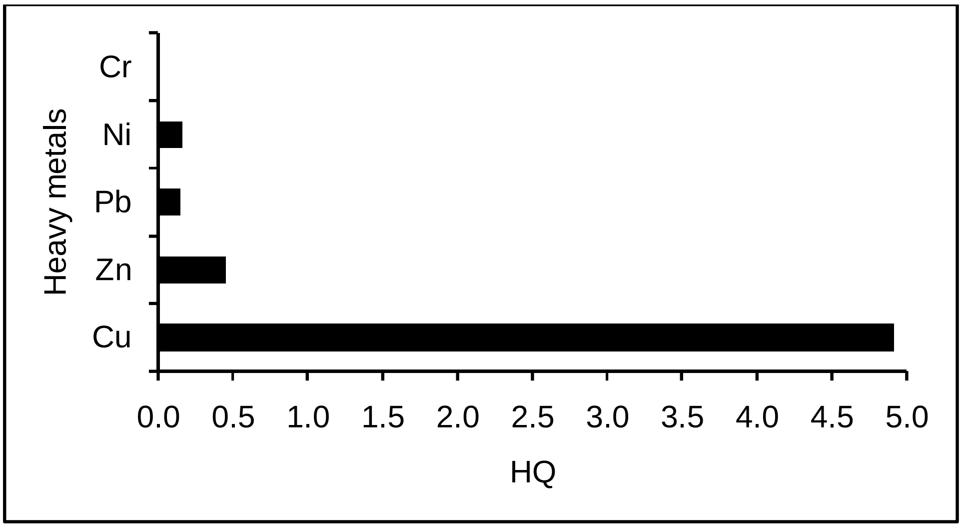


Fig. 4.77 Calculated values of hazard quotient (HQ) with respect to heavy metal concentration

In Khetri region, the residents do not prefer to grow vegetables in their household gardens due to scarcity of water. According to local people, the supply of vegetables is from distant locations approximately 30-40 km away from mining. Hence, the impact is not be the potential and health impacts are minimum due to consumption of vegetables. Cu is present in the aerosol hence the impacts on health are due to inhalation of Cu or through drinking of contaminated groundwater.

Chapter 5

Conclusions

Conclusions

Systematic field and laboratory studies on the distribution and behavior of heavy metals in general and Cu in particular in mine tailings, surface soils, ground water, surface water and vegetables from the Khetri copper mining region of Rajasthan were carried out to understand the impact of copper mining on the immediate environment. Based on field and extensive laboratory data along with the calculated pollution indices (i.e. HPI, CI, WQI, MPI, I_{geo}, CF, PLI and EF) of heavy metals, following are some of the salient findings on physiochemical characteristics of tailings; nature, mineralogy and geochemical makeup of soils; behavior of heavy metals in tailings and soils; quality and chemical composition of waters; heavy metal abundances in several types of vegetables; probable source(s) of various elements in both water and soils in addition to the status of heavy metal pollution in the environment of the region. Accordingly, potential management strategies of mine tailings and overburden materials are proposed to prevent and/or reduce heavy metal pollution for a sustainable ecosystem.

Khetri Copper Mining Region, Rajasthan

1. Mining for copper in Khetri, Rajasthan has been going on since several decades and the resulted mine tailings in huge quantities are dumped in an open area of ~1 sq. km.
2. In Khetri, copper occurs in association with sulphides (pyrrhotite, chalcopyrite and pyrite) which constitute ~10 volume % of the rock/ore being mined along with gangue minerals such as quartz, amphiboles, mica, chlorite and magnetite.
3. At Khetri, on an average, to get 1 kg of copper, ~1 ton of sulphide bearing rock/ore is being mined, milled and processed till the froth flotation stage at the mining site, and the waste, thus generated (~25000 tons/year) in the form of tailings are being thrown into the environment.

4. The Khetri copper belt is in the semi-arid zone, and geologically consists of garnetiferous chlorite quartz schist, amphibole chlorite quartzite and quartzite, and the area is covered with a thick layer of wind-blown sandy soils.

