CHAPTER 1

Introduction
1. INTRODUCTION

Among the various anthropogenic sources of pollution in our environment, industrial emissions are the major contributor and have serious adverse effects on the quality of our living environmental quality. A wide range of pollutants released from various industries affect all three components of environment i.e. air, soil and water but cumulatively accumulate in the pedosphere at large. Among the different pollutant, heavy metal stands out be very large (quantitatively) and are very toxic to our environment. Heavy metal such as Cd, Cu, Pb, Ni and Cr are major pollutant, particularly in the region of high industrial pressure (Nagajyoti et al., 2010). These metals, once released from industrial activities enter the plants (dominantly through soil and water) and then affect the human being and other life forms (Blaylock and Huang, 2000; Nagajyoti et al., 2010). The industrial activities not only impact the surface soil but also sub-surface soils through leaching with time. The effluent drainage affects the soils of the distant regions too via horizontal spread of pollutants. The deposition of pollutant on soil can be either through the fall out of solid atmospheric emission or through the dumping of solid waste or through the drainage coming out of a particular industry. Thus soil acts as an easily available potential sink for the pollutants. Soil (surface and sub-surface) in the area will have signatures of solid waste (s), air emission, and the water drainage. So the study of heavy metals in soil offers an ideal means for monitoring the pollution of soil itself and the overall environmental quality is also reflected in soil (Banat 2005; Chen et al. 2005; Krishna and Govil 2005; Kachenko and Singh, 2006). Soils being the environmental interface of hydrosphere, lithosphere, atmosphere and biosphere with complex inorganic processes and the most productive part of the earth, deterioration in its quality have
serious impact on life forms. Such soil pollution not only affect the biological productivity of ecosystem but also becomes a main contributor to air and water pollution. Therefore, the heavy metal pollution in soils caused by anthropogenic activities is very critical and needs immediate attention and detailed study to improve our understanding.

Although a general thinking prevails that agricultural soil is more important for the pollution point of view as it is used for the food production and a pollutant present there can reach in biosphere including human though the food chain. But the soil of a town, particularly of a residential part not used for food crops production, may also have a direct impact on health. Dermal, ingestion and inhalation are important pathways for the pollutants to enter into human systems (De Miguel et al., 1997; Mielke et al., 1999; Madrid et al., 2002). Particularly for surface dust and soil, ingestion is one of the key pathways, through which humans get exposed to toxic pollutant (Meyer et al., 1999; Rasmussen et al., 2001). Children, old age persons, persons already suffering from some chronic disease and the workers in the industrial area are the most vulnerable to the health effect from re suspension of such polluted dust. The re suspension activity constitutes nearly 26% of the total dust load in a given area (Tandon et al., 2008). Several studied has shown the need for a better understanding of urban soil pollution (De Kimple and Morel, 2000; Manta et al., 2002). This is also reflected in number papers published on the metal contaminants in surface dust and soils (Kelly et al., 1996; Chen et al., 1997; Bhuiyan et al., 2010; Wei and Yang, 2010 and references therein). Surface dust metal pollution is also one of the key sources of heavy metals accumulation in urban soils (Li et al., 2001). Therefore, it is imperative to study metal related surface dust as well as soil pollution in an industrial township.
The term Heavy metal is used very frequently in the research because these metals very significant environmental pollutant and their toxicity is a serious problem for the environment as a whole. Literal meaning of heavy metal is used for a group of metals and metalloid elements with atomic density greater than 4 g/cm³ or 5 times or more than water (Hawkes, 1997). But their chemical properties are more important compared to their higher density as far the environmental studies are concerned. In general the metals that have high toxic potential to the living system are studied under the heading heavy metals which mean the toxicity factor overrules the density factor. Therefore, sometimes the metal having less density than 4g/cm³ or not greater than 5 times that of water are also reported under the heading heavy metal in the environmental research (Nagajyoti et al., 2010). Some of the heavy metals (Fe, Cu, Ni and Zn) are essential for the life system and others are non essential. In both the case any increase above the threshold value result in the environmental pollution and the health effects. These elements are also sometime termed as trace elements due to their presence in low amounts (10 mg/kg) or ultra trace (1 microg/Kg) in the environmental matrices. Thus we can say that the heavy metal is a larger term which includes the metal present in high i.e. Fe, Ti, Al, Mn present in % amounts and the low concentration i.e. PPM or mg/Kg in the environmental samples. In the present study we have taken 9 transition metals and the alkaline earth metal Ca, Mg, Pb and Ba.

In most of the cases industrialized or urbanized surroundings receives flow of pollutants from that. Soil is one of the most important receivers due to various reasons. In the most general cases a discard is dumped on the soil. These get degraded by chemical, physical, and biological factors as sunlight, microbes, heat etc. The heat may be supplied by sun, earth surface, anthropogenic activities (as thermal power
plant) etc. Chemicals are supplied by soil, rain, atmosphere, organisms etc. Physical force may also be supplied by the activity of organisms including humans. This degradation releases secondary pollutants into Environment including soil. In addition to this some of the metal pollutant are non biodegradable and persistent in the nature. At first the pollutants get into the topmost soil and get transported horizontally as well as vertically with time by different physiochemical processes. Thus not only the soil gets contaminated but both surface and ground water and atmosphere get polluted in the affected area.

