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SEASONAL VARIATION OF HEAVY METAL IN INDUSTRIAL ZONE SOIL OF MYSORE CITY, KARNATAKA, INDIA

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ABSTRACT
The main aim of this study to analyze the total concentration of Fe, Cu, Cr, Zn and Ni in the industrial zone soils of Mysore city, Karnataka, India, during different seasons of the year. Nine representative soil samples were collected from the industrial area of Mysore city, Karnataka, India. Total heavymetal concentration has been determined by aquaregia method. For pre monsoon season the metal concentration for iron is 2.6gm/kg to 6.1gm/kg , copper 13.9mg/kg to 25.2 mg/kg, chromium 8 mg/kg to 18.4 mg/kg, zinc 60.7 mg/kg to 119.8 mg/kg and nickel 10 g/kg to 17.1 g/kg. For monsoon season the concentration was iron 2.44 g/kg to 5.9 gm/kg, copper 12.9 mg/kg to 20.6 mg/kg, chromium 5.6 mg/kg to 16.8 mg/kg, zinc 60.8 mg/kg to 107.4 mg/kg and nickel 8.5 mg/kg to 14.1 mg/kg and finally for post monsoon season the heavymetal concentration was iron 2.5 gm/kg to 6.1 gm/kg, copper 14 mg/kg to 19.7 mg/kg, chromium 7 mg/kg to 22.2 mg/kg, zinc 63 mg/kg to 111.4 mg/kg and nickel 9.7 mg/kg to 18 mg/kg. Finally it reveals that heavy metal accumulation has been observed from the different processes involved in the industries. Due to the dilution factor in the rainy season the metal ions will get diluted with the water and the concentration of the heavymetals will be less in monsoon season than pre monsoon and post monsoon season. Finally we found the heavy metal concentration in the sequence of Fe>Zn>Cu>Cr>Ni and Monsoon < post-monsoon < pre-monsoon season.

Key Words: Aquaregia, Industries, Monsoon, Metal Ion, Soil Pollution

INTRODUCTION
Heavy metals are considered to be one of the main sources of pollution in the environment, because of their significant effect on the ecological quality (Sastre *et al*., 2002). The main sources of heavy metal pollution in the environment are man-made effects, including combustion of fossil fuels, mining activities, wastewater discharges of manufacturing industries, and waste disposal (Friberg *et al.,* 1986). High levels of heavy metals in the sediments and soils may pass to the aquatic environment, groundwater, and plants through the transfer processes and reach to the animals and humans. Heavy metal pollution is a problem associated with areas of intensive industry. However, roadways and automobiles now are considered to be one of the largest sources of heavy metals. Zinc, copper, and lead are three of the most common heavy metals released from road travel, accounting for at least 90 of the total metals in road runoff (Khalid Farooq Akbar *et al.,* 2006). Lead concentrations, however, consistently have been decreasing since leaded gasoline was discontinued. Smaller amounts of many other metals, such as nickel and cadmium, are also found in road runoff and exhaust.

About half of the zinc and copper contribution to the environment from urbanization is from automobiles. Brakes release copper, while tire wear releases zinc. Motor oil also tends to accumulate metals as it comes into contact with surrounding parts as the engine runs, so oil leaks become another pathway by which metals enter the environment.

On the road surface, most heavy metals become bound to the surfaces of road dust or other particulates. During precipitation, the bound metals will either become soluble (dissolved) or be swept off the roadway with the dust. In either case, the metals enter the soil or are channeled into a storm drain. Whether in the soil or aquatic environment, metals can be transported by several processes. These processes are governed by the chemical nature of metals, soil and sediment particles, and the pH of the surrounding environment.

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Lead would be released by leaded gasoline, tire wear, lubricating oil and grease, bearing wear. The tire wear, motor oil, grease, brake emissions, corrosion of galvanized parts results in discharge of zinc. Copper enters in to environment by bearing wear, engine parts, and brake emissions. Chromium found in air conditioning coolants, engine parts, brake emissions. Nickel comes from the usage of diesel fuel and gasoline, lubricating oil, brake emissions and Aluminum can expect by the auto body corrosion.

