

REVIEW OF LITERATURE

2.1 Overview

This chapter imparts a significant appraisal of the earlier work published in the literature related to trace elemental contamination and speciation in terrestrial environment around coal fired thermal power plants.

Coal fired thermal power plants are important stationary (point) sources of heavy metal contamination of terrestrial environment in their surroundings. Thermal Power Plants (TPP) may introduce heavy metal contamination into the natural environment via gaseous and particulate matter emissions, coal ashes (fly ash and bottom ash) and leaching of metals to groundwater and surface water. Fly ashes are largely produced in the power plants and their disposal causes a serious environmental problem by the release of metals to soils and ground waters.

The first part of review focuses on approaches /designs to investigate heavy metal mobility/bioavailability in soils around power plant and coal ashes generated thereof. The various approaches usually adopted are:

- Soil profile and spatial distribution of metal concentrations
- Geostatistical approaches
- Mineralogical characteristics of soil and coal ash
- Metal transport and leaching in coal ashes

The second part highlights the role of chemical speciation. Single and sequential extraction procedure (SEPs) from 1970's to so far have been discussed. Different nominally extracted fractions in SEPs along with the commonly used extractants, criticism/limitation of sequential extraction procedure have also been reviewed. Heavy metal distribution in vegetation and water around TPPs also has been discussed.

2.2 Soil profile and spatial distribution of metal concentrations

The heavy metal (HM) pollution is a key environmental problem because of their non-degradable and resistant nature in environment. The toxicity and bioaccumulation affinity of heavy metals in the environment is hazardous to the health of living organisms. Unlike organic pollutants, HMs cannot be degraded or destroyed by

chemical or biological processes. Consequently, they can only be altered or transformed into less toxic species. The accumulation of heavy metals in water and soil is of rising concern due to the safety problems of drinking water as well as food. It is not only causing possible health risks to human beings but also unfavorable for the ecosystem.

The kinetics and reactivity of heavy metals differentiate from each and every soil because of soil heterogeneity and the composition complexity (Filgueiras et al., 2002). Environmental studies need accurate use of elemental transport in soils. The chemical properties of soil and soil profile distribution are then investigated to determine metal retention and transport of metals in soils. Heavy metals usually occur naturally in soil at low concentration as a result of weathering and other pedogenic processes. The natural occurrence of heavy metals varies between certain bed-rocks and rock types, which provide high metal concentration to overlying soils.

The atmospheric deposition and several soil amendments for example sewage sludge, fertilizers, liming materials, pesticides, manures, and compost are the various source of heavy-metal in to the agricultural soils (Raven and Loeppert, 1996). Elements originated from a point source may be deposited close to the source or transported over great distances subjected to dominating environmental conditions. It is important to prevent the possible loss of the soil functions as well as contamination of water due to introduction of contaminants and to examine the development of soil quality around the area affected by the coal fired TPP (Popescu, and Stanca, 2008).

The distribution of metal contaminants within the depth of soil can indicate the mobility of metals originating from surface. The distribution and movement of metals within the soil profile indicates the relative mobility of metals. The surface and sub surface soil profile distribution of metals and physicochemical properties of soils are investigated to determine metal availability in soils. Metals are primarily considered to be deposited in surface soil horizons by many researchers (Buchauer, 1973, Kabal and Singh, 2001; Garcia-Sanchez et al., 1999). The vertical distribution along with downward mobility of many metals like Cd, Pb and Zn, in soils was evaluated by Sterckeman et al. (2000). The majority of heavy metal contamination was observed in the surface horizons (20 to 30 cm) of soil and Pb, Zn and Cd enhancement was found to depth of 1.2 to 2 m. The distribution of heavy metals in the soil profile presents a relative accumulation in the surface layer (Sahuquillo et al., 1999). Akinyemi et al (2011) showed that trace metals, such as P and Zn, show increasing trends down the

depth, while Ba, Ni, Pb, Sr, V, and Cr increased up the depth of the core (20-year-old ash). The trace metals distribution patterns in 1-year-old ash showed increasing trends down the depth of the core for Cr, Ni, Pb, Y, S, and P, while Ba and Sr decrease down the depth of the core. Li and Shuman (1996) observed that the soluble form of Zn and exchangeable fraction migrated down to 100 cm in depth, whereas Cd was found in the sub surface soil from 30 to 75 cm.

The emissions from Novocherkassk power station (NPS) has increased in the total metal content in the soils located near the power station along with the main wind direction in soil samples (Minkina et al., 2009). The HM contents decreased with distance; most pollutants are deposited on the surface of soils within 5 km along the main wind direction from the source of contamination. The contents of total Cu, Pb and Zn in these soils exceeded their maximum permissible concentration values.

The total metal content in a soil is the sum of the natural and technogenic elemental content. It is the technogenic constituent that controls the decreasing total content of a given element in a technogeochemical group. The technogenic origin of an element can be identified when its distribution decreases exponentially with the increasing radial distance from the contamination source. Technogenic pollution may be hydrogenic or aerial. The hydrogenic pollution may be more dangerous because it occurs in limited areas and has been studied much more poorly than aerial pollution (Vodyanitskii et al., 2008). A hot point is taken to mean a place with an abnormally high total metal content in the technogenically contaminated area (Vodyanitskii, 2009). The effect of natural and technogenic issues on the mobility and transformation of metal was studied by Minkina et al. (2009) in the soils of areas around the Novocherkassk power station. The soils with low buffering capacity have found higher metal mobility.

Metals in soils are related with number of physicochemical properties that function as sinks or reservoirs of metals present in the environment. Although, soils are very important sinks for metals, they can also discharge metals into the natural ecosystem. The mobility of various elements in soils is highly dependent on the heavy metals' properties as well as the physical and chemical characteristics of soils.

The mobility as well as bioavailability of heavy metals in soil ecosystem depends on the properties of soil solution as well as the strength of the bond between metal and soil surface. The dissolution of trace elements, mineral mechanism, and the activities of various dissolved components were controlled by behavior of the dissolved species,

pH, and Eh values of soil. The role of pH is in the acid base characteristics of the soil system, and the Eh decides the relative stability of different multivalent species in soil. Soil pH value is considered the important factor controlling heavy metal distribution in soils. Acidic soils have a much higher proportion of metal in soil solution (Alloway et al., 1988). Alkaline soils have low heavy metals mobility as compared with acidic soils. Ion exchange properties in the soil are strongly dependent on soil pH. Under neutral or slightly alkaline soil conditions, the surfaces of organic matter will act as cation exchange sites and also become points of net negative charge. With decrease in pH, an H^+ ion moves towards these exchange sites, and aqueous metal concentrations should be expected to increase (McBride, 1994). Concentration of many metals like Al, B, Be, Ca, Cd, Cu, Co, Mg, Mn, Ni, Si, Sr, and Zn increased at low pH; whereas K, Mo and Na is more soluble at high pH values (Griffin et al., 1973).

The behavior of cadmium is regulated by several physical and chemical processes taking place in soils. Cadmium may be preserved in soils via precipitation and adsorption reactions. Transport of cadmium depends on the release properties of the soil as well as on the environmental conditions. However, Cd may be found in complexes with different organic acids, in soil solution (Krishnamurti et al., 1997). Cadmium solid-solution fractionation is dependent on soil organic matter (OM), soil solution pH, and total metal content. Adsorption of Cd is highly dependent on pH, it enhances with pH and sorbed Cd may become irreversible. Therefore, possible mobility for Cd is highest in acidic soil (Dijkstra et al., 2004).

Chromium is the most toxic in its highly oxidized form (VI), the hazardous effect of Cr reduces with the decrease of Cr (VI) to Cr (III). There are different chemical reducers of Cr (VI), including dissolved organic substances, sulfides, and minerals enriched in Fe(II), and Fe(0). The chromate adsorption increases with decreasing pH due to the protonation of surface hydroxyl groups and chromate CrO_4^{2-} . The soil colloids retain chromate ion at the expense of outer sphere coordination at the particle surface (Vodyanitskii, 2009b).

The mobility and effect of metals in soils are reflected by the partitioning between the soil and soil solution and also affected by soil properties (Sparks, 2003). The main features that influence the mobility of HMs in soils are redox reaction, amount of dissolved organic matter and pH in soil.

Organic matter is generally insoluble at low pH or acidic conditions, thus high pH accelerates the dissolution of organic matter. At alkaline conditions the bonds between trace metals and organic matter get disturbed and thus acidic constituents of organic matter are changed into soluble salt forming soluble metal-oxide complexes in soil (McBride, 1995). The dissolved organic matter has a significant effect on metal solubility (Sauve et al., 2000). The metal binding to the dissolved organic matter can influence the solubility of heavy metals to a significant level and enhance the concentration of dissolved metals (Weng et al., 2002). The distribution and amount of carbonates effect soil fertility. The higher concentration of calcium carbonate in soil usually promotes many difficulties related to fertilization and nutrient availability (Auburn, 2000).

The soils irrigated with the different discharges from Coal-Fired Thermal Power Plant exhibited an increase in pH, water soluble salts, electrical conductivity, organic matter, calcium carbonate, cation exchange capacity, and nitrogen and phosphorus, while potassium content decreased, because of being leached downward in the soil. Also, elevated concentrations of heavy metals Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, and Zn in different effluents from Kasimpur coal-fired thermal power plant have been reported by Ajmal et al. (1983).

The trace element partitioning concentration of Pb, Sb, Cd, Se, As, Ni, Cr, and Zn increases with reducing particle size was studied by Davison et al. (1974). The pH (7.6 – 9.2), EC (0.83-1.20mmhos/cm), organic carbon (0.18-.042%), organic matter (0.31-0.72%), nitrogen and phosphate content in the soil samples have remarkable variability.

The average metal content ($\mu\text{g g}^{-1}$) of contaminated soil was found in the order of Fe (816.41) > Zn (117.61) > Mn (59.14) > Cu (30.14) > Pb (26.48) > Ni (8.96) > Cr (6.41) > Cd (2.98) around a coal based thermal power plant, Uttar Pradesh, India (Singh et al., 2010). The authors investigated deposition of heavy metals in field soils contaminated with fly ash from the thermal power plant, and consequent uptake in different parts of naturally grown plants. Generally, the concentrations of heavy metal in Indian coal ash are found less as compared to coal ashes from other parts of the world (Sushil and Batra, 2006). The findings of heavy metals around Thermal power plants reported in literature at National and International level are given in Table 2.1 and Table 2.2, respectively.