A close co-relation between heavy metal concentrations in dust falls and soils also validate it (Sakagami et al., 1982). Although the presence of a pollutant in the atmosphere depends on various factors including climate/weather (Yadav and Rajamani 2006), but the importance of the presence of pollutant on soil can never be neglected. Water also works as an important vehicle of pollutants. Apart from transferring a pollutant from the one part to another, this also discharges and accumulates pollutants into the soil. Lastly Biosphere receives the pollutants from all the three previously mentioned components apart from itself. This indicates a very paradoxical and complicated situation for the soil pollution i.e. soil get contaminated by direct discharge of pollutants, receives them from water as well as dust deposition and the polluted soils affects surface and ground water by leaching of pollutants and add to the atmospheric pollution through re-suspension (Tandon et al., 2008). A pollutant on the soil surface also pollutes atmosphere by surface wind lifting the particulate matters from the top of the soil (Chen et al., 1997; Bandhu et al., 2000; Cyrys et al., 2003; Gray et al., 2003). Thus, pollution of the any one also pollutes the other. Therefore, studying soil pollution in important and gives the overall idea about other types of pollution i.e. air and water in the area.
1.1 Sources of heavy metals

Trace metals are released into the environment from a wide spectrum of natural as well as anthropogenic sources (Nriagu, 1978; Moore and Ramamurthy, 1984). The natural sources of trace elements include volcanic eruptions, forest wildfires, sea-salt emission, rock weathering vegetation and wind blown dusts. Emissions from industry, vehicles, power plants, agriculture, domestic effluents are prime sources of metals in the environment (Nagajyoti et al., 2010 and references therein). Industrial direct emission, solid waste generation and water effluent are largely responsible for polluting soil. Heavy metals can accumulate in the soil up to toxic levels due to several reasons including long-term application of waste water in irrigation, use of pesticide and fertilizer in an agricultural field, dumping of municipal and industrial solid wastes (Nagajyoti et al., 2010 and references therein), burning of fossil fuel (Anju and Banerjee, 2003), mining (Yang et al., 2010; Dudka and Adriano, 1997; Bridge, 2004), metal processing industries including smelting industries (Burta et al., 2003; Wei-Xin et al., 2008), petrochemical industries (Li et al., 2009), leather industries (Tariq et al., 2005 and 2006; Bini et al., 2008; Gowd et al., 2010), coal based thermal powered plant (Mandal and Sengupta, 2006), transportation and accumulation of heavy metal in soil by air loaded air heavy metals, accidental discharge of heavy metal loaded effluent from the industries (Grimalt et al., 1999), ship braking industries (Reddy et al., 2003, 2004, 2005), spray painting industry (Fergusson and Kim, 1991), battery manufacturing, metal plating, textile industries (Sekhar et al., 2006), Veterinary chemicals, pharmaceuticals and pesticide industries (Sekhar et al., 2003). It is clear from the figure 1.1 that soil becomes the obvious sink for all kind of emissions i.e. air emission and water drainage coming out of industries.
or any other sources in addition to those directly added to the soil. The polluted soils make the route of metals to human via food chain or direct inhalation or ingestion pathways. The greatly increased contribution of toxic metals by anthropogenic sources and their subsequent circulation in the environmental system has resulted in inevitable buildup of such toxins in the plant as well as in the animal food chains and hence, affects the life system adversely. Various possible pathways and exposure roots of heavy metals to humans are shown by schematic diagram in Figure 1.1.

![Diagram showing route of trace elements from sources to humans. Source: modified after Nriagu, (1984)](image)

Fig. 1.1 Schematic figure showing route of trace elements from sources to humans. Source: modified after Nriagu, (1984)

