

# INTRODUCTION

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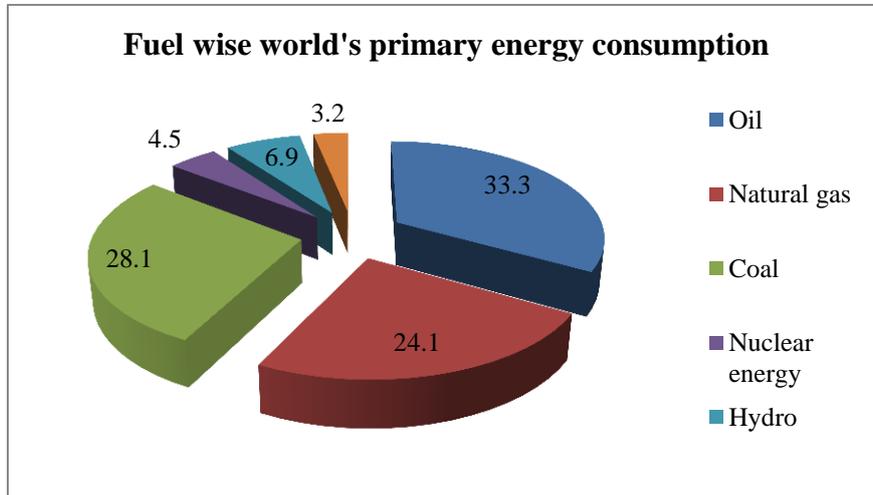
## 1.1 General Introduction

In the last few decades, a phenomenal advancement in industrial sector has occurred worldwide. The world energy consumption has been increasing along with rapid industrialization. Industrial and technological advancements have put enormous pressure on our valuable natural resources. Progress of power sector is important to the economic development of a country as it makes possible development across various sectors of the economy, for example manufacturing, agriculture, railways, and commercial activities etc. Fuel wise world's total primary energy consumption in 2016 was: Oil (33.3%), Coal (28.1%), Natural Gas (24.1%), Hydro (6.9%), Nuclear (4.5%) and renewables (3.2%) (Fig. 1.1). In 2016, fossil fuels contributed to 85.5% of the total world energy (British Petroleum, 2017). World electricity and energy demands are escalating at a rapid pace. The escalating demand of energy to a huge extent has been fulfilled by fossil fuels. Fossil fuels mainly coal and natural gas are exhaustible energy sources, which play an important role in meeting the constantly rising energy demands of countries all around the world.

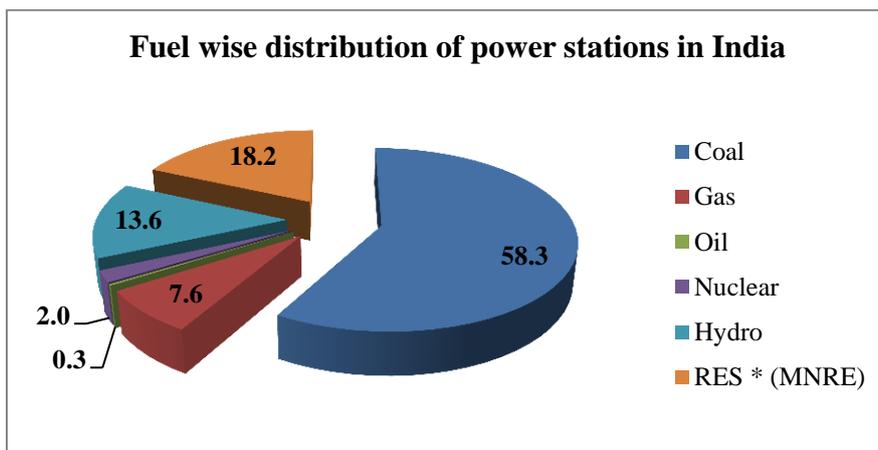
In recent decades, an enormous growth in the Indian energy sector has been noticed. This has brought electricity to hundreds of millions of population who were formerly without electricity supply. In India, the installed capacity of Power Plant Utilities in 1950 was 1713 MW (CEA, 2016), which has increased to about 3,30,861 MW in 2017 (CEA, 2017; as on 31.12. 2017) (Fig 1.2). The electricity generation has also improved from about 5.1 BU in 1950 to 1,107 BU in the year 2015-16. Parallely, per capita utilization of electricity has increased from 15 kWh in 1950 to about 1,010 kWh in the year 2014-15 (CEA, 2016). The share of coal in the total installed capacity of all the power stations is an overwhelming 58.3% (Fig.1.2), followed by Renewable Energy Sources (18.2%), Hydro (13.6%), Gas (7.6%), Nuclear (2.0%) and Oil (0.3%) (CEA, 2017).