Table 2.1: Findings of various studies on Indian thermal power plants

Area/Location	Matrix type	Observations and Findings	Reference
Patratu TPP Jharkhand India	Fly ash	Cu, Mn, Ni had high ecological risk. Pollution Load Index (>1) and Ecological Risk Index (>600) signify that fly ash dump sites was highly polluted and thus the fly ash causes high risk of metal contamination to the environment. Thus, implementation of remediation techniques is necessary to reduce the ecological risk of the fly ash.	Pandey and Bhattacharya, 2016
Barsingsar TPP in the region of Bikaner, Thar Desert, Rajasthan, India	Soil, fly ash, bottom ash, feed lignite coal	Ba, Co, U, Cu, Cd, and Ni are enriched in fly ash and Co, Pb, Li, Ga, Cd, and U in bottom ash, as compared to the feed lignite. The concentration of trace elements in the study area was relatively much less than that in both fly ash and bottom ash.	Ram et al., 2015
Farakka, West Bengal, India	Soil	Average level of heavy metal content followed the order Fe > Zn > Pb > Ni > Cu > Cl > As > Cd in affected soils. The EF values of heavy metals were larger with higher fraction of manmade sources. Even though, I-geo values indicated moderate to unpolluted condition of the soils except Pb, Cd and As. Thus, significant degree of enrichment of toxic heavy metals was found in the soils.	Sengupta et al., 2011

Thermal Power Plants, Singrauli, Madhya Pradesh	Coal combustion by products	Average concentration of Cadmium, Lead, Arsenic and Nickel was 0.69, 13.69, 17.76, and 3.51 mg/kg, respectively, within 2–4 km distance from TPP. It was also observed that concentration of metals was higher in the prevalent wind direction.	Agrawal, et al., 2010
Angul,, Farakka and Sarni, India	Fly ash and soils	Trace elements such as K, Ca, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Se, Rb, Sr and Pb have been analyzed in fly ash samples by EDXRF technique and K, Ca, Ti, V, Mn, Fe, Co, Cu, Zn, Sr and Pb were quantified in the soil samples by EDXRF technique.	Rautray, et al., 2009
Delhi, India	Flyash and bottom ash from three major power plants in north India	Ashes were analyzed for the presence of Cr, Mn, Pb, Zn, Cu, Ni and Co. The concentrations of metals like Cr and Zn were found highest while Co was less. Marked differences were also observed between the heavy metal concentrations of the coal ashes from the three power plant chosen in the study.	Sushil and Batra, 2006
Kolaghat, India	Coal and Flyash	The trace elements like As, Cu, Pb, Ni, Zn, Co, V, Sc, Be, Cs, and Zr have moderately high amount in Kolaghat ashes.	Mandal and Sengupta, 2005
Indraprastha Power Station, Delhi, India	Flyash, Topsoil and Vegetation	Trace elemental concentrations were determined by ICP-AES. Observed elemental enrichment in soils and vegetation.	Mehra et al., 1998
Kasimpur coal-fired TPP, India	Effluents from TPP and soils	Found high concentrations of HMs Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in various effluents from Kasimpur coal-fired thermal	Ajmal et al., 1983

Table 2.2: Findings of various studies on thermal power plants outside India

Location	Matrix studied	Objectives and Observations	Reference
Coal-Fired Power Plant, China	Bottom ash, fly ash and gypsum	Cd is evenly distributed in bottom ash, fly ash, and gypsum samples.	Zhang et al., 2017
Matla, Lethabo, and Rooiwal, TPP South Africa	Surface soil and Plant (Digitaria eriantha)	Fe, Cu, Mn, Ni, Cd, Pb, Hg, Cr, and Zn were determined using ICP-OES and GFAAS. Accumulation factors (A) was less than 1 at all power plants showed a low transfer of metal from soil to plant (excluder). Enrichment factor values obtained (2.4–5.0) suggested that the soils are reasonably enriched with metals excepted of Pb that had enrichment of 20. Geo-accumulation index (I-geo) values of metals showed that the soils are quite polluted (0.005–0.65), except for Pb that showed moderate to strong pollution (1.74–2.53).	Okedeyi et al., 2014
Jamshoro, Pakistan	Soil around TPP	Surrounding soils contaminated with Cr, Fe and Zn	Rind et al., 2013
Cienfuegos Bay, Cuba	Bottom ash from TPP and Oil refineries	Large amount of Cr, Ni, Pb, Ti, V and Zn were found in the bottom ashes. Elements were measured using X-ray fluorescence (XRF). According to Cuban regulations these ashes are classified as hazardous waste. This study represents the first report of heavy metals in bottom ashes from power plants and oil refineries in Cuba.	Alonso-Hernandez et al., 2011
China	Feed Coal and Bottom ash	Metal content observed by using XRF technique. The elemental mass of combusted bottom ash showed strong enrichment of many elements that exist naturally in coal.	Ma et al., 2010

Canadian Power Plant, Canada	Milled coals, ashes, stack-emitted materials from TPP	The concentrations of elements (As, Cd, Cr, Hg, Ni, and Pb) in milled coals, ashes, stack-emitted materials are found of environmental concern. PAHs emitted from the stack were also measured. The rates of trace elemental input for As, Cd, Cr, Hg, Ni, and Pb were 28, 0.94, 230, 0.44, 44, and 88 kg/day. Cr being the highest, while Cd has the lowest contributor to this group. In both bottom and fly ashes, more than 95% of the total arsenic is present as As ⁺⁵ . Chromium in the milled coal and bottom ash is mostly non-toxic (Cr ⁺³).	Huggins and Goodarzi, 2009
Bucharest, Romania	TPP, Soil around TPP	Monitored the regional distribution of HMs viz. Cu, Zn and Ni in soils. In the soil samples metal contents were naturally present however, at some sample collection points, a higher level of metal was observed in relation to the natural content. Also, soils in the area indicating less amount of HMs than thresholds limit i.e. not significantly contaminated.	Popescu and Stanca, 2008
LodzEC4 Power Plant, Poland	Soil around TPP	Determined Pb, Zn, Cr, Co and Fe levels in soils	Jankiewicz and Adamczyk, 2007
Seyitomer, Turkey	Vegetation (<i>Salix alba</i> L.) and Soils	Intense concentrations of pollutants i.e. Fe, Cd, Cr, Cu, Zn, Pb, Ni and S in both soils and leaves in the direction of prevailing wind.	Cicek and Koparal, 2006
West Macedonia, Greece	TPP, Soil	Moderate enrichment for Cr and Ni, to a lesser extent for Mn and relatively high PAH pollution. The prime source of most of PAHs and trace elements were found lignite coal combustion residue and other anthropogenic activities or soil composition.	Stalikas et al., 1997

2.3 Geostatistical Analysis

Routine statistical methods and geostatistics based approaches are the criteria used for the technogenic origin of heavy metals. The geochemical criteria are based on the statistical relationship between the content of the particular heavy metal and its principal mineral phase carrier in the background soils. The chemical criteria are based on the different solubility/ mobility of natural and technogenic heavy metals by reagents.

Particular Geostatistical methods for the geosciences are present and these methods are broadly employed in the study of soil (Chen et al., 2009; Zheng et al., 2008). Wang et al. (2006) suggested that though, geostatistical techniques can be applied in the studies of soil system, classical multivariate techniques are still desirable for a focused approach. The increasing use of Chemometrics in environmental studies responds to the severe research committed to test and show the power of data processing techniques and the availability of suitable software. There are three main areas of interest which can be investigated by chemometric studies: monitoring for environmental quality evaluation and quantitative chemical analysis, modeling, and prediction of toxicological effects. Multivariate calibration methods concentrate on the establishment and relevance of mathematical models that connect multivariate instrumental signals with analyte concentrations or properties of sample (Massart, 1997).

Qishlaqi et al. (2009) studied the pearson correlation between physicochemical parameters and total elemental concentrations in Iranian agricultural soils. Lu et al. (2010) observed pearson correlation in heavy metals in street dust. Anju and Banerjee (2012) found statistical association between physico-chemical parameters and total elemental concentrations in soils.

Principal component analysis (PCA) is a multivariate statistical data display method applied in exploratory data analysis (Jolliffe, 1986). PCA extracts the main principal components which explain most of the variance of the data matrix. The abstract principal components (PC) may be rotated to increase interpretability. For every variable, each principal component shows a characteristic value known as score, and, for each variable, a characteristic value known as loading. Both scores as well as loadings may have positive and negative values for variable (Mostert, 2010). In some studies, the rotated profiles can be quantitatively read as possible sources, such as in absolute principal component analysis (Thurston and Spengler, 1985). Occasionally,

the interpretability of PCA is increased by the so-called varimax rotation (Pere-Trepat et al., 2006), a change of coordinates that increases the sum of the variance of the loading vectors. Multivariate analysis has been used for source apportionment for trace elements in soils (Qishlaqi et al., 2009; Anju and Banerjee, 2012; Bhuiyan et al., 2010; Sengupta et al., 2010) and dust (Lu et al., 2010; Anju and Banerjee, 2003).

Bhuiyan et al. (2010) used principal component analysis on coal mine agricultural soils and extracted five principal components (PCs) with eigenvalues greater than 1 and also found that Pb and Zn is associated with PC1. Source of first factor was anthropogenic source, specifically derived from coal mine effluents. The statistical analysis of the heavy metals observed by Sengupta et al. (2010) observed the two probable sources (Eigen values) in affected soils are dependable for metal distribution. Cu, Ni and Zn are associated with factor 2 with variance of 32% of the total from thermal power plant (TPP) in India located at Farakka, West Bengal. It is also evident that the levels of toxic metals Cu, Zn, and Ni showed less variability than Pb, Cd, in control soils were considerably lower Cr and As. Lu et al. (2010) applied PCA in street dust and found five principal components. Anju and Banerjee (2012) applied PCA to multi-elemental data in soils from mining and smelting area and found three principal components.

2.4 Mineralogical characterization of soils and coal ashes

Mineralogical methods can be used to estimate potential solubility and transport of a metal contaminant in soils and coal ashes. Heavy metal potential solubility and mobility is estimated from the mineral forms and binding of metals with various phases in soil and coal ashes. Trace elements binding with solid phases can be investigated by direct or indirect methods. Direct methods use spectroscopic instruments such as scanning electron microscopy coupled with EDX (SEM-EDX) and X-ray diffraction (XRD), to quantify mineral components. Indirect methods are qualitative predictions based on solution species and their input into chemical equilibrium models. Now some spectroscopic techniques such as transmission electron microscopy and reflectance spectroscopy are used to identify metal mineral phases, heavy metal contamination, and speciation in contaminated soils.

The mineralogical compositions of the fly ash were observed by X-ray diffraction by Akinyemi et al. (2011). The minerals identified were quartz and mullite in the fly ash. Other phases characterized were anorthite, calcite, enstatite, hematite, lime, and mica in the matrix.

Morphological and compositional identification was identified by X-ray diffraction and scanning electron microscopy (SEM) in fly ashes collected in a thermal power plant of Argentina (Smichowski et al., 2008). Fly ash samples were analyzed by EDAX for elemental determination. Similar composition was found for fly ash particles. The Predominant minerals found in the matrix were lime, mullite, iron oxides and quartz. The other mineral phases present as minor were lime, anhydrite, hematite, magnetite, gypsum and rutile. The mineral and chemical composition shows that the presence of quartz (SiO_2) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) indicates the coal burned in the power plant generates class-F type fly ash. Commonly, all the fly ashes particles could be observed, porous and irregular shapes, fine solid and hollow spheres, due to an incomplete combustion of coal and molten glassy materials as well as due to presence of char.

Qian and Ma (2014) characterized the change in surface chemistry of fly ashes by XRD, TEM, FTIR and potentiometric titration. According to the XRD analysis it is determined that quartz was the main component present in FA, whereas other minerals cannot be identified in terms of low intensity of peaks. The components of fly ashes were characterized by ICP-MS method. It is found that the main components in fly ashes are SiO_2 , CaO and Al_2O_3 , which may result from the quartz, carbonate and clay minerals, respectively.

X-ray diffraction method was used by Verma et al. (2015) for the mineralogical characterization of coal, fly ash and bottom ash samples collected from the National Thermal Power Plant of Unchahar, Uttar Pradesh, India. The predominant minerals identified were quartz and kaolinite in the coal, whereas quartz, mullite, and anhydrite in the ashes. XRD analysis identified that feed coal has siliceous minerals mainly kaolinite and quartz. $\text{Si} > \text{Al} > \text{Fe} > \text{Ca}$ are the main elements present in coal and its ashes.

Ram et al. (2015) performed mineralogical characterization (by XRD) of lignite and its ashes from Barsingsar power plant located in region of Bikaner-Nagaur road, Thar Desert, India. The main minerals identified were Kaolinite, quartz, and gypsum in lignite. Both the fly ash and bottom ash contained quartz, mullite, anhydrite, and albite. Also, both the ashes of lignite belong to class-F with $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{CaO} > \text{MgO}$.

Bodog et al. (1996) carried out morphological investigations on fly ash by X-ray powder diffraction. The analysis showed that the fine and coarse particles of studied sample were very similar to each other. Small amounts of sulfates, quartz, anhydrite,

and syngenite were observed in the coarse fraction. Large amounts of amorphous phase along with the crystalline compounds were also observed.

Morphological investigations were carried out on a scanning electron microscopy analyzer (SEM) coupled with an energy-dispersive X-ray analyzer by Cheng et al. (2009). SEM was carried out on the original and solvent leaching samples, and their elemental compositions were semi-qualitatively analyzed with EDX spectrometry.