Some of the essential as well as the potentially toxic heavy metals for the plants and animals are tabulated in Table 1.1 along with their potential sources in the soils. The metals remain chemically bound to the aluminosilicate structure of the sediments in nature and are therefore not readily bioavailable to the plants.
Table 1.1 Essentiality and potential toxicity of few trace metals to plants and animals and their sources in the terrestrial environment:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Essential or beneficial to Plants</th>
<th>Essential or beneficial to Animals</th>
<th>Toxic form</th>
<th>Toxicity to Plants</th>
<th>Toxicity to Animals</th>
<th>Comments</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>As*</td>
<td>No</td>
<td>Yes</td>
<td>As⁺³</td>
<td>No</td>
<td>Yes</td>
<td>Toxicity to form</td>
<td>Sealed and toxic</td>
</tr>
<tr>
<td>Cd</td>
<td>No</td>
<td>No</td>
<td>Cd⁺²</td>
<td>Yes</td>
<td>Yes</td>
<td>Carcinogenic</td>
<td>Itai:itai disease</td>
</tr>
<tr>
<td>Cr</td>
<td>No</td>
<td>Yes</td>
<td>Cr⁶⁺</td>
<td>No</td>
<td>Yes</td>
<td>Speciation</td>
<td>Important: Cr⁶⁺</td>
</tr>
<tr>
<td>Cu</td>
<td>Yes</td>
<td>Yes</td>
<td>Cu⁺²⁺</td>
<td>Yes</td>
<td>Yes</td>
<td>Fungicides</td>
<td>Electrical, paints, pigments, fertilizers.</td>
</tr>
<tr>
<td>Mn</td>
<td>Yes</td>
<td>Yes</td>
<td>Mn⁺²⁻ at &lt;pH 5</td>
<td>Yes</td>
<td>Yes</td>
<td>Fertilizers</td>
<td></td>
</tr>
<tr>
<td>Hg*</td>
<td>No</td>
<td>No</td>
<td>Hg⁺²⁺</td>
<td>Yes</td>
<td>Yes</td>
<td>Enriched in food chain</td>
<td>Minamata disease</td>
</tr>
<tr>
<td>Zn</td>
<td>Yes</td>
<td>Yes</td>
<td>Zn⁺²⁺</td>
<td>Yes</td>
<td>Yes</td>
<td>Toxic at &gt;200mg/Kg</td>
<td>Zn smelting, fertilizers, manure etc.</td>
</tr>
<tr>
<td>Ni</td>
<td>No</td>
<td>Yes</td>
<td>Ni⁺²⁻</td>
<td>Yes</td>
<td>Yes</td>
<td>Toxic for plants at &gt;50mg/Kg, carcinogenic</td>
<td>Diesel oil, tobacco smoke, chemicals and catalysts, steel and non-ferrous alloys.</td>
</tr>
<tr>
<td>Pb</td>
<td>No</td>
<td>Yes</td>
<td>Pb⁺²⁻</td>
<td>Yes</td>
<td>Yes</td>
<td>Cumulative poison</td>
<td>Poisons and poison</td>
</tr>
</tbody>
</table>

Metals marked with star* are not studied herein.
Whereas, the metals of anthropogenic origin are more loosely bound in the soil and thus become readily available to organisms (Schropp and Windom, 1988). Once added to soil and water, they enter into various food chains via plant and finally cycle back to living organisms. Other than occupational exposure and inhalation, the primary route of entry of trace elements into humans is via ingestion of metal contaminated foods of plant and animal origin.

1.2 Metal toxicity

Heavy metals are non biodegradable and non thermodegradable. By nature they are extremely persistent in environment and get accumulated up to toxic levels. Metal toxicity is not related to just total metal concentration (Tessier and Campbell, 1987), but to a number of other environmental and biological processes (Prosi, 1989). Toxicity is a function of form of metal and change in oxidation state of a metal can also have a profound effect on its essentiality, toxicity and bioavailability. The heavy metals are neither always essential nor harmful to biota but a narrow 'concentration window' exists between the toxic and essential levels of heavy metals (Schwarz, 1978). Therefore, any increase in the metal concentration of metal in the soil is going to have toxic effect over a period of time. According to Sherwin (1983) a large segment of the "well population" is suffering from metal poisoning without even realizing it. The ill effects of heavy metals in human are metal specific and has been recently reviewed by Nagajyoti et al., (2010) and others. They also induce oxidative stress and disorders in the related cellular processes (Prasad and Hagmeyer, 1999). Thus, reliable and adequate knowledge of metal content in the soil matrices, especially in industrial areas is imperative. Metals tend to accumulate in the biologically active region of soils, where they can be taken up by plants as well as
crops. Metal input rate to the biological system depends on the amount of the element present in soil and the physical parameters of soil like pH, soil type, TOC etc. There is a general consensus that the free (hydrated) metal ion is the most toxic and bio-available form (Bubb et al., 1991), which has been related to its affinity for various biological functional groups (Rudd, 1987). However, some inorganic complexes may also be directly available to biota.