The fast development of electric power industry has promoted the boost up of national economy. Fossil fuels (especially coal) are playing a key role in powering India's economic development, therefore, making India the world's fourth-largest

source of energy related CO<sub>2</sub> emissions. Coal-fired power plants are the most widely used plants for electricity generation worldwide. In India Renewable energy will become the primary source of electricity by 2030, but subcritical coal-fired capacity falls off only slightly (Howells, 2015)



**Fig. 1.1: Fuel wise world's primary energy consumption in 2016**



**Fig. 1.2: Fuel wise distribution of total installed capacity of power stations in India (Central Electricity Authority; as on 31.12.2017)**

Coal is the only fossil fuel and natural resource existing in abundance in India. Therefore, it has been used widely as a thermal energy source as well as fuel for thermal power plants producing electricity (International Energy Agency, 2009). Indian coal (Gondwana coal) is of poor quality. Indian coals have greater ash content (30-50%) and less calorific value (averaging 3603 kcal/kg in 2010-11) (Guttikunda and Jawahar, 2014; Lokeshappa and Dikshit, 2011; Aswathanarayana, 2008; Senapati, 2011 and Mishra, 2004). Also, the sulfur content in Indian coal is less than those observed in coals from United States and China. However, in North Eastern region of India

particularly in Assam substantial deposits of tertiary origin low rank sub-bituminous coal with high sulfur content (organic sulfur 75-90% and remaining pyritic sulfur) are found (Saikia et al., 2009; Baruah et al., 2006; Baruah and Khare, 2007; Khare and Baruah, 2010 ). In Indian coals the sulfur content has a consumption-weighted mean of 0.6% (Reddy and Venkataraman, 2002). The poor quality of coal (high ash content and low calorific value) has an effect on the thermal power plant's operational efficiency and increase in emissions per kWh electricity generated (Guttikunda and Jawahar, 2014). India's coal is mined by means of open cast methods and it is considered that coal obtained from opencast mines has high ash contents (Bhangare et al., 2011).

Around the world, about 550Mt/annum of fly ash is produced through coal combustion in thermal power plants (Querol et al., 2001). In 2012, about 170 Mt of coal ash was produced in India (Bhangare et al., 2011) from more than 110 thermal power plants. As per the estimates, present generation of fly ash is about 300 million tons/year in 2016-17 and is expected to increase to 700 Mt/year by 2031-32 (Ram and Masto, 2014). After municipal solid waste the coal combustion waste constitutes the India's second largest waste stream (Sturgis, 2009). Up to 90% of the ash generated in many coal-fired plants is fly ash (Klein et. al., 1975.) India has been the ranked the fourth producer of fly ash after China, Russia and USA (Ram and Masto, 2014). In India, approximately 176.7441 Million-ton of flyash was generated in 2015-16, out of which only 61% was utilized and a major fraction (39%) still needs to be disposed off (CEA, 2016). Indian flyash has found a number of uses viz. Cement (24.54%) Mine filling (5.85%), Bricks & Tiles (8.35%), Reclamation of low lying area (7.09%), Ash Dyke Raising (6.00%), Roads & flyovers (2.83%), Agriculture (1.25%), Concrete (0.44%), Hydro Power Sector (0.02%), and others (4.60%) (CEA, 2016).

## **1.2 Environmental impacts of coal fired thermal power plants**

Although, coal-fired power plants are the most widely used plants for electricity generation and can bring much economic prosperity, the legacy of mass emissions of solid particles and hazardous gases into the atmosphere, the discharge of chemicals, ash, contaminated waters, as well as the large energy currents, heat and the different mass flows of various substances are ancillary to various operations in these power plants (Xu and Li, 2009). The influences of power plants on the environment are manifold. Environmental pollution associated with burning of fossil fuels has a serious threat on ecosystem and human health. Environmental pollution because of the release

of smoke, gases, various effluents, and solid wastes from power plants is one of the crucial issues of global concern.

The thermal power plants are considered as stationary point source of pollution, which directly pollute soil via the coal combustion products released by their tall stacks, flue gases such as oxides of sulphur, nitrogen and carbon, polynuclear aromatics (Popescu and Stanca, 2008), and indirectly through the windblown dispersion of dumped coal ash.

Combustion of coal for generation of electricity in thermal power plants produces various types of hazardous as well as complex heterogeneous mixture of pollutants in the natural environment, which are commonly known as coal combustion by-products (CCPs) (Vom Berg, 1998; Meawad et al., 2010). With the rising energy demand and dependence on coal for electricity generation, large volumes of coal combustion byproduct (CCPs) produced in thermal power plants is one of the key issues to the nation along with other environmental aspects. The major pollutants emitted from coal fired power plants are:

- Gaseous pollutants, including CO, SO<sub>x</sub>, NO<sub>x</sub> and acid gases
- Organic compounds mainly Polyaromatic Hydrocarbons (PAH)
- Particulate matter
- Flue gas desulphurization (FGD) materials and fluidized bed combustion (FBC) waste materials
- Solid wastes such as fly ash and bottom ash
- Coal gasification ash etc.

Environmental effects of solid wastes generated from coal combustion are mainly associated with ash disposal and its interactions with surface and ground waters and effects of this waste on biota.

The combustion of lignite coal results principally in release of hydrocarbons, the major part being polyaromatic hydrocarbons. The emissions of PAHs and various metals into atmosphere and their deposition onto soil are considerable (Stalikas et al., 1997).