2.5 Metal transport and leaching of coal ashes

Environmental hazards due to heavy metals are related to their movement and leaching behavior in soils and coal ashes. The leaching and extraction procedures provide the necessary information for a correct evaluation of the eco compatibility of the soils and ashes. A variety of standardized leaching tests with variable reagents, and experimental conditions such as complexity, agitation method, temperature, contact time, liquid to solid ratio (L/S) are used. Generally four types of leaching procedures are commonly used to evaluate the leaching behavior of coal ash (Izquierdo and Querol, 2012):

- (i) Batch leaching analysis by means of deionised water or similar leachant
- (ii) Column/flow-through tests: elements are released under unrestrained pH conditions
- (iii) Toxicity Characteristic Leaching Procedure (TCLP) proposed by US EPA
- (iv) Acid extractions: operated under aggressive situations.

A study by Yuan (2009) in fly ash samples, the distribution of metals in different fractions was impacted by different combustion processes. The metals released from fly ash in groundwater mainly depend on bonding between the fly ash and element, physicochemical properties of water and chemical form of the flyash (Fulekar and Dave, 1991).

The mobility of the majority of elements found in ash is pH sensitive. The alkaline condition of fly ash decreases the release of concerned metals for example Cd, Co, Cu, Hg, Ni, Pb, Sn or Zn among others. Various metals are strongly bound to fly ash and could not be easily released to the environment, in spite of the nature of the coal ash (Izquierdo and Querol, 2012). Most of the chromium was found as Cr (III) ion; noticeable amounts of Cr (VI) were not found in the coals tested (Huggins et al., 2000). Cr was enriched in the Fe-oxide phases whereas, 70% of Cr was found in the glassy silicate. Most of metal concentration like As, Pb, and Cd were observed in fly ash.

However, Se and Hg get vaporized in flyash. The bituminous coals contain approximately 50% of Cr in the organic bound phase as an amorphous fine-particle oxyhydroxide. The majority of the remaining Cr is associated with the residual or silicate illite fraction (Huggins et al., 2000). Antimony, beryllium, chromium, nickel, manganese, zinc and uranium were associated with silicates bound phase. Whereas, 50% of the antimony, beryllium, selenium, mercury, chromium, uranium, lead, thorium, cobalt, and nickel are found to be in the organic bound fraction.

The concentration of trace elements in fly ash were observed higher than the elements found in bottom ash. Because fine particle size of fly ash provide greater surface area for condensation as compared to bottom ash, thus increasing the trace elements concentration in the fly ash than bottom ash (Cao et al., 2008). The major elemental concentrations of fly ash and bottom ash were indistinguishable. The composition of trace element signify that fly ash contain volatile elements (As, B, Cl, F, S and Se). The fly ash generated from burning of bituminous coal was found to have higher concentration of trace metal (EPRI, 1987).

Xu and Li (2009) concluded that As, Cr, Ni, Mn and Zn were released when coal ash being transported to the dumping site, however Cu and Fe did not cause any environmental threat due to elemental leaching taking place during and after the coal ash suspension and transport. It is feasible to recover metals like Al, Ga, Ge, Ca, Cd, Fe, Hg, Mg, Na, Ni, Pb, Ra, Th, V and Zn, etc., from solid wastes of TPP. Reutilization of heavy metals and recovery of heavy metals from TPP solid wastes are necessary for protecting for the environment and conserving metal resources (Meawad et al., 2010).

Indian coal ashes did not contain any humus and SiO₂ has been found as a major component with significant contents of Ca, Mg, K, P, and a low amount of N (Ram et al., 2006). Presence of heavy metals like Pb, Ni, Co, and Cr in the Indian fly ash has been reported by various researchers (Praharaj et al., 2002; Mukherjee and Zevenhoven, 2006; Ram et al., 2000). The difference in the concentration of trace elements, based on particle size, is associated to physicochemical properties and the combustion conditions of the coal (Davison et al., 1974).

The fly and bottom ashes from fuel oil power plants may consist of a large concentration of silicon, iron, aluminum, calcium, magnesium, carbon, as well as copper, lead, cadmium, mercury, arsenic, chromium, nickel, manganese, with small amount of cobalt and other hazardous trace elements. These heavy metals have a

harmful effect on the environment with time because of potential leaching via acid rains into groundwater (Guo et al., 2009).

In thermal plants, gaseous emissions are also of most serious concern. Burning of coal and the consequent emission to the surroundings produces the re-distribution of toxic trace elements in the environment (Mahur et al., 2008).

The major pollutants generated from power plants are PM, sulfur dioxide, and nitrogen oxides. In US, 51% of total power plant boilers are coal fueled which contribute to emissions of 93% of NO_x, over 96% of SO₂, over 88% of CO₂, and 99% of mercury in the entire electricity industry (Frema and Hong, 1999). The concentration of ²³⁸U, ²³²Th and ⁴⁰K radionuclide in fly ash samples from Kolaghat Thermal Power Station (WB) have been identified by Mandal and Sengupta (2005). Combustion of coal enhances the radioactivity in ash. These pollutants are extremely harmful to both public health and to the environment.

Different reagents like water, 0.1M MgCl₂, 0.11M acetic acid and few drops of concentrated HCl were used by Izquierdo and Querol (2012). Leaching behavior of different elements from pond ash samples was pH dependent. Higher leaching of Al, Ti, V, Ni, Zn, Mo, Ba, Ce and Pb; moderately high leaching of Cr and low leaching of Cd, Cu and As were observed. Further study can be done on pH and time dependent leaching behavior of the elements detected during SEP and TCLP (Paul et al., 1994).

Lau and Wong (2001) found that different elements have different leaching behaviors due to different elemental properties, leaching time and pH of the solution, which strongly influence leaching behavior.

The leachability of heavy metals (i.e. Zn, Ni, Cu, Fe, Pb, Mn, Mg, and Cd) from fly ash, bottom ash, dumping site of ash, cement, and brick samples admixture with fly ash was studied by using batch leach test and toxicity characteristic leaching procedure (TCLP) to verify the prospect of ground water pollution. Mg, Mn, and Fe were leached to a larger extent while Zn, Cu, and Pb to moderate amount, and Ni to a lesser amount from the ash and admixtures. Both in TCLP and batch leach test Cd was not extracted or leached from any sample (Sarode et al., 2010).

The concentrations of different elements in each step of TCLP was carried out by Ghosh and Goel (2014) on pond ash samples around Kolaghat Thermal Plant in West Bengal, India to assess the hazardous nature of the samples to the environment. The toxic elements showed varied potential of getting leached from moderate to high ranges

of concentrations by SEP. Pond ash samples are recognized as hazardous by TCLP test. The fraction of Co accessible for leaching under TCLP test (pH 5) is estimated at 1.5–2.5 % (Ward et al., 2003).

Izquierdo and Querol (2012) suggested that various elements are strongly bound to fly ash and may not be certainly leached to the environment. Single step extraction method was applied to optimize the leaching time to attain optimum leaching of trace elements. The assessment of the optimum time for leaching of the toxic metals and metalloids in the fly ashes was found out using the single step extraction method by Lokeshappa and Dikshit (2012). Both for the water soluble step as well as for ion exchangeable step, 4 hours favorable time while in the acid soluble and reducible steps the favorable time of 24 hours for agitation was determined.

To check the ground water contamination around Bhusawal Thermal Power Plant extraction and leaching of various heavy metals (Cu, Cd, Fe, Pb, Mg, Mn, Ni, and Zn) was carried out by using batch leach test and toxicity characteristic leaching procedure (TCLP) by Sarode et al. (2010). Results revealed that Fe, Mn, and Mg were leached to a larger; Cu, Pb, and Zn to moderate amount, and Ni to a smaller level, from the ash samples. Cd was not leached at all from any sample in batch leach as well as in TCLP tests.

In open leaching systems loss of alkalinity occurs in comparison to closed leaching systems thus heavy metals are more mobile in open systems in fly ash. Thus, water soluble trace elements are also highly mobile or soluble in open system (Querol et al., 2001). Also, the alkalinity or calcium content as well as the solid–liquid ratio of an ash sample highly influences the leaching behavior. At low pH higher mobility of the elements have been found and less leaching was observed at a high pH (Dutta et al., 2009).

2.6 Trace elemental speciation

Trace elemental speciation in soils and sediments assists in comprehending the geochemical processes and allows us to evaluate: (i.) The distribution pattern of heavy metals according to their affinity towards various soil constituents and the strengths with which they are bound to the matrix, (ii.) The potential of remobilization with changes in pH and Eh, (iii) the bioavailability and toxicity of an element to plants and living organisms (iv) The importance of multiple sources, and (v) The effectiveness of soil as a sink for metals.

The operational methods of chemical speciation can be used to determine the toxicity of metals in different solid matrices, which can be mobilized under different environmental conditions. Even though, no usually accepted definition of the speciation exists, firstly, it is the active process of the identification and quantification of the various defined species, forms or phases in which an element is found in a material. Secondly, the term “speciation” may be defined as the description of amounts and types of forms or species, or phases occurring in the material. The various types of defined species can be broadly defined, in the context of soils: *Functionally* (by their role), *Operationally* (the reagents or procedure used to isolate and quantify them), and *Classical speciation* (where specific chemical compounds or oxidation states are defined) (Ure, 1991).

The identification of species is likely to be more difficult than determination of total elemental concentrations due to:

- i. Difficult to isolate the compound of interest from different complex matrices
- ii. The majority of the speciation techniques perturb the equilibrium existing between the different chemical species found in the matrix under study
- iii. For species which exist in ultra-trace levels, not many analytical procedures acquire the required degree of sensitivity, and
- iv. Non-availability of suitable standard reference materials (Pickering, 2002).

The nature of difficulties changes with type of environmental matrix, i.e. different methods are required for speciation analysis in different types of matrices (Pickering, 1994). The analytical activity of identifying and quantifying various chemical and physical forms of an element present in a sample is defined as *Speciation analysis* (Kot and Namiesnik, 2000). This endeavor is important to biomedicine, environmental science, geology and material sciences.

The analysis of various elements in soils is often performed with the use of extraction fractionation. Trace element speciation in solid matrices such as soils, sediments, dusts, and wastes is often accomplished by various empirical single as well as sequential extraction methods. In single extractions a large spectra of extractants have been used to extract the “mobile” or “bioavailable” forms of metals, viz. very strong acids (aqua regia, nitric acid), Chelating agents (EDTA, DTPA), Buffered salt solutions (ammonium acetate - pH 7) and Unbuffered salt solutions (CaCl₂, NaNO₃, BaCl₂ etc.).

Extractants used in single extractions are hypothesized to evaluate the exchangeable fractions of elements in soils which is believed to be available for uptake by soil organisms (Rauret, 1998).

For harmonizing the single extraction methods applied to soil analysis and defining common extraction techniques to test three different procedures, namely acetic acid, ammonium acetate and EDTA were tested in European laboratory (Quevauviller et al., 1997). EDTA is thought to extract metals from all the non-silicate-bound soil fractions and it is probably to reveal the metal availability in short-term and long-term processes (Ure, 1996). Acetic acid possesses similar qualities but it is limited to utilize in highly calcareous soils. The choice of ammonium acetate, extracting the exchangeable species, is applicable to neutral and alkaline soils (Ure, 1996).

Single-extraction schemes are generally used to investigate the bioavailable metal fraction and the mobility of metals in coal ashes. Several researchers suggested that a single step extraction method is simple, fast, easy, and cost effective involving only one step to remove the available metals and to determine bioavailability of metals in contaminated solid matrices.

EDTA plays a key role in solubilizing Cd, Ni, and Zn in some soils, thus these three metals were observed to have high tendency to form metal complexes with EDTA (Li and Shuman, 1996). It is also found that metal-chelate complex formed in soil could increase metal solubility and elevate metal diffusion and thus promote metal uptake and toxicity. Many other research studies have established the capability of EDTA to extract a large quantity of total soil Pb (Sposito et al. 1982; McGrath and Cegarra, 1992; Abdel-Saheb et al., 1994; Pichtel et al., 2001). Cheng and Bray (1953) have discussed the use of EDTA at pH 5.0, for determining the available Cu in soils. From the literature it can be concluded that 0.05M EDTA (pH 7) has least effects on aluminosilicates and crystalline iron oxides, though some dissolution may take place from Fe-oxides bound weakly at corners or edges and usually found in poorly crystalline forms of Fe-oxide (Borggaard, 1992).