In India industrial revolution took place in the last two decades and the impact on environment is being realized now. Studies related to metal pollution in the industrial regions have started in this decade and getting impetus. High concentrations of heavy metals are found in the Kattedan industrial area near Hyderabad, in Andhra Pradesh. In this area battery manufacturing, metal plating, textile and pharmaceuticals production and others types of industries were present. Here high percentages of Zn, Cu, and Cr were associated with the mobile fractions. Therefore, correspondingly high concentrations of Zn, Cr, Cu, and Pb were found in forage grass samples. High concentrations of Pb, Zn, and Cr were also found in blood and urine samples from the residents of the study area (Sekhar et al., 2006). High amount of heavy metals are found in soil, industrial wastewater and vegetables in Lohta village, India. Here four plots were irrigated by treated or untreated wastewater coming from the DLW (Diesel Locomotive Works) sewage treatment plant. Samples of irrigation water, soil and the edible portion of various vegetables were collected monthly during the summer and winter seasons. Later it was found that particularly members of Brassicaceae (e.g. turnips, cabbage and radish) can efficiently accumulate the heavy metals (Rai and Tripathi, 2006). High amount of heavy metals was found on the top soil around the coal-fired thermal power plant in Kolaghat, West Bengal due to ash disposal. The contamination was more nearer to the plant. The concentration levels of heavy metals
Mn, Ba, V and Cr in the nearby soils was similar to that found in pond ash (Mandal and Sengupta, 2006). Heavy metals were enriched in soils in the industrial area of Surat, Gujarat. The heavy metal loads in the top soils of the study area was 471.7 mg/kg for Ba, 137.5 mg/kg for Cu, 305.2 mg/kg for Cr, 51.3 mg/kg for Co, 79.0 mg/kg for Ni, 317.9 mg/kg for Sr, 380.6 mg/kg for V and 39.0 mg/kg for Zn (Krishna and Govil, 2007). Localized mercury pollution was found in the vicinity of the chloralkali plant (~40 years old) at Ganjam, Orisa. Significant correlation between mercury levels in soil and plant were found in the area with the exception of C. bonplandianum. Among the tested plants, the highest tolerance to mercury toxicity was found in C. barbata followed by C. dactylon and C. rotundus. The rice plants did not show any significant levels of bioconcentration for mercury. Cabbage (Brassica oleracea) and amaranthus (Amaranthus oleraceus) were found to bio-concentrate mercury (Lenka et al., 1992). The soil of Thane–Belapur industrial area of Mumbai was found contaminated with the high amount of heavy metals. The soils in the study area were enriched with Cu, Cr, Co, Ni and Zn (Krishna and Govil, 2005). Heavy metal pollution is also found in the Kanpur-Unnao industrial region of the Ganga Plain, India. There are high contents of organic C, Cr, Pb, Cu, Ni and Cd were found in the sediments and soil (Ansari et al., 2005). Soil was found polluted due to heavy metals in the Patancheru industrial development area in Andhra Pradesh. The soil had two to three times higher level of toxic elements. Many heavy metals such as Cr, V, Fe, Cd, Se, Ba, Zn, Sr, Mo, Cu and As were above the normal level (Govil et al., 2001). Krishna and Govil found high level of Pb, Cr, Cu, Zn Sr and V on the top soil of Pali Industrial Area and the surrounding (Krishna and Govil, 2004). There are many more industrial areas where the studies have not yet started.
Faridabad region in Haryana adjoining the national capital territory is another prominent industrial area in north India. The township host the large scale well organized industries along with small and medium level unorganized units. In addition to its own industrial set, a large chunk of small and medium scale industries that were operational in the capital city of Delhi were shifted to this region after the Supreme Court of India order in the year 2004-05. The location of the township, water availability through Yamuna catchment, cheap land and cheap labor from adjoining states of UP, MP and Bihar made it a suitable hub for mixed type of industrial setup. Large numbers of industrial units are operational in Faridabad township and are continuously polluting the environment through release of hazardous materials. The small scale and medium scale industries are interwoven with the residential area. There are 2471 registered factories. The major industrial products include Tractors, steel re-rolling, scientific instruments, power looms, agriculture implements, JCB crane etc. The industrial production reported during the year 2000-01 was 12880 tractors, 24230 metric tones of sugar and 4240 numbers of bikes (motorcycle, moped, scooters) and agriculture implements of Rs. 5666 lakhs. The nature of emissions is quite variable depending upon the product formed by a particular industry and their scale of operation (small, medium and large scale; See Annex table AT 1.1). The effects are very much visible and evident during physical visit to the region. To the best of my knowledge no scientific study has been carried out in this region on heavy metal pollution in soils in this area housing the mixed type of industrial set up.

The present study deals with impact of industrial pollution on soil quality with special reference to selected heavy metals (Cu, Cr, Zn, Pb, Ba, Cd, Ni, Fe, V, Mn, Ti and few other elements like Al, Ca, Mg Carbon in Faridabad area with the following broad objectives:-
1. Heavy metal determination in the surface dust, surface and sub surface soil in the study area.
2. Understanding the heavy metal contributions by different industries.
3. Seasonal and temporal variations in metal related pollution.
4. To see the horizontal and vertical spread of heavy metals in soil in the study area.

1.3 Possible Outcomes:

The present study is likely to show the quality of soil, especially around the industrial set up, is affected by the high levels of heavy and trace elements released from industries. The present study will give a picture of the present day pollution, post-pollution inputs and leaching of pollutants to the soil around the industrial set-up. We will be able to find out the contribution in the heavy metal content of the soil by specific type of industry. This will also serve as data base for industrial impact on soil quality in Faridabad, one of the industrial areas in India.