Mine Tailings at Khetri

1. The mine tailings at Khetri are medium grained with ~65 volume % of the bulk is +63 mesh size, and the rest ~35 volume % is -63 mesh size.
2. Relatively new tailings are grey and the old tailings are oxidized and show reddish/yellowish tinge, both new and old tailings are acidic with an average pH of 3.5 and 5.2 respectively.
3. Tailings consist mainly of quartz, K-feldspar, Na-plagioclase, amphibole, pyroxene, garnet, goethite, calcite, mica, chlorite, chalcopyrite, pyrrhotite and pyrite.
4. They contain 56 wt. % SiO_2, 17 wt. % FeO, 11 wt. % Al_2O_3 and LOI ranges from 2.89 to 13 wt. % with an average of 5.49 wt. %. Higher concentration of iron is due to the presence of pyrite and pyrrhotite.
5. The average concentrations of heavy metals (Zn = 299 ppm; Cr = 153 ppm; Co = 53 ppm and Mn = 1492 ppm) in the tailings are higher than those reported for North American Shale Composite, world average shale and Upper Continental Crust.
6. The tailings contain an average concentration of 2047 ppm Cu, which is 82, 46 and 280 times higher than that of Upper Continental Crust (25 ppm), world average shale (45 ppm) and the regional background reference soils (7.3 ppm) respectively.
7. The observed ~5000 ppm copper in some tailing samples is surprising, because, it is ~50 % of the total copper present in the unprocessed ore

indicating incomplete recovery of copper from the bulk ore, and ineffectiveness of the beneficiation method being followed.

8. The observed positive correlation among Cu, Zn, Co, Fe and Ni in the tailings confirms the presence of sulphides, which by their fine grained nature and aerial exposure, will not only get easily be oxidized and release with their heavy metal content, but also get carried by the strong desert winds and contaminate the local environment (i.e., air, soils, and water etc).
9. The observed lower concentrations of Cu (1253 ppm) and Zn (202 ppm) in old tailings compared to new tailings (2542 ppm Cu and 360 ppm Zn) are due to leaching of heavy metals during oxidation process.
10. Absence of correlation between pH and heavy metal abundances in tailings indicates oxidation and dissolution of sulphides present in the tailings.
11. The calculated average I_{geo} values for heavy metals, particularly for Cu (7.28) and Co (4.00) indicate that the tailings are in the extremely contaminated zone.
12. According to calculated average PLI (2.3) values, the tailings of the Khetri region falls in the heavy pollution zone.
13. The huge quantities of tailings being piled up at Khetri, by virtue of their heavy metal rich sulphides and fine grain nature form a potential source of contaminants.
14. Additionally, the semi-arid climate (i.e., higher temperature and stronger winds) and the sparse vegetation cover in the region promoted the aerial dispersal of heavy metal bearing tailings and overburden materials into the surrounding soils and surface water bodies.

Soils in and around Khetri

1. The soils in Khetri area are medium to coarse grained with ~73 volume % of the bulk is +63 mesh size, and ~27 volume % is –63 mesh size.

2. Soils are acidic to alkaline (pH = 6.1 to 8.2 with an average of 7.5).
3. They consist mainly of quartz, mica, chlorite, K-feldspar, Na-plagioclase, amphibole, pyroxene, garnet and calcite.
4. They consist dominantly of SiO_2 (66 wt. %) and Al_2O_3 (13 wt %) with relatively lower concentrations of CaO (2.6 wt. %), MgO (4.6 wt. %), K_2O (1.68 wt. %), P_2O_5 (0.14 wt. %), MnO (0.05 wt. %) and LOI (5.1 wt. %). Thus these soils are typical of those found in sub-tropical semi-arid regions, being leached, low in nutrient and of poor fertility.
5. The calculated CIA (69) of the representative soil samples reveals a moderate chemical weathering of the parent lithologies.
6. The average concentration of heavy metals (Zn = 88 ppm; Cr = 83 ppm; Co = 14 ppm and Mn = 469 ppm and Ni = 32 ppm) in the soils are higher than those reported for North American Shale Composite (NASC), world average shale (WAS) and Upper Continental Crust (UCC).
7. The distinct characteristic of these soils is their high Cu (an average of 231 ppm) content, which is 9, 5 and 32 times higher than that of the UCC, WAS and LS respectively.
8. Soils proximal to active mines (Banwas) and overburden materials (1224 ppm) have higher concentration of Cu compared to those from distal locations (14 ppm).
9. The correlation matrix and Principal Component Analysis (PCA) suggests a common source (i.e. mining activities) for Cu, Zn, Cr, Co, Ni, Mn and Fe in the soils, except Pb and Cd. For Pb and Cd, the source is weathering of parent rock along with other anthropogenic activities. The source for Cr in soils is both mining activities and weathering of parent rocks.
10. The observed strong negative correlation between pH and heavy metals (Cu, Zn and Fe) in soils indicates the role of sulphides in controlling the pH and heavy metals abundances i.e. high sulphide content lowers the pH and thus more heavy metals.