Powerful chelating agents (EDTA, DTPA, CaCl_2 , NH_4NO_3 , and NaNO_3) are used to evaluate the availability of trace elements in soils and ashes which are likely to dissolve/mobilize non-labile metal (Degryse et al., 2004). A number of extractants have been used for single extractions by various researchers (McGrath 1996; Quevauviller 1998; Lu et al., 2003; Gupta and Sinha 2006; Menzies et al., 2007). In several studies

EDTA extracted greater amount of heavy metal than DTPA and NaNO_3 irrespective of the soil properties due to its low pH (Hammer and Keller, 2002; Sahuquillo et al., 2003).

Amount of Cu and Zn extracted by EDTA is dependent on the pH of the extract, larger amounts being removed at higher pH values. The amount of metal extracted at pH 5 was smaller than at pH 7. The recovery of added Cu and Zn was about 90% at pH 7. Also, this method is hardly suitable for calcareous soils because EDTA can dissolve water-insoluble carbonates that are not a part of the exchangeable complex. Thus, EDTA method is best fitted for acidic soils (Viro, 1955).

Borggaard (1976) stated in his review that EDTA is a universal extractants for the most of soil nutrients. EDTA is a weak organic acid having complex and chelating power to sequester divalent and trivalent cations (Chao, 1984). The conversions of cations into chelate ions enhances their release from various solid matrices like sediments, sludge and soils (Pickering, 1986). Borggaard (1982) observed that 0.02-0.1M EDTA at pH 8-10 upto 240 days extracted only negligible amounts of Fe from silicates. In addition, 30-100 days were necessary to remove only amorphous Fe-oxides from synthetic mixtures of amorphous and crystalline Fe- oxides. Therefore, it is concluded from the literature that 0.05M EDTA (at pH 7) has least effects on crystalline Fe-oxides and alumino-silicates. EDTA extracts of soils are likely to correlate with the plant-available fraction for Cd, Cu, Ni, Pb and Zn (Sanders et al., 1986), Cd (Lag and Elsokkary, 1978) and Cu (Sanders et al., 1987). Thus, EDTA is normally used to extract mobilizable metal fraction in solid matrices (Gupta et al., 1996).

EDTA has been widely used for identification of extractable metal content of polluted as well as unpolluted soils (Viro, 1955; McGrath, 1996; Schramel et al., 2000; Tokalioglu and Kartal, 2005), road sediments (Sutherland et al., 2001), municipal and industrial sludge's (Lo and Chen, 1990) and also used in the recovery of contaminated soils and sediments (Mench et al., 1994; Cline and Reed, 1995; Sun et al., 2001).

Lokeshappa and Dikshit (2012) used single step extractions of metals by using ultrapure water, 1 M NH_4NO_3 and 0.11 M acetic acid in coal fly ash collected from electrostatic precipitator's hoppers of Indian power plants around Maharashtra. A single test will never allow a response to be obtained for long-term risk assessment (Quevauviller, 1996). The mobility of metals from coal fired TPP fly ashes was

evaluated by Lokeshappa and Dikshit (2012) by using sequential extraction procedure showing an extensive compositional range.

Determination of specific binding forms or chemical species is not easy and often almost impossible. It is necessary to consider that contamination is more related to the mobile fraction of metals than to their total content. Total metal analysis may provide information concerning potential enrichment of different solid matrices (soil, sediment etc.) with heavy metals. The behavior (e.g., bioavailability, toxicity, and distribution) of metals in the environment cannot be predicted by only the total metal concentration of an element (Rauret, 1999). It is consequently necessary to understand the composition, chemistry, and geology of metals in soil as well as their chemical forms (Adamo et al., 1996). Complete information of the interactions among HMs and soil matrix is necessary to evaluate their environmental impacts.

HM are specified into loosely bound compounds and those firmly bound compounds with the soil. Both firmly and loosely bound HM are not uniform and may be further fractionated. Loosely bound HM are subdivided with respect to the mechanism of their interaction with the soil components i.e. exchangeable, complex, and specifically adsorbed compounds. To determine the content of firmly bound HM compounds, they are dissolved in various extractants together with their organic substances and nonsilicate compounds of Fe, Al, and Mn. The content of HM bound with silicate minerals is associated with the residual fraction.

Sequential or parallel extraction of trace elements is often used to determine their particular compounds. The extracting agents may transfer different metal compounds into solution (Minkina, 2008). SEPs are generally employed to investigate the bioavailability/mobility of heavy metals in soils, coal ash and sediments under various environmental conditions (Rauret, 1998). Finally, sequential extraction procedures provide useful additional information or knowledge about the portioning of metals in the matrix (Brunori et al., 1999).

2.7 Sequential extraction procedures

The behavior of the trace elements in a soil-water-plant ecosystem is based on the chemical forms of elements. Trace element speciation in soils is often accomplished by different single as well as sequential extractions schemes. The term “fractionation” is normally used interchangeably with speciation, but highlights the concept of subdividing a “total content”.

To explain the fractionation of heavy metals among different forms sequential extraction or fractionation schemes have been developed, several of which have been derived from the work of Tessier's scheme. SEP do not give a direct characterization of metal speciation, but are planned to simulate the chemical reactivity of metals under various feasible natural and anthropogenic alterations of environmental systems. It is assumed that mobility and bioavailability of metals decline in the order of extraction in a SEP, indicating that metals in the exchangeable phase are most mobile and bioavailable, while metals in residual phase are tightly bound and thus are least mobile under natural environmental system. These procedures engage a variety of fractions subjecting the solid samples to consecutive attacks with stronger reagents having dissimilar chemical properties (redox potential, acidity, and complexing behavior) (Gibbs, 1973; Gupta and Chen, 1975; Brannon et al., 1976; Tessier et al., 1979; Forstner, 1993).

Initially, developed to observe trace metal fractionation in soils and sediments, Sequential Extraction Procedures (SEP's) are being used by numerous scientists (Table 2.3) to find out the extent of contamination based on partitioning of metals in soil, (Gupta and Chen, 1975; Tessier et al., 1979; Tessier and Campbell, 1988; Shuman, 1985; Rauret et al., 1989; Ramos et al., 1994; Pueyo et al., 2003; Anju and Banerjee, 2011), sediments (Jain, 2004), mine tailings (Anju and Banerjee, 2010), and street dusts (Anju and Banerjee, 2003). In all of the sequential extraction methods reported in literature, different chemical reagents are applied in order of ever-increasing reactivity (Tessier et al., 1979; Smeda and Zyrnicki, 2002; Jegadeesan et al., 2008; Smichowski et al., 2008). BCR method has also been modified (Raksasataya et al., 1996) to comprise aqua regia digestion of the residual material (Table 2.3).

A broad review of more than 33 different reagents applied in various sequential extraction methods have been presented by Gleyzes et al. (2002). Sequential extraction was applied by Ma and Rao (1997) to fractionate Cd, Cu, Ni, and Zn from nine contaminated soils. The residual phase was found the main dominant fraction for all the metals examined.

Table 2.3: Some representative sequential extraction schemes cited in literature

Sequential extraction procedure	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
Forstner (Forstner, 1993)	NH ₄ OAc 1 M pH=7	NaOAc 1 M/ HOAc pH=5	NH ₂ OH.HCl 0.1 M	0.1 M Oxalate buffer	H ₂ O ₂ 8.8 M/ HNO ₃ and NH ₄ OAc 0.8 M	HNO ₃
Tessier (Tessier et al., 1979)	Exchangeable MgCl ₂ 1M pH=7	Carbonatic NaOAc 1 M/ HOAc pH=5	Oxides Fe/Mn NH ₂ OH.HCl 0.04 M in 25% HOAc		Organic matter and sulfidic H ₂ O ₂ 8.8 M/ HNO ₃ and NH ₄ OAc 0.8 M	Residual HF/HClO ₄
Shuman (Shuman, 1983)	Mg(NO ₃) ₂	NaOCl	NH ₂ OH.HCl		NH ₄ Ox/HOx	
Meguelliati (Meguellati et al., 1983)	Exchangeable BaCl ₂ 1M pH=7	Carbonatic NaOAc 1 M/ HOAc pH=5	Oxides Fe/Mn NH ₂ OH.HCl 0.04 M in 25% HOAc		Organic matter and sulfidic H ₂ O ₂ (8.8 M)/ HNO ₃ and NH ₄ OAc (0.8M)	Ashing and digestion HF/HCl

Forstner (Forstner, 1993)	Exchangeable and carbonatic NH ₂ OH.HCl pH=2				Organic matter and sulfidic H ₂ O ₂ 8.8 M/ HCl and NH ₄ OAc (0.8 M)	Residual HF/HClO ₄
Modified BCR (Rauret et al., 1999)		Exchangeable and carbonate HOAc (0.11M)	Oxides Fe/Mn NH ₂ OH.HCL (0.5M) pH=2		Organic matter H ₂ O ₂ (8.8 M) and NH ₄ OAc (1.0 M) at pH=2	Residual HF/HNO ₃ /HCl
Original BCR (Ure et al., 1993)		Exchangeable and carbonate HOAc 40ml (0.11M)	Oxides Fe/Mn NH ₂ OH.HCL 40 ml (0.1M)		Organic matter H ₂ O ₂ (8.8 M) and NH ₄ OAc (1.0 M) at pH=2	Residual Aqua regia digestion
Hall and Pelchat (Hall and Pelchat, 1999)		Exchangeable and Carbonatic NaOAc 1 M pH=5	Am Fe oxy hydroxide NH ₂ OH.HCl in (0.05M HCl)	Cry Fe oxy hydroxide NH ₂ OH.HCl in 25% HOAc	Sulphides and organics KClO ₃ /HCl HNO ₃	Residual (Silicates)

Despite the wide range of sequential extraction schemes cited in literature, only two schemes are applied frequently, namely the Tessier's SEP given by Tessier et al. (1979) and the BCR SEP, originally proposed by the Community Bureau of Reference (BCR) (Ure et al., 1993) now the Standards, measurements and testing Programme, (formerly BCR) of the European Community (Quevauviller, 1998). The extractants convert the metal bound in the solid phase into a soluble form. The proportion of the each element extracted in individual fraction is based on the chemical reagents applied, the chemical and physical operating parameters such as pH, time of contact, reagent type, concentration, particle size, temperature, stirring system etc. (Smichowski et al., 2005). Many of the sequential extraction methods are actually the variants of the Tessier's procedure (Tessier et al., 1979), in which the exchangeable metals and those associated with carbonate, Fe-Mn oxides, organic material, and silicate residues fraction are extracted with diverse reagents (Quevauviller, 2002). The reagents given by BCR for sequential extraction scheme are appropriate for quantification using ICP-MS and ICP-AES. Particular recommendations for metal determination in extracts by usually used techniques such as ICP-OES and ETAAS have been given (Rauret et al., 2000).

On the basis of the Tessier's procedure, the Community Bureau of Reference of the Commission of the European Union proposed the definition of an extraction protocol (the BCR protocol) and a purely operational definition of sequential fractionation. The scheme of the European Community Bureau of Reference, generally known as the BCR method (Ure et al., 1992), look for reducing the errors in the treatment and analysis of environmental samples. This method is considered to be more operationally effective than others anticipated formerly, for example that of Tessier (Tessier et al., 1979).

Modification in SEPs

The observations from the literature conclude that large diversity of SEPs has been applied for the chemical partitioning of metals from various solid matrices (Table 2.3). The major differences in SEP's are in the utilization of reagents, operating conditions and number of steps involved. A little variation in the experimental conditions (e.g. pH, temperature, contact time, solid to reagent volume ratio, particle size, speed etc.) can create huge changes in the fractionation pattern, which makes it complicated for comparisons among results of two different schemes.

Numerous modifications to the Tessier's scheme have been suggested by several authors to improve the selectivity of the extracting agents towards definite geochemical processes of the soils and sediment samples. To meet specific needs and to resolve the problems of Tessier's procedure, modifications or amendments have been designed (Forstner and Salomons, 1980; Meguellati et al., 1983; Schultz et al., 1998).