1.4 Literature Review:

The research on heavy metals in urban soils, urban road side dust and agricultural soil is much debated among the scientific community. This is well reflected in the number of research articles being published on this issue. The attempt has been taken to review the existing scientific information related to the present study and presented here below at both international as well as national level.

1.4.1 International status:

In the urban and industrial area various stationary as well as mobile sources releases huge amount of heavy metals into the atmosphere and soil, and enhances their enrichment in soil compared to the natural background levels (Nriagu, 1989;
These industrial activities including energy production, construction, vehicular exhaust, waste disposal, combustion of fuels including coal and other fossil fuel etc. (Ikeda and Yoda, 1982; Ritter and Rineferd, 1983; Chon et al., 1995; Wong and Mak, 1997; Martin et al., 1998; Li et al., 2001; Anju and Banerjee, 2003). In an urban soil heavy metal pollution is a time (Pfeiffer et al., 1991) and space (Albash and Cottenie, 1985) dependent phenomenon, and in those areas their levels are related to the intensity of various anthropogenic activities (Zheng et al., 2002).

Metal contaminations in the surface dust and soils is not a recent phenomenon, though its level has been more in the recent times as the industrial revolution took place across the world in the last two decades. Very early Helen and Jessie (1962) reported the presence of average 80 to 115 PPM tetraethyl lead in the vegetation grown along the high way of Maryland. They also found 3000 ppm (in ash) of tetraethyl lead in washed grass near Denver on the major intersections of road. Later Chaw (1970) has reported the lead accumulation in the road side soil and grass due to lead alkyl derivatives in petrol along the high way of Maryland in U.S. High concentration (2–1500 mg kg⁻¹) of Zn was found in the soil of residential sites surrounding a sheltering plant in Port Pirie, South Australia (Cartwright et al., 1976). Chen (1991) found the Cadmium and lead contamination in the soils near plastic stabilizing materials producing plants in Northern Taiwan. He also found that the Correlation between concentration of Cd or Pb in the brown rice cultivated in this area and contents of Cd or Pb in the polluted soils were not significant.

Bojinova et al., (1996) found very high concentrations of heavy metals Cd, Cr, Ni, Cu, Pb and Zn in the soil along the downwind side from the smelter in southwestern outskirts of Plovdiv, Bulgaria. Burta et al., (2003) studied the trace
element speciation in some smelter-contaminated soils in Anaconda and Deer Lodge Valley, USA. They found that Cu, Zn, Pb, and Cd were elevated in surface layers with respect to the underlying sub-soils. But Co, Cr and Ni had a more uniform distribution in surface layers and underlying subsoil. Rodriguez et al., (2009) have shown the high presence of heavy metals in the cropping and farming area surrounding an old Spanish Pb–Zn mine.

Olajire et al., (2003) studied the heavy metals status in the soils of the four different areas (commercial metal smelting, battery production site, agricultural site with high fertilizers and pesticides use and the area receiving the discharges from untreated sewage flow and dumping of domestic wastes from neighboring villages) of industrial region in Southern Nigeria. They found among these areas the highest levels of Pb and Zn in battery smelting area, and the highest level of Cu in the iron smelting area. The concentrations of Cu and Pb found in these soils were significantly higher than typical values of any general agricultural soils. Ferrous mining and processing, including the dumping of wastes, usually produces the most severe cases of heavy metal pollution (Wong, 2003; Freitas et al., 2004). Bacon and Dinev (2005) reported the high concentration of heavy metals e.g. Cd, Pb and Zn in soil at the vicinity of non-ferrous metal smelter near Plovdiv, Bulgaria. Soil along the transportation route of ore also contained high concentrations of the same metals. This indicates that the transport of ores also could be a source of contamination.

Li et al., (2009) has found high concentration of heavy metals Cu, Zn, Pb, and Cd and Hg in an agricultural field near a petrochemical complex in Guangzhou, China. They also showed that there is a correlation between land use type and heavy metal concentration in soil. Yang et al., (2009) found the concentration of Pb in surface soils of Guangdong area affected by land mining was much higher than that of
global level. Fayun et al., (2009) has studied the heavy metals distribution in Tiexi Industrial District of Shenyang City in the Liaoning province. They found that the soil of this area was extremely polluted by Cu, Zn, Pb and Cd. Some of the metals were even 100 times higher than the threshold limits provided by the State Environmental Protection Administration of China. Sometimes accidentally release of heavy metals from industries causes heavy metal pollution in soil. Grimalt et al. (1999) found the The investigation of soil heavy metal concentrations in parks and green areas in Seville, Spain, indicated that the concentrations of Pb, Zn and particularly Cu in the soil often exceeded the acceptable limits for residential, recreational and institutional sites (Madrid et al., 2002). In the Dinajpur District of northern Bangladesh at Barapukuria coal basin, soils of mine drainage and surrounding agricultural fields were reported with exceeding concentrations of Mn (Igeo value 1.24±0.38), Zn (Igeo value 1.49±0.58) and Pb (Igeo value 1.63±0.38), Ti, As, Fe, Rb, Sr, Nb and Zr than normal averages for the world (Bhuiyan et al., 2010). Some of the cases Mn, Zn, As and Pb were exceeding the toxic limit. Among the studied parts, particularly the extreme proximal to the source is heavily polluted (most polluted with PLI value of 4.02).