The particulate matter causes pollution of the surrounding waters and degradation of land due to deposition of ash and slag. Coals from different areas may give an idea

about distinctive trace element characteristics. Trace elements partitioning in CCPs have been described by many researchers based on coal's boiling points as well as the phase change temperature of coal oxides (Germani and Zoller, 1988; Meij et al., 1986; Yokoyama et al., 2000). In a conventional coal-fired power plant, which is just designed for electricity generation, 2/3 of fuels energy is wasted all the way through stack gases and also from cooling water of condensers (Erdem et al., 2010). When coal is burned in power plants, its noncombustible mineral content is divided into bottom ash (remains in the furnace) and fly ash (rises with flue gases). Generally, fly ash constitutes almost 80% of solid residues generated from coal combustion in a pulverized coal-fired power plant (Jankowski et al., 2006; Wagner and Hlatshwayo, 2005). The fly ash generated from coal fired thermal power plant is a complex mixture of crystalline and amorphous phases and is very fine powdered ferroaluminosilicate substance with Al, Ca, Mg, Fe, Na, and Si as the major elements. The fly ash also contains significant amount of toxic heavy metals such as As, Ba, Hg, Cr, Ni, V, Pb, Zn, and Se (Adriano et al., 1980). The physical, chemical, and mineralogical characteristics of fly ashes depend on various aspects such as parent coal's geological origin, the efficiency of particulate removal, combustion conditions, types of emission control devices and degree of weathering before final disposal (Adriano et al., 1980; Saikia et al., 2006; Kutchko and Kim, 2006).

The disposal of huge quantity of fly ash is a major crisis, probably due to leaching of various pollutants into surface as well as ground waters (Nalawade, 2012). Coal ash is usually stored in huge coal ash dumps, either in dry or wet state (Martinez-Tarazona and Spears, 2006). The fly ashes are discarded into landfills and fly ash basins in dry disposal method. In the wet disposal method, the fly ashes are washed out with water into artificial lagoons and thus, called pond ash. Storage of wet coal ashes generally protects from wind spreading, however, decreases the time required for leaching of various elements. Both methods finally lead to dumping of fly ashes on open land, which degrades the soil quality and endangers human health and the natural environment. The unmanaged landfills or illegal dumping on the land may serve as a possible source of ash contamination all through leaching, windblown or atmospheric deposition on the nearby soil and agricultural plants (Kim and Kim, 1998; Sharma et al., 2000). The fly ash gets through to the sub-soil and eventually causes siltation, clogs up the natural drainage system and ultimately contaminates the ground water with

heavy metals. The fly ash particles are very fine particles to escape in emission restrain or control devices and thus, easily get suspended in the atmosphere. Frequent exposures to fly ash can cause irritation in skin, eyes, nose, throat, and respiratory tract of human beings (Carlson and Adriano, 1993; Belkin et al., 1999; Finkelman et al., 2002). Consequently, coal fired thermal power plant pollute our air, water, and land ecosystem.

Power plants have a significant effect on the environment due to generation of slag and sludge from flue gas desulphurization (FGD) systems and huge amounts of coal ashes, which are disposed off in huge ponds in the vicinity of the thermal power plants (Omana et al., 2002).

The effects of power plants on the environment are manifold. Environmental pollution associated with burning of fossil fuels that has a serious threat on ecosystem and human health. The major global environmental concerns associated with coal fired thermal plants include (Nelson et al., 2010):

- Particulate and gaseous emissions produced during coal combustion, particularly SO<sub>2</sub>, NO<sub>x</sub>, PAH (polyaromatic hydrocarbons) and trace elements
- Carbon dioxide emissions due to implications on global warming
- Pollution of air, water and land from operations associated with combustion of coal and the subsequent disposal of coal ash.

### **1.3 Thermal power plant as source of trace elements**

There are a number of explanations for heavy metals, some definitions are based on the specific gravity such as any metallic element that has specific density more than 5gcm<sup>-3</sup> and is toxic or poisonous at very low concentrations (Berkowitz et al., 2008), whilst others are based on atomic weight of metals. Bennet (1986) described them as metals of atomic weight greater than sodium (Na). There are also some definitions which are based on the atomic number. Venugopal and Luckey (1975) defined the term “heavy metal” as any metal with an atomic number beyond calcium (Ca). Lyman (1995) described them as metals with an atomic number in between scandium (at number 21) and uranium (at number 92). Generally, the term “heavy metals” is used to deal with those elements which have a high density and also belong to the transition group of the periodic table.

The term “heavy metals” has been used interchangeably with "trace elements" in literature. The element whose concentration is less than 1000 ppm (0.1%) in a matrix (rock, soil, or any natural product) is known as Trace element. The majority of heavy metals are termed as trace elements, stressing their quite low abundance in soils (De Vries et al., 2002). Trace elements include micronutrients and heavy metals. The trace elements which are needed by plants in small quantities (i.e., below 50 mg/g in the biomass) are known as micronutrients. Some of these micronutrients are required in small amounts by plants or animals for normal nutrition and health (Wu et al., 2006). Some micro-elements can be found generally at trace levels in soils and vegetation and in living organisms (Onder et al., 2007). The knowledge of distribution of trace elements in soil profile and their availability to plants is essential for maintaining as well as improving crop production and food quality.

Once heavy metals are introduced and contaminate the environment or soil, they will remain there. Unlike carbon-based (organic) molecules, heavy metals do not degrade in the environment and most of these metals have toxic and hazardous effects on living organisms, when they go beyond a critical concentration (Ghrefat and Yusuf, 2006).