Most heavy metals are cations, meaning they carry a positive charge. Zinc and copper, for instance, both carry a 2+ charge. Soil particles and loose dust also carry charges. Most clay minerals have a net negative charge. Soil organic matter tends to have a variety of charged sites on their surfaces, some positive and some negative. The negative charges of these various soil particles tend to attract and bind the metal cations and prevent them from becoming soluble and dissolved in water. The soluble form of metals is thought to be more dangerous because it easily is transported and more readily available to plants and animals. By contrast, soil bound metals tend to stay in place.

Metal behavior in the aquatic (streams, lakes and rivers) environment is surprisingly similar to that outside a water body. Streambed sediments exhibit the same binding characteristics found in the normal soil environment. As a result, many heavy metals tend to be sequestered at the bottom of water bodies. Some of these metals will dissolve. The aquatic environment is more susceptible to the harmful effects of heavy metal pollution because aquatic organisms are in close and prolonged contact with the soluble metals.

pH tends to be a master variable in this whole process. pH is a measure of the concentration of hydrogen (H+) ions dissolved in water. H+ is the ion that causes acidity; however, it is also a cation. As a cation it is attracted to the negative charges of the soil and sediment particles. In acid conditions, there are enough H+ ions in to occupy many of the negatively charged surfaces of clay and organic matter. Little room is left to bind metals, and as a result, more metals remain in the soluble phase.

The effects of pH are even more pronounced in the Washington, DC metropolitan area because of the problem of acid rain. Acid rainfall can cause a large increase in acidity and a corresponding increase in the amount of heavy metals becoming soluble.

Soil Pollution

In a general sense, soil pollution definition is the presence of toxic chemicals (pollutants or contaminants) in soil in high enough concentrations to be of risk to human health and/or ecosystem. Additionally, even when the levels of contaminants in soil are not of risk, soil pollution may occur simply due to the fact that the levels of the contaminants in soil exceed the levels that are naturally present in soil (in the case of contaminants which occur naturally in soil).

Soil pollutants include a large variety of contaminants or chemicals (organic and inorganic), which could be both naturally-occurring in soil and man-made. In both cases, the main soil pollution causes are the human activities (i.e., the accumulation of those chemicals in soil at levels of health risk is due to human activities such as accidental leaks and spills, dumping, manufacturing processes, etc.). Accumulation due to natural processes is also possible, but it has only been recorded in few cases (such as the accumulation of higher levels of perchlorate in soil from Atacama Desert in Chile which is purely due to natural processes in arid environments). Natural processes, however, may have an influence of the human released toxic chemicals (pollutants) in the soil, overall decreasing or increasing the pollutant toxicity and/or the level of contaminated soil. This is possible due to the complex soil environment involving the presence of other chemicals and natural conditions which may interact with the released pollutants.

Heavy metal contamination of soil results from anthropogenic such as mining (Navarro *et al.,* 2008), smelting process (Brumelis *et al.,* 1999) and agriculture issues (Vaalgamaa *et al.,* 2008) as well as natural activities. Through the Chemical and metallurgical industries the most of the important heavy metals will be released to the environment (Cortes *et al.,* 2003).

Soil Pollution and Its Effects

Soil pollution may affect all of us as well as plants and animals. However, children are usually more susceptible. This is because kids are more sensitive to various pollutants and they may come in close

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contact with soil by regularly playing in the ground for example. Thus, soil pollution for kids always involves higher risks than for adults. While anyone is susceptible to soil pollution, soil pollution effects may vary based on age, general health status and other factors.

A more detailed explanation of various processes contributing to soil pollution, along with concrete examples of the most common soil pollutants generating soil poisoning issuesare given below. Additionally, soil poisoning prevention, a summary of the main health issues associated with contaminated or polluted soils (also referred to as soil poisoning) is also included.

All soils (weather polluted or un-polluted) contain a variety of compounds (contaminants) which are naturally present. Such contaminants include metals, inorganic ions and salts (e/g., phosphates, carbonates, sulfates, nitrates), and many organic compounds (such as lipids, proteins, DNA, fatty acids, hydrocarbons, PAHs, alcohols, etc.). These compounds are mainly formed through soil microbial activity and decomposition of organisms (e.g., plants and animals). Additionally, various compounds get into soil from the atmosphere (with precipitation water, as well as by wind activity or other types of soil disturbances) and from surface water bodies and shallow groundwater flowing through the soil. When the amounts of soil contaminants exceed natural levels (what is naturally present in various soils) pollution is generated. There are the following main mechanisms that generate soil pollution:

Antropogenic – Through Human Activity Including:

• Accidental spills and leaks during storage, transport or use of chemicals (e.g., leaks and spills of gasoline and diesel at gas stations).
• Foundry activities and manufacturing processes that involve furnaces or other processes resulting in possible dispersion of contaminants in environment.
• Mining activities involving crushing and processing of raw materials (such as mining activity).
• Construction activities.
• Agricultural activities involving the spread of herbicides/pesticides/insecticides and fertilizers.
• Transportation activities. (e.g., vehicle emissions)
• Dumping of chemicals (accidental or intended – such as illegal dumping).
• Storage of wastes in landfills (which may leak to groundwater or generate polluted vapors).
• Cracked paint chips falling from building walls, especially lead-based paint.

Natural:

• Natural accumulation of compounds in soil due to imbalances between atmospheric deposition and leaching away with precipitation water. (e.g., concentration and accumulation of perchlorate in soils in arid environments)
• Natural production in soil under certain environmental conditions. (e.g., natural formation of perchlorate in soil in the presence of a chlorine source, metallic object and using the energy generated by a thunderstorm)
• Leaks from sewer lines into subsurface. (e.g., adding chlorine which could generate trihalometanes such as chloroform).

MATERIALS AND METHODS

Study Area

The study area Mysore is having more than 10 lakh populations and was capital of former state and 11^o6^1 latitude and 77^o7^1 longitude and general elevation is little more than 1800 feet above sea level. The climate of the city is moderated throughout the year with temperature during summer ranging from 30^oC to 34^oC. The rainy season is from June to October. The winter season starts from November to February. The source of water for domestic purpose is mainly from the Cauvery River and ground water. Mysore is having industrial areas, which have been majorly divided in to 3 regions as follows:

• Metagalli industrial area
• Hebbal Industrial area

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● Hootagalli Industrial area

Metagalli Industrial area consisting of industries like tyre manufacturing, aluminium industries, electric appliances manufacturing industry and metal industry. In Hebbal industrial area small scale industries are more in number than Metagalli industrial area. Hootagalli industrial area is smaller in its size as compared to Metagalli and Hebbal industrial areas. Here the industries like textile, heavy earth movers manufacturing industry and very few small scale industries are situated.

The samples were collected in polythene covers and brought to the laboratory for analysis. All the samples were dried in oven and passed through a 2-mm sieve. One gram of each air-dried and sieved soil sample was digested in 10 ml Aqua regia (1 part conc. HNO_3 to 3 parts HCl) in a digestion tube on the heating blocks at different temperatures and times (2 h at 25°C; 2 h at 60°C, 2 h at 105°C, and 3 h at 125°C), spreading over a total of nine hours. After the digestion, the digests were first centrifuged and then made up to the volume. The concentrations of Fe, Cu, Cr, Zn and Ni were determined by using atomic absorption spectroscopy. In the present study, sampling locations are included in all the three major industrial areas of Mysore city. Sampling site from 1 to 5 belongs to the Hootagalli and Hebbal industrial area and 6 to 9 samples were belonging to different industrial site of Metagalli industrial area. The samples were collected during pre monsoon, monsoon season and post monsoon season. The samples were analysed using standard methods to determine the concentration of heavy metals of the soil and the results were tabulated.

Figure 1: Location map of study area

RESULTS AND DISCUSSION
Table 1: Heavymetal concentration in Industrial area of Mysore city during Pre monsoon-2010

Station code	Fe	Cu	Cr	Zn	Ni
P1	4.5	25.2	10	72.5	14.2
P2	3.069	13.9	8.0	70.6	15.6
P3	5.441	19.3	12.0	60.7	15.5
P4	6.1	14.4	15.2	98.3	12.2
P5	5.24	19.8	16.8	119.8	17.1
P6	4.43	17.8	12.2	112.6	13.5
P7	4.2	20.9	15.3	103.5	11.3
P8	2.667	17.8	18.4	105.6	10.3
P9	3.76	19.0	13.9	105.5	10.0

Note: All the results are expressed in mg/kg except Fe (gm/kg)

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Table 2: Heavymetal concentration in Industrial area of Mysore city during Monsoon-2010