Failure of tailings dike at the Aznalcollar mine lead to high amount of heavy metals in the alluvial soil of Agrio and Guadiamar river basin, and Guadalquivir marshland. Due to this accident about 6 million m$^3$ of acidic waters with sludge, high amount of heavy metal and other toxic elements get released and polluted 4000 ha of soil. Later the sediments were physically removed after this accident. But even after removing the sediments the affected zone remained polluted with trace metals. Thus physical removal of sediments is not fully effective in controlling pollution in this type of condition (Simón et al., 1999).
1.4.2 Indian context

The modern world is almost impossible to imagine without heavy metals and alloy. Almost all the applications as material production, transport, construction, power transmission, jewelry and catalyst require metals in one or other form. The association and importance of metals in the development of human civilization is very old and is such that some periods in history are named after some of these metals. i.e. iron age, bronze age. Like any developing country lack of political will in Government towards Environment, high population pressure, lack of environmental friendly technology and social responsibility in corporate bodies, along with lack of environmental awareness and preparedness in people are common derivers of soil pollution in India. Industrial growth to meet the demand of growing population particularly in the last two decades has resulted in severe case of soil pollution at different places in India. Among the soil pollutants heavy metals are very common and have serious implications to the health of soil as well as to the living systems (plants and animals including human). Due to the serious nature of metal related soil pollution, the scientific work in different parts of the country has been done in the past and is being done to understand it in more details.

In northern India, Heavy metal related soil pollution has been reported in Jajmau and Unnao industrial areas of Kanpur (Rawat et al., 2009; Gowd et al., 2010) Varanasi, (Sharma et al., 2007), Raebareli (Bajpai et al., 2010) and Delhi (Anju and Banerjee, 2003). In Kanpur, the soil of Jajmau and Unnao industrial areas had high Cr and Zn. Cotton and wool textile mills, tanning and leather manufacturing industries, and fertilizer and arms factories were mainly situated there. These industries were either dumping their waste directly on soil or releasing them into uncontrolled effluents on to the ground unscientifically and contaminating the soil and water bodies.
in the area (Gowd et al., 2010). Rawat et al., (2009) also found high level of heavy metals in solid wastes, soil and road dust of the same Jajmau and Panki industrial areas of Kanpur.

Although irrigation water had heavy metals (except for Cd) lower than the internationally recommended (WHO) maximum permissible limits set for the irrigation water for agricultural, in Dinapur, Shivpur and Lohta of suburban Varanasi but both untreated as well as treated wastewater-irrigated vegetables were Cd, Pb, and Ni contaminated. The mean heavy metal concentrations in the soil of this region were also below the Indian standards with the exception of Cd, of which maximum value was recorded in January and that was higher than the standard (Sharma et al., 2007). Lohta was receiving treated waste-water from a large diesel engine manufacturing unit apart from untreated sewage and industrial effluents from more than 100 industries. The main industries were fabric and newspaper printing, various manufacturing industries including iron gates, window nets, table fans, bicycle tires, and heavy agricultural equipments. In Shivpur, untreated domestic and industrial sewage (mainly coming from fabric printing and dyeing, food processing, and electrical cables and paint manufacturing industries) was used in irrigation. In Dinapur, industrial waste treated in a waste water treatment plant was used for irrigation. The plant was receiving waste water from fabric printing, batteries, and paint-like various types of industries. Heavy metal pollution in soil was found in the vicinity of a coal based thermal power plant in Raebareli resulting in affecting the physiology of the lichen P. cocoes significantly (Bajpai et al., 2010). The street dusts of Wazirpur Industrial Area in Delhi were found with high Cr, Ni, Cu, Cd, Zn and Pb, but environmental mobility and bioavailability of Ni and Cr were limited. The
chromium, copper and nickel in the dust were from the same origin, which can only be industrial (Anju and Banerjee, 2003).

In southern India, soil pollution has been found due to heavy metals in Pichavaram mangrove forest of Tamil Nadu (Agoramoorthy et al., 2008), Muthupet mangroves (Janaki-Raman et al., 2007), Chennai (Jayaprakash et al., 2008), Patancheru in Hyderabad, (Dhar et al., 1998; Gurunadha Rao et al., 2001; Govil et al., 1997, 1998, 2001; Sekhar et al., 2003, 2006), Bangalore (Ha et al., 2009) and Goa (Ratha et al., 1994; Yellishetty et al., 2009).