11. The calculated average I_{geo} values for Cu (2.58) and Co (1.39) indicate that the soils are in the highly contaminated range compared to regional reference soil.
12. According to PLI (1.5), the soils of the Khetri region falls in the moderate pollution zone.

Groundwater in and around Khetri

1. The groundwater of Khetri is neutral to slightly alkaline in both pre and post monsoon season (pH =7 to 8). It is hard (TH = 1110 and 782 mg/L post and pre monsoon respectively) with an average EC of ~2000 and 1900 µs/cm in post and pre monsoon respectively.
2. The groundwater consists dominantly of Ca^{2+} (units are in mg/L: post monsoon = 166; pre monsoon = 176), Mg^{2+} (post monsoon = 170; pre monsoon = 89), Na^{+} (post monsoon = 243; pre monsoon = 166), HCO_3^- (post monsoon = 328; pre monsoon = 360) and Cl^- (post monsoon = 259; pre monsoon = 518) and all exceed the WHO (2011) and BIS (2012) permissible limits.
3. The concentration of cations in decreasing order of abundance is $Na^+ > Mg^{2+} > Ca^{2+} > K^+$ and that of anions is $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$ during post monsoon, and it is $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ and $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$ in pre monsoon.
4. The abundances of major ions are more in groundwater samples around the mining activities (W23) and downstream flows (W5, W13, W14, W15, W16 and W17) compared to those of upstream.
5. Based on calculated TH (post monsoon = 1110 mg/L; pre monsoon = 782 mg/L) and WQI (post monsoon = 179; pre monsoon = 173), the groundwater in Khetri region is unsuitable for drinking purposes.

6. Higher EC (~1900 and 2000 µs/cm during pre and post monsoon respectively), magnesium hazards (MH) and permeability index (PI) suggest its unsuitability for irrigation.
7. Equal dominance of alkaline earth elements (Ca^{2+} + Mg^{2+}) and alkalies (Na^{+} + K^{+}), along with dominance of strong acids (Cl^{-}) over weak acids (HCO_3^{-}) suggest influence of silicate weathering and anthropogenic activities in the region.
8. The observed significant positive correlation between major cations (Ca^{2+}, Mg^{2+} and Na^{+}) and SO_4^{2-} suggests weathering of sulphides in the region.
9. Absence of correlation between major cations (Ca^{2+}, Mg^{2+} and Na^{+}) and HCO_3^{-} indicates either lack of carbonate weathering or dominance of silicate weathering in the region.
10. The Gibbs plot drawn for cations and anions as a function of TDS indicates the evolution of groundwater from rock-water interaction in both the seasons.
11. The Piper plot shows the dominance of hydrogeochemical facies such as Ca-Mg-Cl, Ca-HCO_3 and Na-Cl in both the seasons. The Ca-Mg-Cl and Na-Cl present in the groundwater are responsible for permanent hardness and salinity respectively in the region.
12. The observed high EC and major ion concentration in the groundwater samples surrounding the mines, overburden materials and tailings are due to dissolution of minerals by AMD. Hence, assessment and monitoring of waste is important to avoid the environmental contamination in the mining region.
13. The heavy metal (Cu, Ni, Co, Fe and Mn) concentration data on majority of groundwater samples for the both pre and post monsoon from the Khetri region indicate that they exceed the desirable limits set by WHO, 2011 and BIS, 2012.

14. Fe is in much higher concentration (1.65 and 1.90 ppm during pre and post monsoon respectively) and exceeds the permissible limit in almost all the samples in both the seasons due to leaching or oxidation of sulphides. In addition, Fe is more mobile in the groundwater relative to Cu due to its high sensitivity to redox conditions.
15. The correlation matrix ($p>0.01$) and PCA (57% of variance) indicates the source of Cu, Co, Ni and Mn in the groundwater is anthropogenic activities (sulphides ores) in the region.
16. Lack of correlation between Fe and heavy metals is due to occurrence of Fe as oxides, silicates, carbonates in addition to sulphides as well as its high sensitivity to changing environment.
17. The observed significant negative correlation of pH with Cu, Co, Ni and Mn at $p>0.01$ confirms the decrease in pH of water with the increase of heavy metal contamination, while EC does not show strong correlation with the heavy metals as EC is mostly controlled by the major ion chemistry.
18. The calculated pollution indices namely CI and I_{ER} indicate groundwater near the mining activities falls in extremely contaminated (W4, W15 and W18) and highly contaminated zone (W14 and W23).
19. The hazard quotient for non-carcinogenic health effects is in the acceptable limit (< 1) for all the samples except samples from Chaandmari mine (~40), whereas the Health Index (HI) is in the medium range (≥ 1 <4) for all the samples indicating the average suitability of water for drinking purposes except few samples.