The main improvement is a change in the sequence in which hydroxylamine and hydrogen peroxide extractions were used (Forstner and Salomons, 1980; Han and Banin, 1995). Common Problems for example the poor reducing power of hydroxylamine hydrochloride (Schramel et al., 2000), and the less oxidizing power of hydrogen peroxide (Hall et al., 1996), its capability to change metal re-adsorption (Schramel et al., 2000; Chomchoei et al., 2002) lead to the foundation of a new sequential extraction scheme by Hall et al., (1996). The scheme given by Hall et al. (1996) replaces the H₂O₂ used in Tessier and BCR schemes to extract heavy metals associated with "organic matter" with potassium chlorate is considered a stronger oxidizing reagent to extract heavy metals associated to "sulfides and organics".

In BCR scheme, a further modification has been established named as modified- BCR scheme based on the systematic study of uncertainty sources (Sahuquillo, 1999). This scheme has been customized in the second step by increasing the concentration of hydroxylamine hydrochloride from 0.1 to 0.5 M, the pH of hydroxylamine hydrochloride was adjusted to pH 1.5 by mixing a fixed volume of HNO₃ and by increasing the speed of centrifugation from 1500 to 3000g (Sahuquillo, 1999). Sahuquillo et al. (1999) observed that pH was of important factor for the extractability of metals in the second step of the BCR sequential extraction method. Cd and Zn are less susceptible to pH-changes; the extractability of Pb, Cu and Cr reduced when the pH of the extract increases. The original BCR procedure has been modified because of irreproducibility mainly in reducible fraction (NH₂OH.HCl) (Sahuquillo et al., 1999; Rauret et al., 1999). Although, an improved precision was introduced when the BCR SES (now SM&T SES), method attempts have been made to reduce the effects of the readsorption and solid-to-solution ratio (Filgueiras et al., 2002).

Several authors have compared the performance of various extraction methods for heavy metals or partially modified existing methods: Kheboian and Bauer (1987), Rauret et al. (1989), Lopez-Sanchez et al. (1993), Fiedler et al. (1994), Mester et al. (1998). A significant difference between the Tessier and BCR schemes occurs in the

first step. Theoretically, the metal contents released in the acid soluble step of the BCR scheme ought to correspond to the sum of metal contents released in the exchangeable and acid soluble fractions of the Tessier's scheme. However, both schemes use the similar extractants for the reducible and oxidisable fractions, but applied experimental conditions are different, therefore, the released metal contents also get changed. It has been established that the reducing agent applied in the Tessier SEP shows higher extraction ability than that of the BCR SEP. As a result fractionation patterns with both schemes differ considerably. Given that extraction of metals are higher in the reducible fraction of the Tessier SES, but they are released in a larger amount in the oxidizable fraction of the BCR SEP (Filgueiras et al., 2002). Different type of conclusions can be drawn when comparing the Tessier's and BCR scheme. It is difficult to carry out a direct comparison between the different methods, since different extractants with different concentrations are used in each method (Table 2.3) (Maiz et al., 1997).

BCR method separates the heavy metals into four fractions: exchangeable and carbonate bound, Fe and Mn oxides bound, organic matter bound, and residual metal fraction. Tessier's scheme extracts the labile elements or metals in to five fractions i.e. exchangeable, carbonates (acid-soluble), iron and manganese oxides (reducible), organic matter (oxidizable) and residual fraction. Operating sequence and conditions for Tessier's and Modified-BCR schemes are described in Fig.2.1 and Fig. 2.2.

Different nominal fractions and reagents used in various SEPs are discussed in the following part:

Exchangeable Fraction

Exchangeable fraction involves water soluble and weakly adsorbed metals, which can be released by ion-exchange process. For this fraction solutions of replaceable cations such as CaCl_2 , MgCl_2 , NaNO_3 , $\text{Ca}(\text{NO}_3)_2$, BaCl_2 , KNO_3 , NH_4OAc , $\text{Sr}(\text{NO}_3)_2$, NH_4NO_3 are usually employed to extract metal fraction bound through weak electrostatic forces to the negative sites on the solid matrix (Stone and Droppo, 1996; Narwal et al., 1999; Ahnstrom and Parker, 1999). Metals equivalent to this fraction typically represent a small content (less than 2%) of the total metal concentration in soil system (Emmerson et al., 2000).

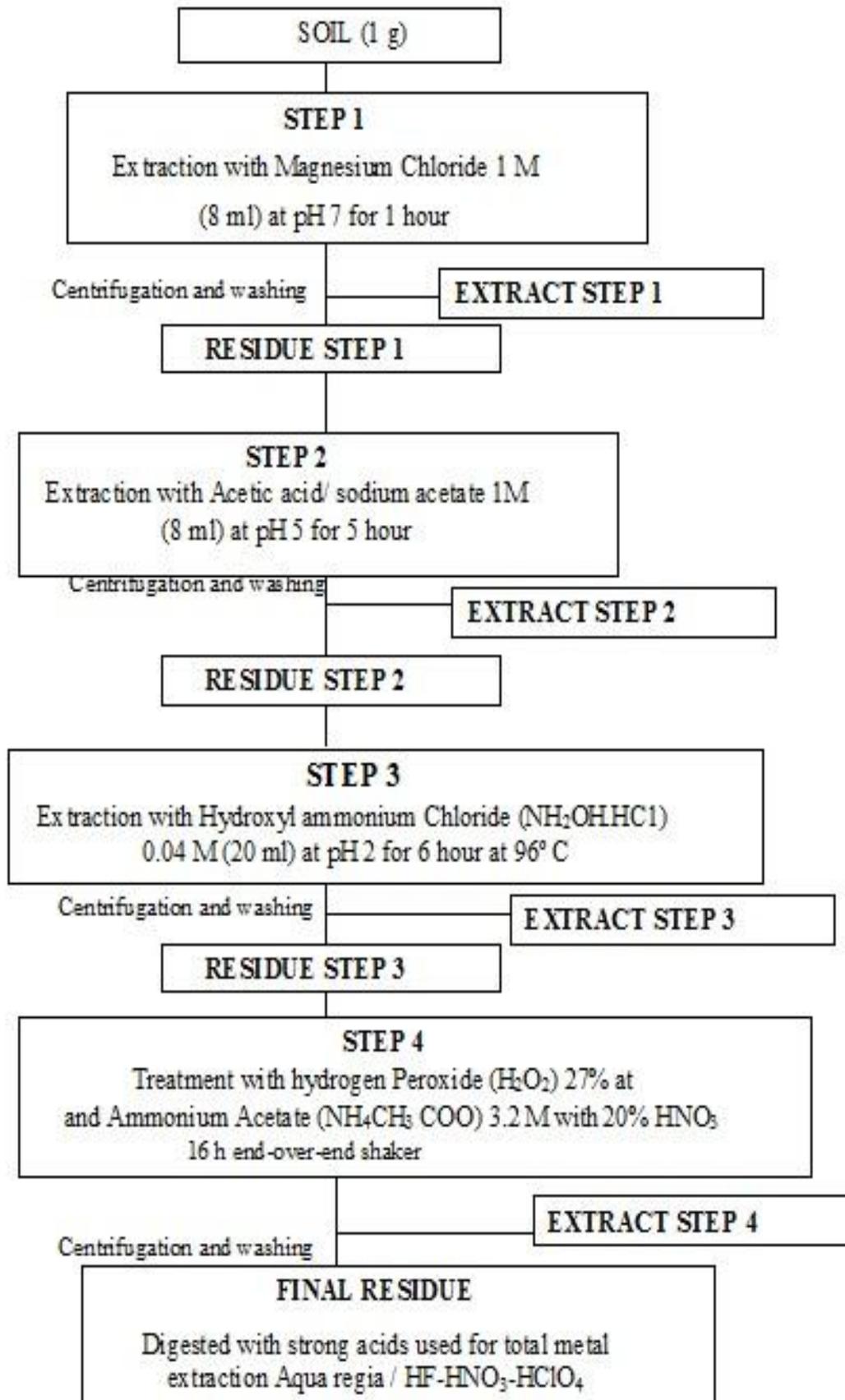


Fig. 2.1: Flow diagram of Tessier's sequential extraction scheme

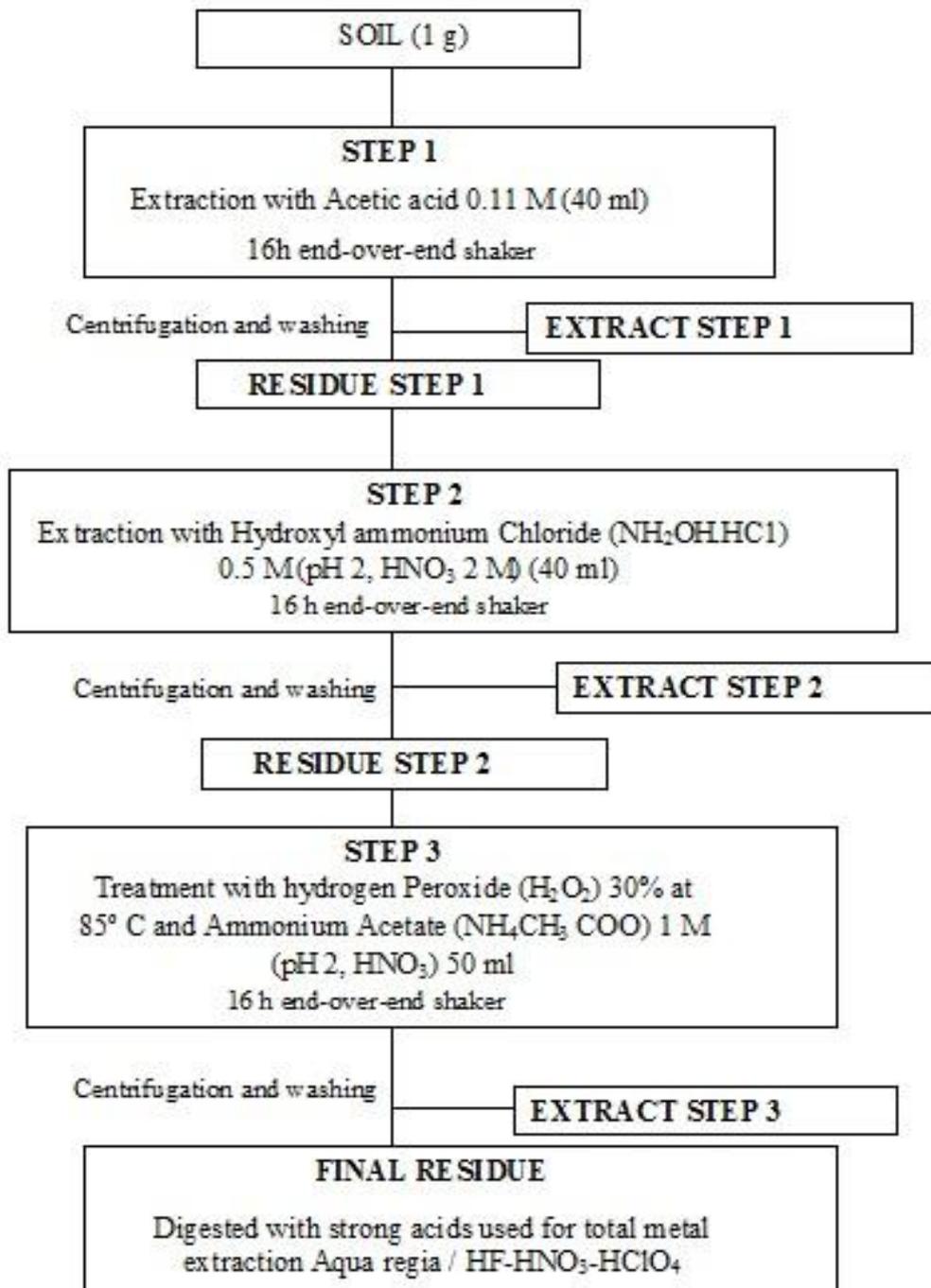


Fig. 2.2: Flow diagram of modified-BCR sequential extractions scheme

Acid soluble fraction

Acid soluble phase is the second fraction that includes the metals which are precipitated with carbonate (Clevenger, 1990). The carbonate is a loosely bound phase that is easily released by use of weak acids or reagents like acetic acid (HOAc) or sodium acetate-acetic acid (NaOAc) with or without buffering pH 5 (Gibson and Farmer, 1986; Lee

and Kittrick, 1984). NaOAc–HOAc reagent is able of dissolving carbonates without considerable attack on organic matter, Fe and Mn oxides and aluminosilicates. For extraction of more than 99.9% of the metal content related with carbonate in sediments, 5 h time is sufficient (Tessier et al., 1979). The acid soluble fraction usually contains a comparatively small percentage of the total concentration of the majority of metals (Emmerson et al., 2000).