Coal contains virtually all the elements of periodic table. Huge quantity of coal consumption in thermal power plants makes it a significant technogenic (man-made) source of a trace elemental contamination in the environment (Wagner, 2005). During combustion in power plants the elements associated with organic and mineral fractions of coal are liberated and redistributed into combustion products, viz. flyash, bottom ash and flue gases. The redistribution of elements largely depends on occurrence and volatility of elements in coal, coal combustion operational parameters (excessive air coefficients, temperature etc.), and air pollution control device used (Tang et al. 2012, 2013; Khare and Baruah, 2010). Fossil fuel combustion in thermal power plants is one of the principal man-made sources of heavy metal contamination in the environment. Since, the thermal power plants are generally situated in densely populated areas; there is possible chance for contamination of soil and groundwater of the adjacent areas with the toxic metals from coal ash (Dahl et al., 2008). By combustion of coal significant amounts of inorganic vapors of toxic metals may be released in environment. Terrestrial application of fly ash may lead to high trace elemental deposition in soil (Adriano, 1986). Land dumping of sewage sludge, coal, fly ash, and other industrial waste products may contribute to the accumulation of metals in soils (Dudka and

Adriano, 1997; Sloan et al., 1997). The ashes from fuel oil power plants may contain not only huge amounts of aluminum, carbon, calcium, silicon, iron, magnesium, but also contain copper, lead, cadmium, mercury, arsenic, chromium, nickel, manganese, and a small amount of cobalt and other hazardous trace elements. These trace elements have a negative impact on the natural environment with time due to possible leaching through acid rains and also into groundwater ecosystem (Guo et al., 2009). Since, coal is the primary source of energy in India and Indian coals have high ash content and coals contain virtually all the elements of the periodic table, so, the relevance of trace elements in coal combustion residues has now become an important environmental consideration.

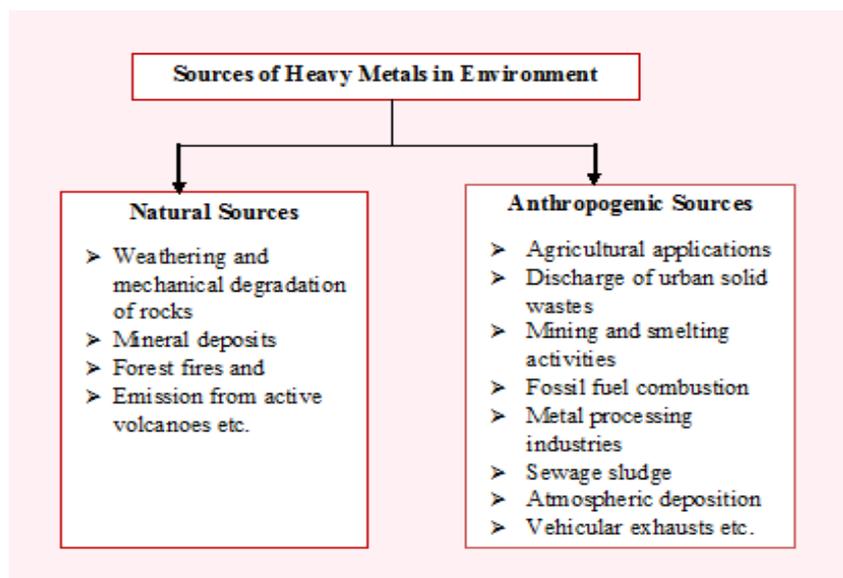
#### **1.4 Metals in the soil environment**

Soil is a geochemical important component of rural as well as urban environments. Soils behave both as a source and sink for trace elemental contamination in the terrestrial environment (Okedeyi et al., 2014). So, there is an immense concern about contamination of the land ecosystem by potentially toxic heavy metal ions because of their hazard to environment and human life. Soil has very complex and critical functions in protecting the universal eco-system against the pollution effects by acting as a buffer, filter, sink and transformation system.

Soil pollution takes place when a substance or an element is available in greater than natural or background concentrations due to human activities and also causes detrimental effects on the environment and its components (Popescu and Stanca, 2008). Therefore, it is necessary to understand the way of occurrence of trace elements in soil system for the assessment of soil contamination (Stumm, 1987). The presence of heavy metals in soils is contributed by a multitude of natural and anthropogenic/technogenic sources. Natural and anthropogenic trace elemental contamination of different compartments of environment is a perpetual problem in industrial sector (Fig. 1.3) (Adriano, 2001; Alloway, 2013).

Heavy metals occur naturally, but rarely at toxic levels in soils. Firstly, these are released by natural phenomena, such as forest fire, mineral deposits, emission from active volcanoes, weathering and mechanical degradation of rocks. The anthropogenic activities including agricultural applications, uncontrolled discharge of urban solid wastes, mining and smelting activities, metal processing industries, fossil fuel

combustion, sewage sludge, vehicular exhausts, and atmospheric deposition etc. also release heavy metals in the environmental systems. With the industrial revolution an exponential rise in heavy metal emissions and their dispersal has become more widespread due to tall chimneys. The contaminated/polluted soils may occur at industrial sites where chemicals may have been disposed off on the open ground, in areas downwind from industrial areas, region surrounding mining waste piles and tailings, or at old landfill sites.