Vegetables Grown in and around Khetri

1. Among the heavy metals (Cu, Zn, Ni, Mn, Fe, Co, Pb and Cd), Fe is the most abundant (143 ppm) followed by Cu (72 ppm) in all the studied vegetables of Khetri area.

2. Cu concentration in the studied vegetables is 2 times higher than the permissible limit (30 ppm) of Prevention of Food Adulteration (PFA) act. Guar (oil seed) and Spinach (leafy vegetable) have relatively higher concentrations of Cu compared to other studied vegetables.
3. Zn concentration in some vegetables (pepper and spinach) exceeds the PFA limit (45 ppm), while Ni, Mn, Fe, Pb and Cd are present within the permissible limit of PFA.
4. The average concentration of heavy metals in leafy vegetables are higher (63 ppm) compared to that of fruit (28 ppm) and root (22 ppm) vegetables. The observed higher concentration of heavy metals in leafy vegetables is due to their high surface area.
5. The rank order of vegetables according to their heavy metal abundances is, Guar > Spinach > Pepper > Ridged gourd > Brinjal > Bottle gourd > Daikon > Lady’s finger.
6. The order of abundance of individual heavy metals in vegetables is:
   Fe >Cu >Zn >Mn >Ni >Pb >Cd
7. Vegetables grown in the Khetri mining area have higher abundances of heavy metals in general, Cu in particular compared to those far from mining area.
8. The heavy metal concentration data on several vegetables will help to assess the impact of consumption of heavy metal bearing vegetables on human health in the region.

Heavy Metal Fractionation and Bioavailability

In addition to knowing the concentration of heavy metals in the environmental samples, knowledge on their bioavailability is equally important to assess their effect on environment and human health. Therefore, the observed higher concentrations of heavy metals in the Khetri environment warrants further systematic studies on bioavailability and their toxic effects.

1. Both in tailings and soils, the fine fraction is enriched in heavy metals compared to bulk for both single regent extracts and sequential fractions.
2. Extraction of Cu with EDTA and AA is more in soils compared to tailings despite its high concentration in tailings which indicates that in tailings, the heavy metals are present in association with sulphides, while in soils they are present as loosely bound pollutant pool.
3. The rank order of heavy metal concentration in different fractions of soils is:
   Residue >reducible >acid leachable >water soluble, and
   In tailings, it is:
   Residue >acid leachable >reducible >water soluble
4. In case of tailings, the acid leachable fraction is more as they are fine grained with sulphides. Hence, acidification or oxidation of tailings (AMD) would enhance the leaching of heavy metals.
5. In soils, reducible fraction dominates over the acid leachable fraction, which indicates occurrence of heavy metals as adsorbed Fe-Mn oxyhydroxides.
6. Concentration of Cu in water soluble, acid leachable and reducible fraction of soils is higher compared to that of tailings indicates that in tailings the heavy metals are present in the crystal lattice of sulphides.
7. In soils, Ni is most mobile followed by Zn >Cu >Pb >Cr. In tailings, the same trend is followed excepting Cr and Pb, which are absent in water soluble fraction.
8. Since, the source for Cr and Pb in soils of Khetri is lithogenic, they are (Cr and Pb) less extracted in water soluble fraction or non residual fractions compared to that of anthropogenic source.

9. Single and sequential extraction method indicates that the source of heavy metals (Cu, Zn and Ni) is anthropogenic as their concentrations are higher in non residual fraction of the soils.

Suggested Management Strategies

The soils, groundwater and vegetables in Khetri and surrounding areas within the limits of this study suggest a significant concentration of heavy metals largely from mining and related activities in the area (Fig. 5). Enrichment factors, pollution load and geo-accumulation indices on the samples studied indicate enrichment of heavy metals above their respective background concentrations as well as permissible limits. The degree of contamination of heavy metals has been observed to decrease farther downstream and away from the contamination sources i.e. tailings and overburden materials. The research highlights the impacts of mining, mine waste, and the improper disposal of mine waste on the quality of soils and water, and effects on food quality. Therefore, in order to ensure no or minimal effects on soils and water resources, the following action plan is suggested.