Fraction Bound to oxides of Fe and Mn

The Fe-Mn oxides bound fraction may be separated into three parts i.e. easily reducible (Mn oxides fraction); moderately reducible (amorphous Fe oxides fraction); and poorly-reducible (crystalline Fe oxides fraction) (Miller et al., 1986; Krishnamurti et al., 1995). Hydrous oxides of Fe/Mn are extracted collectively, identified as ‘sinks’ in the surface environment for metals (Stone and Droppo, 1996). The most successful reagents for determining total metal ion contained with these minerals are reducing agents having capability to attack the various crystalline forms of Fe and Mn oxyhydroxides (Pickering, 1986). Hydroxylamine, oxalic acids and dithionite are mainly popular reagents used in this fraction.

Hydroxylamine

Hydroxylamine is a specific reducing reagent, whose capability to dissolve the dissimilar metallic oxides virtually depends on different conditions like extracting time, concentration, pH, and temperature. A 0.1 mol/l hydroxylamine solution prepared in 0.01 M nitric acid (pH 2) can dissolve Mn oxides, while minimizing Fe extraction (Chao, 1972). Immediate extraction of Mn-Fe oxides can be attained by using a 0.02 M or 0.04 M hydroxylamine solution prepared in 25% v/v acetic acid, at high temperature (Gleyzes, 2002). Hydroxylamine hydrochloride (NH₂OH.HCl) at pH 2 in nitric acid medium is commonly used reagent for extracting the easily reducible fraction. When the pH of the extractant solution is reduced below 1.5, the reagent may moderately release the metal associated with the silicate fraction (Tessier et al., 1979).

Oxalate/oxalic acid buffered solution

Oxalic acid is specific for amorphous iron fraction with a low degree of crystallinity. The solubility of Fe-oxides in oxalate solutions is based on the nature and the concentration of surface hydroxyl groups. Since oxalate process is light sensitive, the UV catalytic effect was applied to increase the attack on crystallised Fe-oxides.

Following the earlier leaching of Mn oxides an attack by 0.2 M oxalate reagent at ambient temperature, in the dark is used. Although, thermodynamically feasible, the reductive dissolution of Fe (III) hydroxides by oxalic acid does not take place quickly in the dark. The buffering effect is more at constant pH 2 - 3 (Gleyzes, 2002). When the pH of the oxalate solution is more than 4.2, pH is no longer buffered during the extraction process, and thus the extracted Fe-oxide decreased (McKeague et al., 1967).

Sodium dithionite ($Na_2S_2O_4$)

Sodium dithionite is a strong reducing agent that can dissolve Fe oxides in the pH range 7–8. Mehra and Jackson (1960) proposed that to avoid FeS precipitation, it is required to use a strong ligand, and the solution is buffered to stabilize the pH throughout the entire extraction process. Shuman (1982) suggested that considerable precipitation of elements due to the formation of sulphides or sulphates leads to underestimation of the amount associated with oxides. Regardless of these criticisms, sodium dithionite reagent remains useful for the assessment of the reactive Fe fraction in soil system and numerous authors still applied it for fractionation studies (Jeanroy, 1984; Kostka et al., 1994, Sirvent et al., 1997).

Oxidizable fraction

In the fourth fraction the metals bound to organic matter and sulfides can be easily liberated under oxidizing conditions (Marin et al., 1997). The oxidizing conditions can destroy the organic minerals and reducing sulfur compounds and thus trace metals associated with them can be leached into the environmental system. Thus, the oxidizing reagents like H_2O_2 and NaClO are commonly used to extract the metals bound with organic matter. The oxidation process is improved by heating the solution for several hours (Pickering, 1986). In this step, for absolute dissolution of organic matter and least changes of silicates, the hydrogen peroxide is heated (e.g. 85°C) for several hours (Tessier et al., 1979). In oxidizable step to prevent readsorption of released metals during the extraction, a soft complexing reagent, such as NH_4OAc in nitric acid is used (Tessier et al., 1979).

Fe-Mn oxide bound and oxidizable fractions are considered the two most important sinks for heavy metals present in environmental samples (Ramos et al., 1994; Baruah et al., 1996; Gleyzes et al., 2002; Wong et al., 2002). Metals in oxidizable fraction are more stable and thus will not take part in the geochemical cycle easily. To extract

metals associated with Mn/ Fe oxides and organic matter, residual and oxidizable fraction, hydroxylamine hydrochloride, and hydrogen peroxide reagents are the mostly used in different sequential methods; because of their reducing and oxidizing properties (Tessier et al., 1979; Quevauviller et al., 1993).

Hydrogen peroxide

In order to avoid heavy metals scavenging by the formation of Fe hydroxides at higher pH values hydrogen peroxide is used with dilute nitric acid solutions. Since, H₂O₂ oxidation is mostly used, but it does not completely destroy organic matter, and sulphides are moderately dissolved (Tessier et al., 1979) therefore, this step cannot be regarded as specific for metals bound to organic matter.

Sodium hypochlorite

The application of NaClO as an oxidising reagent in alkaline conditions leads to improved destruction of organic matter, least effect on amorphous constituents and clay minerals. The extraction usually takes place at pH 8.5 with a 0.7 M NaClO, at high temperature (Glavez, 2002). It can also oxidize some Mn oxides to MnO₄ ions (Pickering, 1986).

Residual fractions

In this step destruction of primary and secondary minerals containing trace metals takes place by digestion with strong acids, such as HF, HClO₄, HCl, HNO₃ etc. are used in different combinations.

2.8 Criticisms of selective extraction procedures

Even though SEPs have been used commonly, they have many criticisms i.e. re-adsorption and redistribution, poor metal recovery, lack of selectivity of reagents, incomplete dissolution of the targeted solid phase (Martin et al., 1987; Shan and Chen, 1993; Raksatayal et al., 1996) etc.

2.8.1 Readsorption

The main problem of readsorption and the consequent metal redistribution between different phases occurs in SEP's. By using a modified Tessier scheme on spiked natural sediments it was observed that As, Cu, and Hg undergo strong readsorption in the most labile fractions by using MgCl₂ and NaOAc/HOAc as extractants (McLaren, 1983).

Shan and Chen (1993) indicated that redistribution in SEP occurred during soil analysis. Cu, Mn, Ni, Pb, V and Zn collected for fractions 1 to 3 were less and for fractions 4 to 5 were higher. This indicates that metals were released in the first three steps, they were reconnecting to the newly available sites of the next fraction. Metals were associated in fourth fraction due to the formation of strong complexes with humic material present in soil. Nature of the metal and soil played a significant role in the redistribution that occurred due to various binding sites available and different binding strengths. Also, the incomplete dissolution of metals and variation in pH can promote to redistribution and readsorption of metals. Martin et al., (1987) has reviewed the various problems associated with different extraction methods.

2.8.2 The lack of specificity of reagents

The requirement of specific reagents has been observed in several experimental researches in solid matrices. Gomez-Ariza et al. (2000) criticized the classification pattern. The author observed that selection of reagent was only appropriate for metal-co precipitated phase but not for metal sorbed fraction. Another alternative is to use a single extraction scheme. Finally, carbonate species have different solubilities depending on various metals, thus dissolution of metals is sometimes incomplete during this step. This will be extracted in next step by using hydroxylamine, thus excess estimation of metals in reducing step take place. Tessier et al. (1982) suggested that metals released with NaOAc/HOAc- buffered solution would be particularly adsorbed on surfaces, specifically on Fe oxides.

2.8.3 Sample Pretreatment

Sample pretreatment should not alter the original metal distribution pattern. The most important concern in the application of SEPs is that the sample should be preserved by a drying method. Despite this fact soil sample handling, homogenization and representative sub-sampling, has also been suggested. To get the appropriate particle size distribution, sieving of soil sample is necessary. After drying, sieving should be done with nylon sieves to avoid metal contamination.

One of the main drawbacks to SEP's is time consuming, laborious and cost. Also, not all the available forms are equally essential from the environmental risk point of view (Maiz et al., 1997). Numerous critical reviews on SEPs have been published (Kersten

and Forstner, 1995; Ure, 1996; Kennedy et al., 1997; Clark et al., 2000; Gleyzes et al., 2002; Filgueiras et al., 2002).

2.9 Applications of sequential extraction procedures

Despite several limitations, sequential extraction procedures for heavy metal fractionation have been applied to soils, sediments, coal ash and other matrices. Some of the studies applying SEPs are detailed in Table 2.5.

Metal mobility in the soil is affected by the soil pH (McBride et al., 1997). Thus, the solubility and mobility of metals is higher at pH <7 and this may enhance the solubilization of trace metals from the carbonate form. Hence, exchangeable + carbonate forms possibly indicate the most essential fraction available to plants. Trace metal bioavailability decreases in the order: water soluble fraction > exchangeable fraction > carbonate fraction > Fe-Mn oxide fraction > organic fraction > residual fraction. This decreasing order is just an overview and indicates only qualitative information about metal bioavailability. Additionally, by above information it can be inferred that metals in the non-residual fractions are more bioavailable than metals bound with the residual fraction. The non-residual fraction is the sum of all other fractions except the residual fraction (Mahur et al., 2008).

Two different sequential extraction procedures were applied by Maiz et al. (2000) to assess Pb availability from polluted soils affected by several anthropogenic sources. It was observed that the mobilizable and mobile phases accounted for 14% of total Pb. However, 15% of the total Pb was associated with exchangeable and carbonate phases. 17% of total Pb was bound with Fe-Mn oxides and 4% with OM/sulfides phases.

A three-stage Cd-extraction scheme by using contaminated sediment samples was evaluated by Carapeto and Purchase (2000). It was observed that the largest proportion (54-65%) of Cd occurred in the residual fraction, followed by the organic phase (26-37%) and the least amount of Cd (6-18%) with exchangeable fraction. The Cu concentrations in a surface soil were greatest in the amorphous and crystalline fraction studied by Ippolito et al. (2009). Mn/Fe oxyhydroxide-bound fraction contained total Cu (51-53%) while; lesser amounts of Cu were present in the organically complexed and residual inorganic phases. Whereas, Ho and Evans (2000) observed that high concentration of Cu was associated with residual fractions (47%), and only 8% was bound with organic carbon fraction in alkaline soils.

The mobility of toxic metals from coal fired TPP fly ashes showing a broad compositional range has been analyzed by sequential extraction schemes in order to evaluate their mobility when these wastes are land filled or dumped (Turiel et al., 1994). From the study of Akinyemi et al. (2011) it is clearly inferred that the results from Sequential Extraction Procedures will provide the information about potential mobility and bioavailability of metals in soils which are likely to be contaminated by fly ash disposal and dispersal.

Pandey and Bhattacharya (2016) found higher proportion of Cd, Cu, Mn, Ni and Zn, in the mobile fraction, posing greater risk than the other metals. It was also observed that metals viz. Cr, Pb, Zn, Cu, and Cd are more extracted in residual fraction.

Filgueiras et al. (2002) discussed the applications of sequential extraction procedures in identifying the binding sites of metals for evaluating metal pollution, accumulation, metal mobility, bioavailability and characterization of pollution sources and transport mechanisms of metals. Metal toxicity depends on chemical associations in solid matrices. Application of SEP's at different thermal power plant is given in Table 2.4.