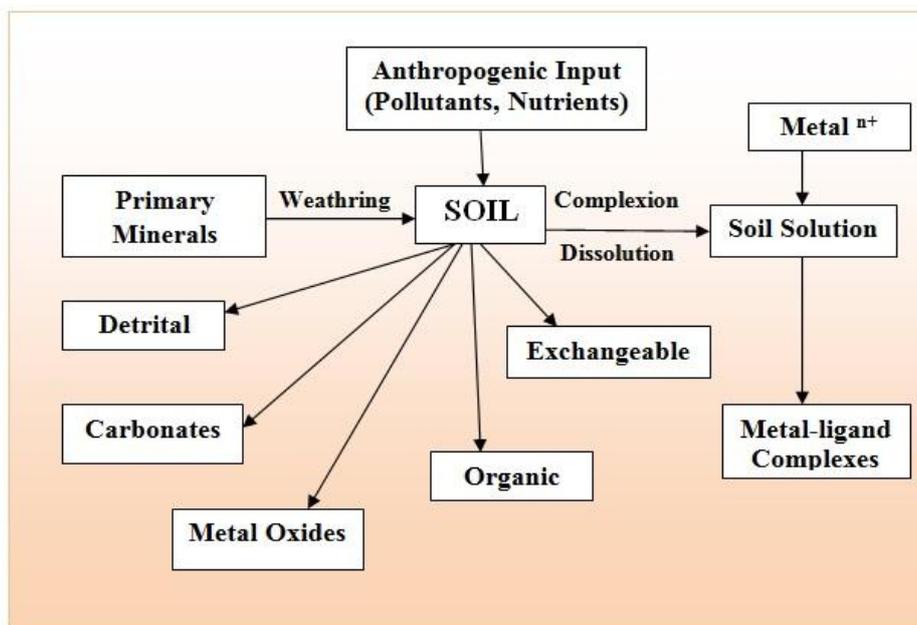


**Fig. 1.3: Sources of heavy metals**

The fate of trace elements in the soils is element-specific and governed by both the soil properties and environmental factors. Geochemically, an element added into soil may end up in the following physicochemical forms (Fig. 1.4): in the crystalline lattices of primary minerals; in the lattices of secondary minerals (i.e. carbonates, phosphates and sulphates); adsorbed to the surfaces of clays/organic matter that are easily exchangeable; sorbed in amorphous materials (viz. Fe and Mn oxyhydroxids, Fe sulphides or organic matter) and; finally may be introduced as free or complex ions/colloids in soil solution as metal-ligand complexes.

It is important to ascertain which physicochemical forms are really present in soils, because the mobility and bioavailability of these metals in the complex and dynamic soil-plant-water systems changes with environmental conditions and time. It is not easy to predict the fate and behavior of trace elements in soils without understanding the factors due to soil heterogeneity and natural variability in chemical, mineralogical, and physical properties of the soil.

Some metals are essential to plants, animals, and human beings and their deficiency may result in the impairment of certain biological functions (Ross, 1994). Copper and zinc are biologically essential elements, whose paucity may give rise to deficiency symptoms both in plants and animals. Whilst, if present in excessive amounts, they may also become toxic.



**Fig. 1.4: Effects of pollutant and nutrient ions in soil ecosystem (adapted from Naidu et al., 2001)**

Also, some non-essential elements such as lead, chromium and cadmium become toxic when their contents exceed critical levels in living organisms. Excess heavy metal accumulation or deposition in terrestrial ecosystem is toxic to humans and other animals. Chronic exposure (over a longer period of time) to heavy metals occurs because of food chain transfer and acute (immediate) poisoning from heavy metals is scarce only through dermal contact or ingestion by human beings and animals (Auburn, 2000).

Alloway (1995) found that Cu toxicity depends on properties of soil that manage Cu reactivity in soil ecosystem. All over the world, commonly the average Cu contents in dissimilar soils are observed to vary between 20 and 30 mg kg<sup>-1</sup>. Lead is a naturally occurring trace element found in all environmental system i.e. water, air, soil, and sediment. Lead enters in to the soil system via natural processes (weathering of parent materials) as well as anthropogenic activities. Pb concentration varying from 100 to

500 mg kg<sup>-1</sup> is considered to be excessive in soils from plant toxicity point of view (Kabata-Pendias and Pendias, 2001).

The soil-plant system is the primary and constructive unit of the biosphere and geosphere. Thus, heavy metal pollution of the soil has a significant influence not only on the quality of atmospheric and water environment, but also on the yield and quality of crops, and even on the human health through food chains. The heavy metal distribution between soil and vegetation is the main concern in assessing the effect of metals in environmental system (Abulude and Adesoje, 2006). The distribution of metals between the soil and soil components is essential for assessing the ability of soils to supply enough micronutrients for crop growth and to maintain toxic quantities of heavy metals (Adriano, 2001). Uptake of elements by plants reflects their levels in soils, particularly for those elements which are mobile. Agricultural crops or plants represent a necessary pathway for the movement of potentially toxic or harmful trace elements from soils to human beings. Some trace elements (e.g., Zn, Cd, Mn, Mo, Se, and B) are weakly chelated when present in soils and thus easily absorbed by plants and hence, translocated to food-chain through different plant tissues (Logan and Chaney, 1983).

Many researchers have measured the amounts of trace metals present in the terrestrial environment in the vicinity of coal-fired power plants at international level (Bolton et al., 1973; Anderson et al., 1975; Connor et al., 1976; Bradford et al., 1978; Strojjan and Turner, 1978, Stalikas et al., 1997, Huggins and Goodarzi, 2009, Ma et al., 2010, Alonso-Hernandez, et al., 2011, Rind et al., 2013, Okedeyi et al., 2014).