Heavy metal contaminated mangroves and halophyte were found in protected Pichavaram mangrove forest reserve along the coastal Tamil Nadu. Concentrations of Pb were higher than the normal in the 13 studied plants. Among the studied plants, halophytes were seven times more polluted with Hg than mangroves (Agoramoorthy et al., 2008).

Diagenetically modified Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn and Cd were found in Mullipallam Creek of Muthupet mangroves. Anthropogenic processes were controlling the concentration of Pb, and up to some extent Ni, Zn and Fe also. Acid leachable fractions of these metals were increasing and the sediments were working as a sink for them. Positive relation of carbonates with trace metals was indicating that secondary carbonates absorb them. Trace metals were also found associated with Fe-Mn oxy-hydroxides. Carbonates were found dissolving in the upper layer and re-precipitation in reduction zones suggesting that the nature of oxides and oxidation reduction condition do play a vital role in concentrating metal content in soil (Janaki-Raman et al., 2007). Due to surrounding industrial activities, the sediments of Ennore Creek in north Chennai were found Fe, Cr, Cu, Ni, Pb and Zn contaminated (Jayaprakash et al., 2008)
In Andhra Pradesh (A.P), industrial region of Patancheru near Hyderabad was arsenic contaminated due to veterinary chemicals, pharmaceuticals and pesticide industries like industrial sources. The arsenic concentration in soil was from 0.87 to 12.8 mg/kg against quality criterion set by EPA for total arsenic 20 mcg/g (Helgesen and Larsen, 1998). The water (surface and ground), soil, fodder, milk, and vegetables in the area had high levels of arsenic. The total arsenic content in the whole blood, urine, hair, and nails of the residents showing arsenical skin lesions and other clinical manifestations (Sekhar et al., 2003). Compared to the reference, e-waste recycling sites of Bangalore had higher level of Cu, Zn, Ag, Cd, In, Sn, Sb, Hg, Pb, and Bi in soil. Even in some of the cases, the soils Cu, Sb, Hg, and Pb were exceeding the screening values proposed by US Environmental Protection Agency (EPA) (Ha et al., 2009). In Chennai, air around e-waste recycling sites had higher Cr, Mn, Co, Cu, In, Sn, Sb, Tl, Pb and Bi level than that of the ordinary city levels. Here high levels of Cu, Mo, Ag, Cd, In, Sb, Tl, and Pb were also observed in the hair of male workers working in the e-waste recycling sites (Ha et al., 2009).

Very high concentration of heavy metals was found in the non-mining of areas of Goa. Weathering, secondary alteration of clay minerals and lateritisation like natural processes along with anthropogenic sources like fertilizers, atmospheric fallout and vehicular exhausts were found responsible for this (Ratha et al., 1994). Surface water of the Codli mining area in Goa was found highly vulnerable to heavy metal pollution. In groundwater, some of the studied metals had higher concentrations in pre-monsoon seasons than post-monsoon seasons. In the studied area, mining and mineral processing wastes were found containing various metals including Cr, Zn, Pb, Cd, Ni, Mn, Fe and Cu. Among these metals, iron and manganese were very high (Yellishetty et al., 2009).
In eastern India, soil pollution has been found due to heavy metals in Domkal block of Murshidabad district in West Bengal (Roychowdhury et al., 2002). In the Domkal block of Murshidabad district in West Bengal, the mean concentrations of As, Fe, Cu, Pb, Ni, Mn, Zn, Se, Mg, V, Cr, Cd, Sb and Hg were within normal limit in the soils of fallow land. But in the agricultural soils, mean concentrations of As, Fe, and Mg were higher and Hg was lower than the fallow land. Among the agricultural land, particularly high arsenic containing water irrigated agricultural soil had significantly higher Arsenic concentration. High ground water withdrawal may be the reason of decomposition to iron pyrites there. Due to this, arsenic and other heavy metals get released in water and get deposit on soil. (Roychowdhury et al., 2002)

When we come to the western part of India, we find that soil pollution has been there due to heavy metals in Alang–Sosiya ship scrapping yard in Gujrat and (Reddy et al; 2003, 2004, 2005).

The largest ship recycling yard of the world is situated on the Gulf of Cambay at Alang–Sosiya in Gujarat. The area along 5 km on both sides of the recycling yard, the intertidal, sub-tidal and marine zone was heavy metals enriched (Reddy et al., 2004). Since ships were broken in the intertidal zone, most enrichment was there, followed by sub-tidal and marine sediments. The metals were first enriched in the intertidal sediments and then slowly transmitted vertically into the sea. In the intertidal region, both bulk and fine sediments were highly enriched with heavy metals. Heavy metals (Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb and Zn) were higher in the fine than bulk fraction there. This is because metals were more bound with fine fraction having high surface area and the presence of complex organic materials.

In the intertidal zone, Zn was enriched 83%; Mn and Pb was enriched from 67 to 83%; Co and Cu was enriched from 50 to 67%; Cr and Fe was enriched 50%; and Ni
was enriched from 33 to 50%. Except Fe and Mn, all the studied heavy metals (Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb and Zn) were almost uniformly distributed throughout the coast. The high variation of Fe and Mn may be due to the nature and type of ships scraped on the yard (Reddy et al., 2004).