Station code	Fe	Cu	Cr	Zn	Ni
P1	3.7	20.6	9.9	72.6	12.5
P2	2.88	13.1	5.6	60.8	13.0
P3	5.449	16.2	9.4	63.6	12.1
P4	5.96	12.9	13.0	82.8	11.7
P5	5.36	17.6	14.4	97.0	14.1
P6	4.04	14.0	9.1	97.3	13.5
P7	3.93	17.4	10.3	92.6	8.9
P8	2.24	18.0	16.8	88.2	8.5
P9	3.55	16.0	12.2	107.4	11.3

Note: All the results are expressed in mg/kg except Fe (gm/kg)

Table 3: Heavymetal concentration in Industrial area of Mysore city during Post monsoon-2010

Station code	Fe	Cu	Cr	Zn	Ni
P1	3.84	19.7	9.6	75.0	12.4
P2	3.62	14.0	7.0	63.0	16.0
P3	5.27	16.8	8.0	67.0	12.1
P4	6.11	15.2	13.4	87.0	11.2
P5	5.47	17.6	22.2	93.0	18.0
P6	4.41	14.7	11.0	98.5	15.1
P7	3.95	17.7	11.8	90.0	11.6
P8	2.59	17.0	14.7	82.1	9.7
P9	3.42	16.8	12.3	111.4	12.3

Note: All the results are expressed in mg/kg except Fe (gm/kg)

Iron
Iron plays an important role in biology, forming complexes with molecular oxygen in haemoglobin and myoglobin, these two compounds are common oxygen proteins in vertebrates. Iron is also the metal used at the active site of many important redox enzymes dealing with respiration and oxidation and reduction in plants and animals.
In the present study the iron level varies from 2.6 gm/kg to 6.1 gm/kg in the Premonsoon season, whereas in monsoon its ranges from 2.44gm/kg to 5.9 gm/kg and 2.5 gm/kg to 6.1 gm/kg in the post monsoon season. It clearly indicates the metal availability is less in the monsoon season due to dilution of metal ion in the water. (Table 1, 2 and 3)(Figure 1)

Copper
Copper is usually present in soils within the range of 0 to 250 µg/gm (Alloway 1995). Its amount in urban and roadside soils, however, is reported to be 5–10 times higher than the normal concentrations (Baker *et al.,* 1995 and Nriagu 1979). Total copper content in most of the roadside soils was below or within the limits of the critical soil concentration of 60–125 µg/gm (ICRCL 1987). In the present study the copper level varies from 13.9 mg/kg to 25.2 mg/kg in the Premonsoon season, whereas in monsoon its ranges from 12.9 mg/kg to 20.6 gm/kg and 14.0 mg/kg to 19.7 mg/kg in the post monsoon season. (Table 1, 2 and 3) (Figure 2)

Chromium
The relative high hardness and corrosion resistance of unalloyed chromium makes it a good surface coating, being still the most popular metal coating with unparalleled combined durability. A thin layer of chromium is deposited on pre-treated metallic surfaces by electroplating techniques. There are two

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deposition methods: Thin, below 1 μm thickness, layers are deposited by chrome plating, and are used for decorative surfaces. If wear-resistant surfaces are needed then thicker chromium layers are deposited. Both methods normally use acidic chromate or dichromate solutions. To prevent the energy consuming change in oxidation state, the use of Chromium (III) sulfate is under development, but for most applications, the established process is used (*Dennis et al.,* 1993).

In the chromate conversion coating process, the strong oxidative properties of chromates are used to deposit a protective oxide layer on metals like aluminium, zinc and cadmium. This passivation and the self healing properties by the chromate stored in the chromate conversion coating, which is able to migrate to local defects, are the benefits of this coating method (Edwards *et al.,* 1997). Because of environmental and health regulations on chromates, alternative coating method are under development (Zhao *et al.,* 2001).

Chromium oxides are also used as a green colour in glassmaking and as a glaze in ceramics. Green chromium oxide is extremely light-fast and as such is used in cladding coatings. It is also the main ingredient in IR reflecting paints, used by the armed forces, to paint vehicles, to give them the same IR reflectance as green leaves (Marrion *et al.,* 2004).