Table 2.4: Application of SEP's at thermal power plant

Location/Area	Matrix	Observations	Reference
Mpumalanga province, South Africa	Dry disposed fly ash	Chemical extractants used proved to be effective for extraction of inorganic metals bound with various physicochemical forms in weathered fly ash. There is little variability between sum of values obtained for five-fractions of analytes and total metal content in the original ash which, suggests that there is small or no sample loss, and the mass balance calculations for the extraction scheme are good and within acceptable limits.	Akinyemi et al., 2011
Fortum Power and Heat Oy Inkoo power plant, Southern Finland	Bottom ash	A five-stage sequential extraction procedure was used to determine the partitioning of 16 metals (Cd, Cr, Cu, Mo, Pb, Zn, As, Co, V, Ni, Ba, Al, Be, Fe, Mn, and Ti), sulfur (S), and phosphorus (P) in bottom ash from a coal-fired power plant. The highest concentrations of the metals found in the residual fraction.	Dahl et al., 2008
Jingangshan thermal power station, Jiangxi province, China	Coal Combustion residue, Flyash from ash field	Used modified BCR sequential extraction procedure. Portions of Zn, Ni and Cr are released, and As and Mn are released continuously after coal ash being transported to the dumping site. Cu, Pb, Cd and Fe do not cause any environmental threat due to element leaching during and after the coal ash suspension and transport.	Xu and Li, 2009
China	Chinese coals Qingshan ashes	Trace element enrichment in the submicron particles in ashes. sequential extraction show low mobility of Cd, Co, Cu and Ni.	Yan et al., 1999
Huaibei Coalfield, China	Coals of different ranks	Chinese coal rich in Selenium. Forms of Selenium determined by Sequential solvent extraction.	Zhang et al., 2007

Table 2.5 Applications of sequential extraction schemes to metal partitioning in different environmental matrices

Matrix	Scheme	Analytical technique	Metal Analyzed	Remarks/Findings	Reference
Chinese Soils	4 step BCR	ICP-AES, XRD	Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn	Partitioning of heavy metals in different soil, particle size fractions was directly related to the soil particle compositions, for example OM, Fe/Al oxides and clay minerals. High concentration of OM and Fe/Al oxides stabilizes anthropogenic HM in fine soil particles.	Liu et al., 2018
Agricultural soils of Pearl River Delta, China	Tessier	ICP-OES, ICP-MS	Co, Cu, Fe, Mn, Pb, Zn, isotopic Pb.	The fractionation pattern indicated that Zn was predominantly found in residual fraction while Pb was associated with residual and reducible fraction. Significant amount of Cu was bound in oxidizable fraction.	Wong et al., 2002
Agricultural soil	5 fractions	FAAS	Cd, Co, Cr, Cu, Pb, Ni, Zn	Cd, Cu and Pb showed highest value of extracted metal and Cr showed lowest value. All metals exhibited in residual fraction	Ahumada et al., 1999
Agricultural soil	3 step	-	Fe, Mn, Cu, Zn	Moderately extracted Reducible Fe-Mn oxide fraction increased the subsequent oxidizable metal fractions.	Luo and Christie et al., 1998
Soil	BCR, Tessier	ICP-OES	Ca, Fe, Mn, Cu, Zn	The results showed significant correlation between the metals extracted in the 3-steps of the BCR and that extracted in the corresponding steps of the Tessier's scheme.	Zhang et al, 1998

Soil	Sequential Extraction Procedures	FAAS	Pb	Pb is mainly associated with residual and reducible fraction. An extractive cleaning solution i.e. EDTA was used to remove Pb from soil samples.	Barona and Romero et al., 1996
Polluted and unpolluted soil	4 Fractions	FAAS, ETAAS	Cd, Cr, Cu, Pb, Ni, and Zn	Three investigations were described: sequential extraction scheme, extractability using chelating agents, geographic delineation using EDTA extraction.	McGrath, 1996
Bottom ash, fly ash and gypsum from coal-fired power plant, China	Five-Step Modified BCR Extraction Procedure	ICP-AES	Hg, As, Cr, Cd and Pb	In fly ash, 60 to 90% of the trace elements exist in the residual fraction. Pb, Cr and As are enriched in fly ash. Residual fraction is most effective fraction for Hg, As and Pb in fly ash and Cr and Cd in both fly ash and gypsum. Cd is evenly distributed in bottom ash, fly ash, and gypsum samples.	Zhang et al., 2017
Bottom ash and fly ash	Three-Step BCR Sequential Extraction Scheme	ICP-OES	P, Ca, Na, K, Mg, Zn and Cu	Low risk is caused by Ba, Cr and Mn in the bottom ash and Co, Cr, Mn, Ni, V and Cu in the fly ash. High risk metals were Cd in the bottom ash as well as As, Cd and Se in the fly ash. Medium risk metals were Co, Mo, Ni, V, Zn, and Cu in the bottom ash and Mo and Zn in the fly ash.	Poykio et al., 2016
Solid waste incineration fly ash, Swedish	A modified four-step Sequential Extraction Procedure	X-ray Fluorescence	Zn, Cu, Pb, Sb, Cr, As, Cd.	Speciation shows that mobility of Cd, Zn, Pb is strongly associated to exchangeable phase. Total content of trace elements in fly ashes decreased in the order Zn > Cu > Pb > Sb > Cr > As > Cd. Cd, Zn, Cu and Sb presented major risk in the fly ash.	Saqib and Backstrom, 2016

Fly ash from Patratu TPP Jharkhand India	Modified Tessier Sequential Extraction Scheme	SEM-EDX , Back scattered electron imaging (BSE), ICP-OES.	Cd ,Cr, Cu, Fe, Mn, Ni , and Pb	Ni, Cd, Mn, Cu, Zn were more in the soluble and exchangeable fraction in flyash therefore, these metals can be easily leached. Cr, Fe, and Pb were potentially less bio-available. Cd and Zn had low ecological risk.	Pandey and Bhattacharya, 2016
Coal ash Kostolac Power Plant, Republic of Serbia	Single-Extraction and Modified BCR Sequential Extraction Procedures	ICP-AES	Al, As, Be, Cd, Co, Cr, Cu, Fe, Mn, Ni and Pb	All the metals were mobile in second and third fraction, indicating that these elements become mobilized at pH less than 5. Cd, Cr, Co and Ni were found dominating in third or fifth fraction. Cu was found dominating in fourth and fifth fraction. Pb was dominating in organic bound fraction.	Tasic et al., 2016
Coal cotton ash from Nigeria	Three Step Sequential Extraction Procedure	FAAS	Cr, Fe, Cu, Ni, Pb, Cd and Zn	High conc. of Pb was found in the exchangeable fraction. High concentration of Cu and Zn were found in the residual fraction. Chromium occurred mostly in reducible fraction while Fe occurred mostly as bound to carbonate fraction. Cadmium was found low in all the fractions analyzed.	Okorie et al., 2014

Feed coals, fly ash and bottom ash from coal-fired power plants, China	Leaching behaviors of elements determined	ICP-AES, ICP-MS, AFS, XRD	As, B, Ti, Mn, Ni, Cd, Co, Cr, Cu, Pb, Sn, V, Zn.	The diameter of ash particle was inversely proportional to the enrichment factor of the trace elements. The smaller the fly ash particle size, the higher the enrichment of elements. Most of the trace elements were concentrated in the fly ash, only Fe and Mn were enriched in the bottom ash.	Tang et al., 2013
Fly ash from power plants, Maharashtra.	Single Step Extraction Procedure	ICP-AES.	As, Ca, Fe, Mg, Na, Si, Cr, Mn, Ni, Cu, Zn, Cd, Se, and Pb.	Most of the metals exhibit more than 90% of their peak leaching concentrations at 4 hours, except Si, Na, Ni, Mn, Cr in water soluble fractions. All major metals exhibit more than 90% of their maximum leaching concentrations at 24 hours in acid soluble fractions, the optimum leaching for the reducible solids step can be fixed as 24 hours.	Lokeshappa and Dikshit, 2012
Fly ash of power plants in West Bengal, India,	Sequential Batch Extraction and Long-Term Leaching Tests	AAS	As, Zn, Ca, Cr, Cu, Fe, Pb, K, Mn and Na.	The leaching pattern depends on the pH as well as the solid-liquid ratio. A much higher mobility of the elements have been observed at low pH.	Dutta et al., 2009

Fly ash of electrostatic filter of a city waste incinerator	Modified Tessier Six-Step Sequential Extraction	ICP-AES, ICP-MS, SEM/EDX	Al, Ca, Fe, K, Mg, Na, and S in	Cr and Ni were bound to silicate /residual fraction. Copper and lead were bound with carbonate fraction. Mn was bound to the organic metal complex while As was bound to carbonate and organic compounds. HF in used in the digestion to destroy the silicate matrix.	Chang et al., 2009
Incinerator Fly ash	3 step BCR	ICP-MS	As, Se, Sb,Cr	The leaching concentration of each element increased by increasing pH and concentration of the extractants.	Kim et al., 2002
Coal fly ashes	4 step	ICP-OES	Al, Ba, Ca, Cr, Cu, Fe, Mg, Mn, Ni, Sr, V ,Zn and B	The efficiency of the extraction process for each step was examined.	Smeda and Zyrnicki, 2002
Tailing waste and Fly ash	Sequential Extraction Procedure	-	Cd, Cu, Pb and Zn	A Sequential Extraction was conducted to determine the chemical fractionation pattern.	Jang and Kim, 2000
Fly ash	Sequential Extraction Procedure	ICP-MS	Al, Ca, Cd, Cu, Pb and Zn	Investigated about leaching conditions were necessary to obtain good extraction results of heavy metals.	Van Herck et al., 2000
City waste incinerator Fly ash, Milan	3 step BCR	XRF-spectrometry AAS	As,Cd, Cr, Cu, Pb, Ni, and Zn	Metal behavior and mobility is related to the material origin than to the total content in the matrix.	Brunori et al., 1999

Coal fly ash (NBS 1633a), soil (NIST 2709), river sediment (CRM 320)	Three-Step Sequential Extraction Procedure	GFAAS, ETAAS	Cadmium	Recommended some modifications in the extraction method. Cd in coal fly ash samples found least in reducible and oxidizable step. Considerable amount of Cd is associated in the residual fraction for the studied samples. The recoveries of total Cd with the sequential extraction procedure are higher than 85% for the studied samples.	Petit and Rucandio, 1999
Fly ash	6 step	ICP-AES	Heavy metal	The use of thermal treatment enables the inertization of heavy metal in residues of waste against leaching	Wunsch, et al., 1996
Fly ash of TPP, Austria & Municipal Waste Incinerator, Hungary	Five-Stage Sequential Leaching Procedure	AAS, XRD	Cd, Cr, Cu, Pb, Zn, and V	Chromium was mostly distributed between the residual and sulfide fractions. High amount of Cu, and Pb was found in the exchangeable fraction. More than 50% of Cd and Zn were present in the residual fraction in coal fly ash.	Bodog et al., 1996
Flyash of coal-fired power plants, Brazil	Sequential Extraction Procedure	Modular Polarographic Analyzer	Cd, Co, Cu, Ni, Pb, Sb, and Zn	Ni, Pb, and Zn are mainly associated with the surface oxide-bound and Fe-oxide-bound fractions. Nickel, Pb, and Sb have low mobility in water-extractable fraction while Cd is associated easily with water-extractable element.	Fernfinez-Turiel et al., 1994

2.10 Metal analysis in vegetation

The plants which are adapted to survive on heavy metal-rich soils (“heavy metal soils”) are called as metallophytes. On the basis of the level of tolerance of plants to metals, plants may be separated into the three categories: hypo tolerant plants, basal tolerant plants, and hyper tolerant plants (Ernst et al., 2008). A hyper accumulator can be defined as the threshold rate which is about a 10 times higher concentration of a metal in the above ground parts as compared to the concentration in a non hyper accumulator growing on the same polluted soil (Bert et al., 2002). A few plant species are clear hyper accumulators for Cu, Zn, or Cd. Zn hyper accumulator is defined as a plant that contains $>10,000 \text{ mg g}^{-1}$ dry weight, and a Cd hyper accumulator may have $>100 \text{ mg g}^{-1}$ dry weight (Baker 1981; Bert et al., 2002). Though, every plant species has a particular threshold value for each heavy metal, above this threshold value the metals become toxic to plant growth (Ernst, 1982). All heavy metals (except iron) higher than a concentration of 0.1% in the soil become toxic to plants and consequently change the structure of plants in a polluted soil system (Ernst, 1974). A high content of Pb was found in Zinc-rich soils (0.1–10.0% Zn), but practically no Cd, while soils with a high copper concentration (0.1–3.2%) have higher concentrations of other metals also for example Zn, Pb, Co, Ni, Cd (Ernst, 1974).