In another study, metals have shown seasonal variations and concentration of all the studied metals (Al, Fe, Pb, Mn, Cu, Zn, Cd, Cr and Co) were highest in winter followed by summer and monsoon (Reddy et al., 2005). The metals were highly positively correlated with pH and among themselves. In factorial analysis, Pb, Fe, Cu, Zn and Mn were found ship scrapping activities dependent, and NO$_3^-$, PO$_4^{3-}$, NO$_2^-$, pH, Cr, Ni, Cd and Co were found tidal and domestic discharge dependent (Reddy et al., 2005). The concentrations of hydrocarbons (both petroleum hydrocarbons and aromatic hydrocarbons) were also higher thrice in winter, twice in summer or monsoon at Alang-Sosiya and about twice in all the seasons at the two stations situated on either side 5 km away from that as compared to the reference station Mahuva, situated at 60 km away towards the south (Reddy et al., 2005).

### 1.4.3 Determination of trace metals in soil

The determination of heavy metals in soil may be carried out for various reasons. These include measurement of the total elementary content which provides base line knowledge of soil components with respect to change in soil composition produced by pollution; plant uptake or agricultural manipulation can be assessed. It also helps in assessing the availability of elements to agricultural crops and hence the likelihood of their entry into food chain of animals and plants. The heavy metal burden in soils can be evaluated by measuring the total metal concentration (Gracia-Miragaya and Sosa 1994; Facetti et. al., 1998; Scancar et. al., 2000). In routine
analysis decomposition with strong acid solutions e.g. a mixture of perchloric and nitric acid (Kada et. al., 1994) or aqua regia digestion (Ure, 1996; Gupta et. al., 1996) was often applied. The concentration of a particular heavy metal determined after aqua regia treatment is considered pseudo total concentration (Ure, 1996; Gupta et. al., 1996). The aqua regia extractable concentration indicates metal pollution at a more advanced stage (Kaasalainen and Yli-Halla, 2003). The total metal concentration can be determined by various methods and are summarized in Table 2.2 below.

<table>
<thead>
<tr>
<th>Dissolution method</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open digestion</td>
<td>Inexpensive, semirapid, high-purity acids available, low salt matrix in final solution, can remove Si as SiF&lt;sub&gt;4&lt;/sub&gt; in open crucible</td>
<td>Loss of volatiles (e.g., Hg and Se) form open crucible, attack glass (HF), corrosive and potentially explosive (HClO&lt;sub&gt;4&lt;/sub&gt;) acids.</td>
<td></td>
</tr>
<tr>
<td>Bomb digestion or fusion</td>
<td>No corrosive and potentially explosive acid.</td>
<td>High salt matrix in final solution, high potential for contaminants in fusion salts.</td>
<td>Pruseth et al., 2005 and references therein</td>
</tr>
<tr>
<td>Microwave</td>
<td>Rapid, high purity acids available, low salt matrix in final solution</td>
<td>Equipment expensive, loss of volatiles from containers, corrosive acids, low recovery of Cr and Ti</td>
<td></td>
</tr>
</tbody>
</table>

More commonly, heavy metal concentrations of soils are determined by the more conventional analytical instruments inductively coupled plasma atomic emission spectrometer (ICP-AES) and atomic absorption spectrometry (AAS). To analyze heavy metal concentrations of soils by ICP-AES and AAS, dissolution of soil samples is a pre requisite. The dissolution is carried out using combinations of strong mineral
acids i.e. acid digestion or fusion agents, which might change the matrix or the chemical status of the chemical species. The acid digestion can be carried out in the close bomb, microwave and open acid digestion (Pruseth et al., 2005). All three have their own merits and demerits. In the close digestion, sample is mixed with known amount of mineral acids in a Teflon bomb and the bomb is put either in microwave or the hot air oven. The digested sample is mixed with the boric acid solution to precipitate the silica content and left for three-four days and then filtered. There could be chances that the metal may get into the colloidal precipitates of silica and boric acids and might result in the wrong analysis. In microwave digestion the boric acid is used in small quantities and does not form any precipitates rather used to neutralize the fluoride content as free fluoride leach the glass wares. But in this techniques sample has to analysed immediately and the instrument is also very costly. In open digestion sample is mixed with mineral acids and heated to dryness (2-3 times) and finally the solution is picked in HCl. In open digestion silica is removed by HF and solution is picked (Shapiro and Branock, 1962). The loss during heating and drying are compensated by digesting the standards by same method. Such digested standards are used in the instrument calibration and also a control samples. There are studies which do leaching rather than following digestion procedures. Leaching might not give the total metal content as some of the metals are part of alumino-silicate matrix which cannot be broken without the HF digestion. Therefore, the leaching results are always lower than the digestion results.