In the industrial area soil showed, the chromium level ranges from 8 mg/kg to 18.4 mg/kg in the Premonsoon season, monsoon its ranges from 5.6 mg/kg to 16.8 mg/kg and 7 mg/kg to 22.2mg/kg in the post monsoon season. (Table 1, 2 and 3) (Figure 3)

Zinc
Normal concentrations of zinc in soil ranges from 1 to 900 mg/g (Alloway 1995). Mcgrath and Loveland (1992) reported that the zinc concentration in the soils of England and Wales ranged from 5mg/kg to 3648 mg/kg. In the present study, the concentration of zinc shows slightly higher range in some soil samples. It may due to due to the higher input of zinc in the roadside environments by motor vehicles surrounding in the industrial area and from the industrial activities and other activities. According to Kiekens (1995) the total zinc levels in polluted/disturbed soils in industrialised countries may account for hundred to thousand times higher than those in unpolluted soils. Here in our soil sample the values shows a little higher range in certain samples. For Pre monsoon it accounts 60.7 mg/kg to 119.8 mg/kg, for Monsoon 60.8 mg/kg to 107.4 mg/kg and for Post monsoon 63 mg/kg to 111.4 mg/kg. (Table 1, 2 and 3) (Figure 4)

Nickel
The metal is chiefly valuable in the modern world for the alloys it forms; about 60% of world production is used in nickel-steels (particularly stainless steel). Other common alloys, as well as some new super alloys, make up most of the remainder of world nickel use, with chemical uses for nickel compounds consuming less than 3% of production (Derek and Kerfoot 2005). As a compound, nickel has a number of chemical manufacturing uses, such as a catalyst for hydrogenation. Enzymes of some microorganisms and plants contain nickel as an active center, which makes the metal an essential nutrient for them. The fraction of global nickel production presently used for various applications is as follows: 60% for making nickel steels; 14% in nickel-copper alloys and nickel silver; 9% to make malleable nickel, nickel clad, inconel, and other super alloys; 6% in plating; 3% for nickel cast irons; 3% in heat and electric resistance alloys, such as Nichrome; 2% for nickel brasses and bronzes; 3% in all other applications combined (Kuck and Peter 2008).

Nickel is used in many specific and recognizable industrial and consumer products, including stainless steel, alnico magnets, coinage, rechargeable batteries, electric guitar strings, microphone capsules, and special alloys. It is also used for plating and as a green tint in glass. Nickel is preeminently an alloy metal, and its chief use is in the nickel steels and nickel cast irons, of which there are many varieties. It is also widely used in many other alloys, such as nickel brasses and bronzes, and alloys with copper, chromium, aluminium, lead, cobalt, silver, and gold (Davis *et al.,* 2000).

In the soil of industrial area of Mysore city having a nickel concentration of 10mg/kg to 17.1 mg/kg in Pre monsoon, 8.5 mg/kg to 14.1 mg/kg for Monsoon and 9.7 mg/kg to 18 mg/kg in Post monsoon season. (Table 1, 2 and 3) (Figure 5)

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Graphical Representation of Heavymetal Concentration in Industrial Area of Mysore City, India:
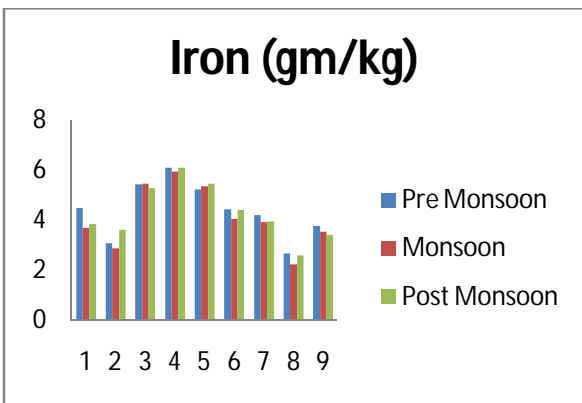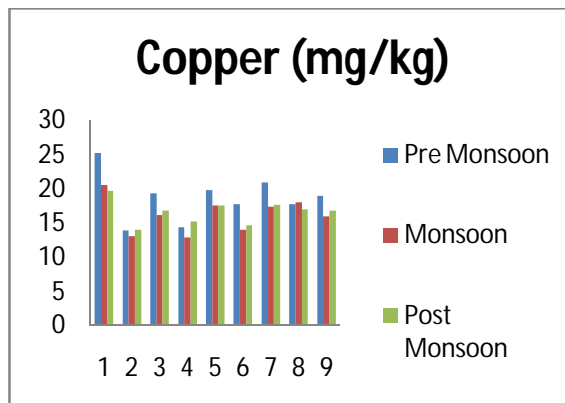