In India, heavy metal contamination of soils and ashes around many coal-based thermal power plants viz.- Singrauli region, Uttar Pradesh (Agrawal et al., 2010), Farakka, West Bengal (Sengupta et al., 2010), Singrauli region Uttar Pradesh (Sharma and Tripathi, 2010), Indraprastha Power Station, Delhi (Mehra et al., 1998) and Kolaghat, West Bengal (Mandal and Sengupta, 2006), TPP Bikaner and Barsingsar lignite coal region of Thar Desert, Rajasthan (Ram et al. 2015), Patratu TPP, Jharkhand (Pandey and Bhattacharya, 2016) has been measured. The soils have been found to be contaminated to varying amounts from coal combustion byproducts.

Most of the earlier studies on metals in the vicinity of coal fired thermal power plants have been restricted only to the determination of their total concentration. However,

total concentrations do not give the information regarding bioavailability, mobility and distribution of potentially toxic trace elements. Metal toxicity or effects also depend on chemical associations of metals in soils and which metal ionic species or compounds are potentially more toxic in soils (Duffus, 2002).

## 1.5 Need for speciation

The necessity to determine distinctive chemical forms of trace elements in environment and biological system is beyond question, because the toxicity and behavior of an element depend to a large extent on its species and amounts present (Kot and Namiesnik, 2000). The biological availability distribution and mobility of trace elements depend not just on their total concentration but significantly on chemical as well as physical association which they undergo in their natural ecosystems. The exemplar shift from mere determination of total elemental concentration to a more advanced fractionation based approach points to the general recognition that information about the physiochemical forms of trace elements is required for understanding their environmental fate and behavior, including mobility, pathways and bioavailability

The speciation has been defined by IUPAC as “the analytical activity of identifying and measuring the quantity of one or more individual chemical species in a sample” and the speciation of an element as “the distribution of defined chemical species of an element in a system” (Templeton et al., 2000). Speciation can be useful in understanding the mobility and bioavailability of trace metals in contaminated soil and coal ash. The analytical technique used in identifying and measuring species is defined as ‘speciation analyses’ (Kot and Namiesnik, 2000).

Speciation techniques can be defined: *functionally* (species are defined by their role); *operationally* (species are defined by the procedure used to isolate metals); and *classical speciation* (determine specific oxidation state/ chemical compounds) (Ure, 1991). Classical speciation is always preferred; however, it is possible only in exceptional cases for solid samples. Thus, elemental speciation in solids is often accomplished by different empirical single and sequential extraction methods. Single and sequential extraction schemes have been intended for the determination of binding forms of metals in solid matrices.

A generally used technique for understanding trace elemental distribution in the solid phase (known as fractionation, following the IUPAC definition; Templeton et al., 2000) is widely based on the application of sequential selective chemical extractions also known as “speciation schemes” (Gleyzes et al., 2002). The term “fractionation” is now frequently used intermittently with speciation but highlights the concept of subdividing a “total content” (Chang et al., 1984; Tack and Verloo, 1995; Gleyzes et al., 2002; Hou et al., 2006). Nowadays, operationally defined speciation has become a necessary tool to acquire the knowledge about the bioavailability of toxic heavy metals and their fractionation.

### **1.5.1 Single extraction schemes**

Trace metals in soils may be present in various chemical forms or ways of binding. The trace metals are mostly bound to silicates and primary minerals, which form immobile species, whereas in polluted soils trace metals are usually more mobile and bound to other soil phases (Rauret, 1998). To understand the heavy metal fate and behavior, quantification of metal proportion bound to different soil constituents is of utmost importance. The mobility as well as bioavailability of metals in soils depends largely on the bond strength between metal and soil surface along with the negatively charged surface particles of soils (Stumm, 1987; Filgueiras et al., 2002).

Single extractions are widely used in soil science. Single extractions tell us about how much of a given quantity of metal in the soil/ash can distribute in the selected fraction and can become bioavailable. The important applications of single extraction of heavy metals in the soils are to evaluate the bioavailability and mobility of metals which is related to soil-plant transfer of pollutants (Rauret, 1998). A wide range of standardized single extraction schemes with different reactants/extractants, temperature, agitation method, liquid to solid ratio (L/S) and contact time have been used in literature (Rauret, 1998). The extractants used in single extractions are hypothesized to extract exchangeable or weakly bound “available” metals in the soils and they include EDTA, DTPA,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$ ,  $\text{CaCl}_2$  etc. Powerful chelating agents such as DTPA or EDTA are used to evaluate the availability of elements in soils and ashes, are also likely to dissolve/mobilize, or desorb non-labile metals (Degryse et al., 2004). EDTA is considered to extract metals from all the non-silicate-bound soil fractions and it is supposed to emulate the metal availability in the short-term as well as relatively long-term (Ure, 1996).

### 1.5.2 Sequential extraction procedures (SEPs)

Sequential extraction procedures are applied to determine the chemical “forms”, in which the element appear to be associated in a particular solid sample (Gupta and Sinha, 2006). The idea behind sequential extraction procedures is that a solid sample (soil, sediment, dust, waste, ash etc.) is subjected to successive attacks with a series of progressively harsher reagents to dissolve increasingly refractory forms. The concept of the sequential extraction procedure is the partitioning of a solid material into a specific fraction from which it can be extracted or released into a solution together with the associated trace metals, by using the suitable reagents, arranged according to increasing order of strenght (Tessier et al., 1979; Tessier et al., 1992). SEP’s are based on the utilization of a series of more or less selective extractants hypothesized to solubilize the various mineralogical fractions considered to be responsible for retaining the larger portion of the trace elements (Gleyzes et al., 2002). These techniques are planned to mimic various possible natural and anthropogenic modifications of environmental conditions. Sequential extraction can offer a good insight into the sequence of metal leaching performance through determination of metal association with various mineral fractions in the coal fly ash (Fernandez-Turiel et al., 1994; Querol et al., 1996; Goodarzi and Huggins, 2001; Soco and Kalembkiewicz, 2007).