Heavy metal extractability is strongly influenced by soil pH and many acids such as citric acid, tartaric and oxalic acid, which are excreted by roots of plants form soluble complexes with metals (Cheng, 2003). The occurrence of micro-nutrients and available sulfur varied from low to high in coal ashes are appropriate for improving the fertility and development of various crops and plant species (Ram et al., 2006). Additionally, the existence of not only secondary and micro-nutrients in the ashes but also toxic metals to the plants has been observed (Adriano et al., 1980). Toxic metals (Pb, Cd and Cr) on an average show higher levels in plants grown in affected sites with different temporal and spatial variation in comparison to samples in control areas (Ajmal and Khan, 1986).

An interaction is found between P, Zn and Cd in plants. The accumulation and transport of Zn and Cd from roots to above ground parts in plants is increased by increasing the content of phosphorus (P) in the media (Hu et al., 1999). Organic fertilizer application enhances an efficient immobilization of Pb, Cu, Zn and Cd phytoaccessible forms in the soil.

Table 2.6: Metal studies in vegetation around thermal power plant reported in literature

Area of study	Vegetation	Observations	Reference
Farakka, West Bengal, India	Plant <i>Mangifera indica</i>	Bioaccumulation of Fe, Cu, Ni, Zn, Pb, Cd and Cr in <i>Mangifera indica</i> tree leaves grown in the periphery of a coal fired TPP. A higher contamination factor (CF > 6) of the toxic metals was observed in plant leaves grown around the TPP. The ash contamination from TPP might play an active role for metals enrichment in plant leaves.	Sengupta et al., 2011
Sonebhadra district of South- Eastern Uttar Pradesh, India	Vegetation and Soils	In the contaminated site, the mean level of all HMs (Cd, Zn, Cr, Pb, Cu, Ni, Mn and Fe) in soil and different parts (root and shoots) of naturally grown plant species were observed to be significantly ($p < 0.01$) higher than the uncontaminated site. The enrichment factor (EF) of these metals in contaminated soil was found to be in the sequence of Cd (2.33) > Fe (1.88) > Ni (1.58) > Pb (1.42) > Zn (1.31) > Mn (1.27) > Cr (1.11) > Cu (1.10).	Singh et al., 2010
Indraprastha power station, New Delhi, India and Ratcliffe-on-solar power station, UK	PFA, leachates, <i>Eichhornia crassipes</i>	Investigated the uptake of Cd, Cu, Ni and Zn by <i>E. crassipes</i> grown in leachates and slurries prepared from two different PFA samples obtained from Indraprastha Power Station (IPP Stn.) in New Delhi, India and the Ratcliffe-on-Soar Power Station in the UK. The plant has a very high accumulation capability for Cd, Cu, Ni and Zn from both leachates and slurries and the uptake of these metals is stronger in the roots than in the tops of the plant.	Cordes et al., 2000
Matla, Lethabo, and Rooiwal TPP South Africa	Plant <i>Digitaria eriantha</i>	Total metal concentration in the plant (<i>D. eriantha</i>) ranged from 0.005 to 535 $\mu\text{g g}^{-1}$ in Matla, 0.002 to 400 $\mu\text{g g}^{-1}$ in Lethabo, and 0.002 to 4277 $\mu\text{g g}^{-1}$ in Rooiwal. Less than 1 Accumulation factors (A) at all power plants indicate a low transfer of metal from soil to plant (excluder).	Okedeyi et al., 2013

However, continuous composting decreases the heavy metal bioavailable contents for plant. The ash contamination from TPP might play an active role for metals enrichment in plant leaves (Sengupta et al., 2011). The accumulation of Cd was more in roots, which appears to be a mechanism of plants to avoid the phytotoxic effects of this element (Barcelo and Poschenrieder, 1992). Alloway (1995) found index of bioaccumulation ratio is less than 1, opposing to the data observed for non-polluted sites. This may be because of a constrained uptake by roots, because competition by the high concentration of Ca and Zn exist in these calcic soils reduces the available sites on the root surface for Cd adsorption (Jarvis et al., 1976). On the other hand, it could be due to a restricted transfer of cations from roots to shoots. The level of bioaccumulation was moderately low with respect to other references of barley grown in sludged or fertilized soils (Chlopecka, 1993). Plants show natural ability to absorb and accumulate trace metals from soil.

The study of Cordes et al. (2000) revealed that *E. crassipes* plant is capable to decrease the pH, particularly the highly alkaline leachates to near neutral conditions. Accumulation of Cd and Zn by the plant was more from the IPP leachates having lower pH than the Ratcliffe leachates, showing that these metals are highly soluble, and bioavailable in the acidic medium.

Eshagberi (2012) studied that wheat (*Triticum aestivum*) is affected by various concentrations of copper (Cu) and zinc (Zn). Heavy metals reduce dry weight of wheat crop and grain yields, with Cadmium (Cd) having the largest effect and Chromium (Cr) the least effect. Copper is a necessary micronutrient for plant growth while zinc has a structural and catalytic role in many proteins and enzymes take part in energy metabolism. Lead is neither a necessary nor a useful trace element for plant growth (Hall and Williams, 2003). Athar and Ahmad (2001) studied the effect of various metals on wheat (*Triticum aestivum*). The phytotoxic effect of heavy metals was in the following sequence Cd > Cu > Ni > Zn > Pb > Cr. The larger concentration of heavy metals in the soil causes toxicity to the plants. Zn and Cu as the necessary micronutrients for plant were the most abundant in wheat grains (Ramesh et al., 2004; Lin and Wu, 1994; Marschnar, 1995). In summer season, *B. vulgaris*, was found to have the higher Cd concentration than the permissible limits of the Indian standard, whereas Pb and Ni concentrations were higher in both summer and winter seasons. The study also observed that by using wastewater (treated and untreated) for irrigation

practices in the long term has enhanced the contamination of various metals (Cd, Pb, and Ni) in edible portion of vegetables causing possible health risk (Singh et al., 2009).

2.11 Water quality and metal transport

Water pollution may be defined as the contamination of water bodies like rivers, oceans, lakes, canals, and groundwater due to anthropogenic activities, which can be injurious to living organisms and plants that live in these water bodies. Water quality is always influenced by both natural (local climate, geology etc.) as well as anthropogenic factors (irrigation practices, pesticide used etc.) (Ramesh and Elango, 2012). Punjab is one of the most productive agricultural state. In Punjab the agricultural fields are cultivated with widespread irrigation by using ground water and the canal water from Beas and Sutlej rivers. Various manmade and natural activities are polluting the terrestrial as well as aquatic ecosystem with heavy metals and chemicals. Most of the drinking water schemes in the Punjab depend on the ground water and the canal water (Bhalla et al., 2011). The mobility of metals in soils is largely based on the heavy metals' properties as well as the physical and chemical soil characteristics. The association of heavy metals with ground water might present hazards to aquatic life and humans (Levy et al., 1992). The heavy metal pollution index in nearby area of Parli Thermal Power Plant indicated that leaching of metals from fly ash has contaminated both the groundwater and surface water (Nalawade, 2012).

A study was carried by Katnoria et al. (2010) on the impacts of industrial wastewater irrigation on soils of Amritsar, Punjab, India. Results of physicochemical characteristics such as pH, bulk density, nitrates, phosphates and potassium etc. and heavy metal content from two industrial effluent contaminated soils indicated that nickel content of zinc coating industry was found to be maximum followed by zinc, cobalt and chromium. The sample of copper sulphate manufacturing industry has showed the highest amount of copper followed by nickel, cobalt, and zinc while Cr was less than detectable limits in the studied sample.

Observation of Nitrate content in different industrial effluents viz. oil refining 140 mg/ha, paper mil 168 mg/ha, distillery 420 mg/ha and cycle industry is 84 mh/ha have been observed by Gupta et al. (1994). These industries may also affect the nitrate content in water samples. High level of nitrate content in ground water may be because

of variation in composition of sewer water, duration of irrigation and inherent variation of soil (Antil and Narwal, 2005).

Mittal and Arora (2014) observed that contamination due to heavy metals was high in groundwater from Bathinda. Water of almost all study points was hard and contaminated. Overall, groundwater quality was not suitable for drinking purposes. The study observed that the groundwater quality of Bathinda and nearby regions did not agree with the Indian standards (ISO 10500) in most of water samples. So, it should not be used for the drinking (Mittal and Arora, 2014). The groundwater may be used for the irrigation purposes but before that proper study should be conducted to ensure that the groundwater will not harm the soil fertility as well as the crop production.

Examination of water samples taken from the villages of Jind district showed significant variations in the analyzed samples with respect to their chemical composition. Majority of the water samples did not meet the water quality standards for fluoride concentration and many other quality parameters. Majority of the water samples did not follow both Indian and WHO water quality standards. Therefore, the ground water was not appropriate for consumption without any prior treatment (Meenakshi et al., 2004).

To assess the quality and suitability of groundwater for drinking and irrigation purpose groundwater samples were analyzed from 16 villages of district Bhiwani Haryana, (India). The groundwater has been contaminated by a large amount of salts. About 78% of groundwater samples have dominance of salt water. Results indicate that majority of groundwater samples can be considered appropriate for irrigation on the basis of absorption ratio of residual sodium carbonate and sodium (Shalu et al., 2015).

The characteristics of ground water changes from place to place, from season to season and with the depth of water table. The high amount of Ca^{++} , Mg^{++} , TH and NO_3^- and F^- in the groundwater is because of anthropogenic sources and geological characteristics of the aquifer in Warora Tehsil, District Chandrapur, India (Deshapnde et al., 2012).

Nalawade et al. (2012) analyzed underground and surface water samples collected from the surrounding areas of fly ash dumping site of Parli Thermal Power Station (PTPS) of the Maharashtra, India. Metals such as As, Hg, Zn, Cu, Cd and Pb contents were determined in both underground and surface water samples. The heavy metal pollution

index (HPI) indicates that leaching metal from fly ash has contaminated the groundwater as well as surface water.

Sarode et al. (2010) has found the concentrations of Cd, Fe, Mn, Mg, and Zn in groundwater samples in the vicinity of Bhusawal Thermal Power Plant and ash dumping sites were less the permissible range of Indian standards and WHO. The concentrations of Ni and Pb were below the Indian standards but slightly larger than WHO permissible range. The concentration of Cu was slightly higher than Indian Standards but within the WHO permissible limits.

Cd, Cu, Zn, Pb, Cr, Mn, and Ni were analyzed in the samples of irrigation water, soil, and the edible portion of the palak (*Beta vulgaris* L. var All green H1) collected from Varanasi, India. Except Cd all other metals concentration in irrigation water samples were below WHO maximum permissible limits. Also, the average metal concentrations in soil samples were less than the Indian standards, but the maximum value for Cd was observed. Pillani et al. (2000) have reported that heavy metal pollution in ground water affects the agricultural soil's properties and thus influences production of crops.

This chapter is a general description of the heavy metal mobility in soil, coal ash, vegetation and water around TPP throughout the entire research. The literature survey shows that so far, numerous studies have been undertaken into trace element contamination derived from coal fired thermal power plant, in soils, plants, waters, and sediments in various countries but little has been done on international and national level on heavy metal speciation in different types of solid matrices (viz. soils, fly ash and bottom ash) in the vicinity of thermal power plants. There is paucity of published studies relating to the levels and speciation of heavy metals in different types of solid matrices viz. fly ash, bottom ash, contaminated soils and vegetation around coal fired thermal power plants in India.