Figure 1: Seasonal variation of Iron
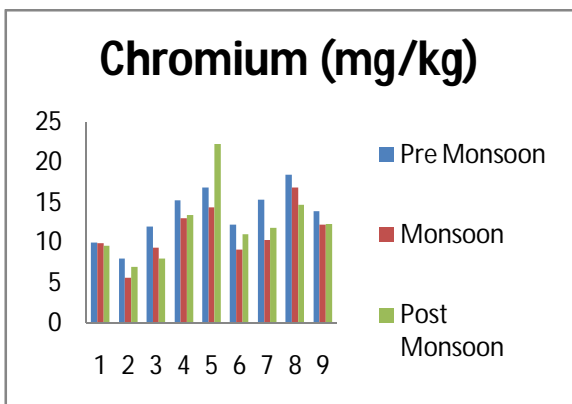

Figure 2: Seasonal variation of Copper

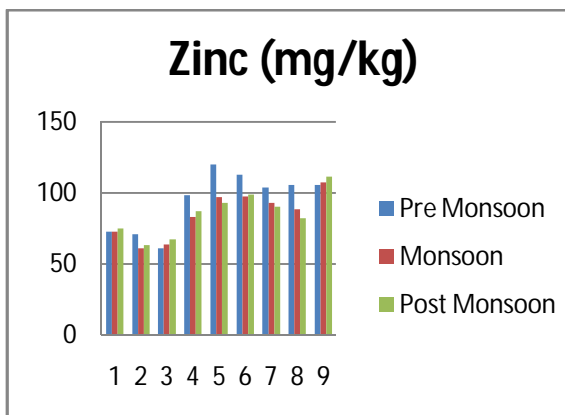**Figure 3: Seasonal variation of Chromium**

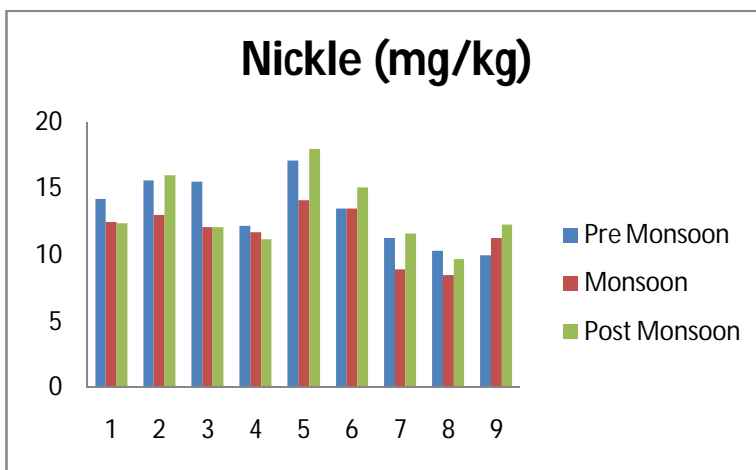
Figure 4: Seasonal variation of Zinc

Figure 5: Seasonal variation of Nickle

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CONCLUSION
Due to activities like Mining, manufacturing, industrial process and the use of synthetic products can result in heavy metal contamination in urban and agricultural soils. Heavy metals will occur naturally for some extent, but rarely at toxic levels. Polluted soils may occur, where the old landfill sites, waste dumping sites, chemical discarded sites particularly those that accepted industrial wastes as the major input waste for landfill purpose, old orchards that used insecticides containing toxic to the environment and non degradable ingredient, fields that had past applications of wastewater or municipal sludge, industrial areas where chemicals may have been dumped on the ground. Heavy metal contamination in the industrial areas of Mysore city showed that the heavy metal concentration is slightly higher in pre-monsoon season compared to Monsoon and post-monsoon season. The main reason behind the seasonal variation of heavymetals is dilution of metal ions in the soil during rainy season and accumulation due to free movement of the metal ion in the remaining seasons. These concentrations however were below the maximum permissible limit and above which causes toxicity to the surrounding environment and vegetation.

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