A plethora of SEP’s quoted in literature employ different reagents with a broad array of experimental conditions including: sample preparation, sample storage, size fractionation, reagent concentration, sequence of extractants, extraction time, pH control, shaking time, solid to solution ratio, filtration vs. centrifugation and temperature. In all of the SEP’s described in literature, various chemical reagents are used in order of increasing reactivity (Tessier et al., 1979; Smeda and Zyrnicki, 2002; Jegadeesan et al., 2008; Smichowski et al., 2008). The most of the SEPs intend to partition the metals into following broad fractions: Water soluble, Exchangeable, Carbonate bound (acid soluble), Fe-Mn oxide bound (Reducible), Organic and sulfide bound (Oxidisable) and Residual. Metal mobility and bioavailability assessment by means of SEP’s believe that mobility and bioavailability decrease in the order of extraction, implying that metals associated with the first fraction are most mobile, whilst metals in last fraction are least mobile.

In sequential extraction procedures the distribution of metals in each phases/steps indicate their availability and mobility, further which allows the risk assessment of metals present in the environment. After all, sequential extraction methods are designed to extract a possible labile or available metal pool in whatever matrix they are applied to and therefore provide useful information in environmental studies. The operationally defined character of sequential extraction means that if a good agreement between fractionations occurs in the results obtained in distinctive labs, then conditions established must be accurately followed. The major factors which influence sequential extraction schemes are: (1) particular matrix effects for example cross contamination, readsorption and pH buffering; (2) the sequence of the individual steps and (3) heterogeneity along with physical associations of the different solid fractions (Davidson et al., 2000).

Although, a number of sequential extraction schemes have been designed to predict the partitioning of heavy metals between various fractions, the sequential extraction method reported by Tessier et al. (1979) and the BCR procedure proposed in 1993 by the Standards, Measurements and Testing Programme (SM&T) and further modified by Rauret et al. (1999) are mainly the representative schemes. The distribution of metals in various phases obtained by sequential extraction procedures suggests their availability, which, consecutively, allows the assessment of the hazard of their existence in the environment.

Furthermore, initially developed to examine trace elemental fractionation in soil and sediments, sequential extraction schemes are being applied to an ever widening spectrum of environmental matrices such as fly ash (Zhang et al., 2017; Pandey and Bhattacharya, 2016; Chaudhary and Banerjee, 2007), mine tailings (Anju and Banerjee, 2010), street dusts (Anju and Banerjee, 2003) etc. In spite of expanding applications, there is skepticism about the reliability of methods and meaningfulness of the results obtained. Foremost amongst the criticisms are conceptual difficulties related to the specificity of the methods applied, operational problems for example reagent selectivity, sequence of individual step, sample handling, specificity, readsorption, interferences, as well as time consuming. The lack of consistency in the procedures used neither permit the results to be compared worldwide nor the methods to be verified. It has been widely recognized that no reagent is perfectly selective, so the

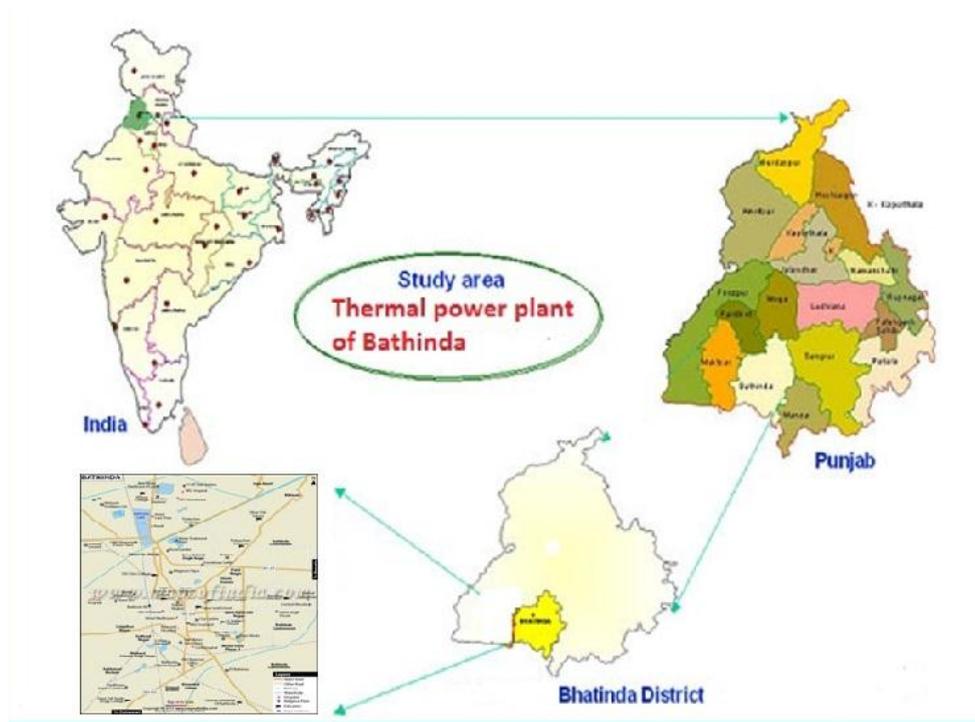
fractions recovered are best defined operationally. In recent years single and sequential extraction procedures along with column leaching systems have been widely employed to determine the geochemical associations of trace elements in coal ash (fly ash and bottom ash) to ascertain their mobility and bioavailability (Jankowski, 2006; Pandey and Bhattacharya, 2016).