1. Studies to explore on the management options for existing tailings and overburden materials to minimise their impacts on human health and environment are warranted.
2. Application of effective and efficient methods of metal milling and beneficiation technologies in order to minimize the concentration of copper in tailings and thus in environment (soils, water, air and crops).
3. It is essential to recover the Cu from the existing tailings so as to minimize their further impact on the environment.
4. Reclamation of the open pit mine areas to the conditions capable of supporting alternative sustainable land uses.

5. The observed higher concentration of Cu in the vegetables of Khetri area is a cause of serious concern, and therefore, its potential toxic effects on the health of the people in the region needs to be studied.

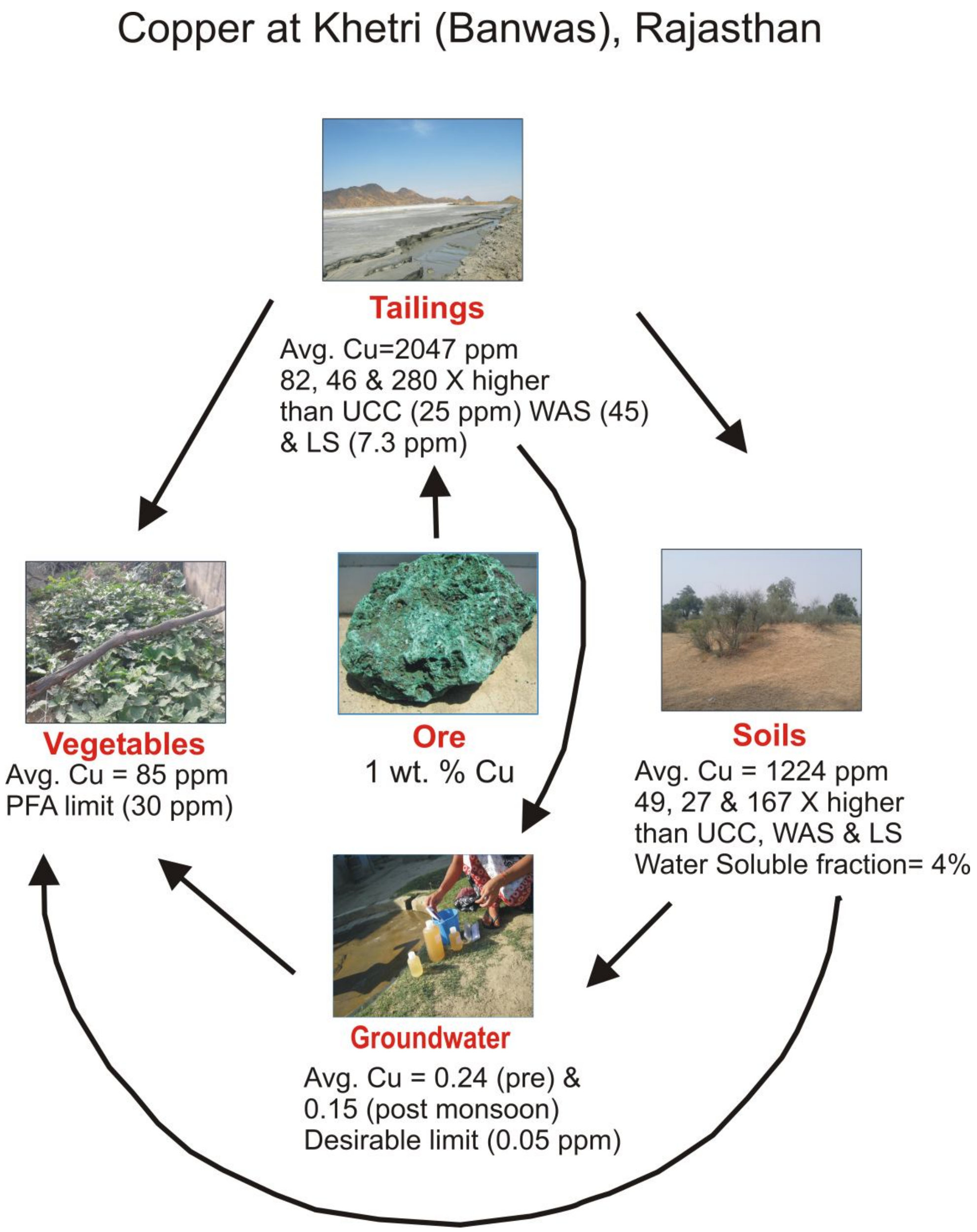


Fig. 5 Schematic diagram showing the concentration of Cu in different components of the environment at Khetri.

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