Because of the above discussed pollution potential of coal fired thermal power plants and importance of speciation, and a paucity of information on them in our country, there is need to obtain information on trace elemental speciation in terrestrial environment particularly in soil and coal ashes (fly ash and bottom ash) for the purpose of assessing comprehensive environmental impacts of coal fired thermal power stations.

## **1.6 Study Area**

The study area investigated - Guru Nanak Dev Thermal Power Plant located in Bathinda (Punjab) - is a coal fired thermal power plant. The foundation stone of G.N.D.T.P.P at Bathinda was laid down on 19<sup>th</sup> November 1969. The project was completed in two phases. The total installed capability of the power station was 440MW with four units of 110MW each. In September, 1974, the primary/first unit of the thermal power plant was commissioned. Afterwards second, third and fourth units got started production in September 1975, March 1978, and January 1979, respectively. When operated at full capacity each unit of GNDTPP, was capable of producing 26.4 lac units of electricity per day. GNDTPP is a coal-based, and the requirement of coal is depending on specific fuel utilization of 0.60 kg / kwh. The coal utilization was about 1500 to 1600 MT per unit based upon the quality of coal. The total per day coal requirement was about 6500 M.T. when the entire units were in operation. Bituminous and sub-bituminous type of coal was used in GNDTPP. To ensure the maximum possible combustion, the coal was crushed and pulverized before it was fired in the furnace. The ash obtained is of two types: Wet ash and Dry ash. The electrostatic precipitators have been installed at GNDTPP to collect fly ash. Coal ash (fly ash and bottom ash) from thermal power plant in Bathinda is one of the contemplated sources of metal pollution in the surrounding environment.

After having generated electricity for 43 years, Punjab State Power Corporation Limited (PSPCL) has shut down all the four units of coal-fired GNDTPP in Bathinda in September 2017, as it was not able to meet the minimum environmental and emission norms (Times of India, Sept.29, 2017). Now, the Punjab government has decided to decommission this plant from January, 2018.



**Fig. 1.5: Map of the study area**

Bathinda is located in the southern part of Punjab State. The area experiences subtropical to semi-arid climate with hot summers and cold winters. The maximum temperature in summers goes up to 45°C and minimum in winter 4°C in December/January. Dusty storms are a common feature in summers. Rainfall is about 60 cm per year. The average annual rainfall for the district as a whole is 411.67 mm.

Bathinda is occupied by Indo-Gangetic alluvium. The district has two kinds of soils first is the arid brown soils and second the siezoram soils. The arid brown soils are poorly to moderately drained having calcareous nature. Alkalinity as well as salinity is the major problems of these soils. In siezoram type soils, the accumulation of  $\text{CaCO}_3$  is in amorphous or concretionary form known as *kankars*. Existence of high amount of calcium carbonate and poor fertility is the major negative aspect of this soil. The siezoram soils are found commonly in the western part and arid brown soils are found frequently in eastern parts of the district (Sehgal et al., 1985).

## 1.7 Objectives

Fossil fuel combustion is a universal activity and certainly may be considered as “global”– to comprise matters of local or regional level that are repetitive with sufficient frequency to give them global importance. Investigations into environmental impact of coal fired thermal power plants have to date been mostly limited to those in industrialized wealthy nations of the west. Main concern in the future should be specified to the investigations in developing countries, where environmental considerations are generally put to second place than the economic growth.

Because of the above discussed pollution potential of coal fired thermal power plants and importance of chemical speciation, and a paucity of information on them in our country, there is need to obtain information on relevant environmental parameters around coal fired thermal power plants in India.

For the present study, a coal fired power plant at Bathinda, Punjab has been selected. Due to coal combustion history which spans four decades, and large quantities of coal ash generated due to use of bituminous and sub-bituminous coal, huge quantities of solid coal ash occurs in the area around GNDTPP, Bathinda. Over the years, the gaseous, liquid and solid emissions from thermal power plant are liable to have contaminated soil, water and biotic community of the surrounding area with heavy metals and other contaminants in excess of their background concentrations. The mobilization of toxic elements from soils and coal ashes differs and therefore, a detailed geochemical study is necessary. In aspect of the above, a broad-spectrum purpose of this study was to study the trace elemental contamination and speciation in the terrestrial environment around GNDTPP, Bathinda. More precisely, the objectives were:

1. Sampling of soil, ash and other material from area near the power plant.
2. Physico-chemical characterization (viz. pH, EC, TOC, PSA, and some heavy metals Cr, Ni, Pb, Zn etc.) of the soil would be undertaken.
3. To investigate the degree of trace metal contamination in soil.
4. To study the level of heavy metal in vegetation near thermal power plant.
5. Single and sequential extraction would be used to assess the operational speciation and fate of metals in soil samples taken from the study area.
6. Extraction selectivity and efficiency of some sequential extraction procedures would be evaluated to assess metal associations in the soils of the study area.
7. Statistical Analysis of the experimentally generated data.