Introduction
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In the last few decades, the accelerated pace of development, rapid industrialization towards economic stability and ever expanding technological advancement have led to the depletion of natural resources. The consequences of this profound economic and sociological change are apparent in the global environment degradation.

The pollutants present in the environment are divided in two main categories i.e. degradable and non-degradable. Among the non-degradable pollutants, a widespread interest in trace element research in the agricultural, environmental and life sciences has emerged especially over the last half century because of their ecological significance due to their toxicity and accumulative behaviour (Purves, 1985).

Trace elements are ubiquitous in the environment, being present usually in small amounts in rocks, soils, air, water and food (Thornton, 1996). However, some geological parent materials, including black sedimentary sulfide bearing shales (alum shales) and basic igneous rocks, often contain large amounts of trace elements. These elements originate into the environment from a wide spectrum of natural and anthropogenic sources. Natural sources are weathering of mineral deposits, emissions from active volcanoes, sea salt sprays, forest fires etc. The main anthropogenic sources are mining activities, metal processing industries, fossil fuel combustion, incineration of wastes and sludge, application of phosphate fertilizers, leaching from garbage dumps and some incidental sources etc. Of the two modes of input, anthropogenic sources are of greater environmental threat as a result of surface inputs to soil system making the metal accessible for plant/animal uptake. Moreover, metal forms from anthropogenic sources are environmentally unstable, thus more soluble and bioavailable than natural forms. Although, some metals (viz.Cu, Zn, Mn, Fe, Ni, Mo, Co) and metalloids (viz. B, Si, Se) have an essential role as nutrients for plants, animals and man, and they are necessary components of some proteins playing important physiological functions, some if present in sufficient quantities and in certain forms may be toxic. Heavy metals severely affect the growth, morphology and metabolism of microorganisms in bulk soils, through functional disturbance, protein denaturation or destruction of the
integrity of cell membranes (Leita et al., 1995). Metals are cycling at low rates within and between bio-, geo-, atmos-, and hydrospheric systems. It is now recognized that the mining of metalliferous mineral deposits and associated smelting and metal processing activities has led to perturbations in the cycling of metals at local level. Even though mining and smelting are not the main sources of global metal input into the environment, the environmental contamination with trace elements is considered a serious localized problem related to these activities.

1.1 Mining and smelting activities as source of metal pollution

Man’s first use of metals for the manufacture of simple tools, weapons and ornaments dates back to Bronze Age, and during the period of Roman empire mining of Fe, Au, Ag, Sn, Cu, and Pb was active. Metalliferous mining associated with exploitation of non-ferrous metals has taken place on a massive global scale for several centuries. An increasing volume and range of heavy metals have been exploited with the growth of the world industry. In particular lead, zinc and copper have been mined extensively. Pb and Zn occur principally as sulphide minerals. Galena (PbS) and zinc blend (sphalerite-ZnS) usually occur together and have been mined in many regions. Cadmium is obtained as by-product of the smelting of ZnS, in which it has substituted for some of Zn and no ores are used primarily as source of Cd (Alloway, 1990). Cd is closely related with Zn in its geochemistry; both elements have similar ionic structures and electronegativities. Although, mines are classified on the basis of their predominant product, they may produce large quantities of other elements as co-products. As a result metal ore processing usually leads to the multi-elemental contamination of the environment. Although heavy metal mining can bring much economic prosperity, the legacy of acid drainage from wastes, mercury pollution from amalgam of precious metals, other heavy metal pollution from residual minerals in mill tailings, and, in some instances, cyanide toxicities from early gold leaching operations are ancillary to various mining and smelting activities. Metal mining, smelting and processing throughout the world have contaminated soils with heavy metals in excess of natural soil background concentrations. These processes introduce metal contaminants into the environment through gaseous and particulate emissions, waste liquids and solid wastes (Dudka and Adriano, 1997). Mining and
milling/beneficiation processes (crushing, grinding, washing etc.) generate four major categories of waste, i.e.

- mine waste (low grade ore, overburden, barren rocks),
- tailings,
- dump heap leach and
- acid mine water,

Which are disposed of in surrounding land and water in more or less environmentally acceptable manner? Mine tailings- a major solid waste, are produced from ore beneficiation. Dump leaching, heap leaching and in situ leaching are the processes used to extract metals from low-grade ore. The mine water is the water that infiltrates a mine and must be removed to facilitate the mining. Metal smelting and refining processes produce gaseous (CO₂, SO₂, NOₓ etc.) and particulate matter emissions, wastewaters and solid wastes (slag). The emissions of SO₂ from smelters contribute to soil acidity.

Commonly referred to acid rock drainage (ARD) or acid mine drainage (AMD), acid drainage from mine waste rock, tailings, spent ore from heap leach operations, overburden materials, sub-grade ore piles and mine structures such as pits and underground workings is dependent on many factors and site specific. Fergusson and Erickson (1988) identified primary, secondary and tertiary factors that control acid drainage. Primary factors of acid generation include sulfide minerals, water, oxygen, ferric iron, bacteria to catalyze the oxidation reaction and generated heat. Secondary factors act to control the products of oxidation reaction, such as reactions with other minerals that consume acid. Secondary factors may either neutralize acid or react with other minerals. Calcite and dolomite are the most common neutralizing minerals. Tertiary factors refer to the physical aspects of the waste management unit (e.g. pit walls, waste rock piles, or tailing impoundments), physical characteristic of the material (particle size, permeability, physical weathering characteristics etc.).

Pyrite (FeS₂), Marcasite (FeS₂), Chalcopryte (CuFeS₂), Chalcosite (Cu₂S), Sphalerite (ZnS), Galena (PbS), Millerite (NiS), Arsenopyrite (FeAsS), Cinnabar (HgS) are some of the sulfide minerals commonly mined for metal extractions. Prior to mining, oxidation of these minerals and the formation of sulfuric acid is a function of natural weathering processes. The oxidation of undisturbed ore bodies followed by release of acid and mobilization of metals is slow. Extraction and
beneficiation operation associated with mining activity increase the rate of oxidation by exposing large volumes of sulfide rock material with increased surface area to air and water. Low pH and high heavy metals concentrations characterize mining influenced waters. Precipitaion of Fe and Al hydroxides ("yellow boy") are common in watersheds. AMD is a serious environmental problem around the world (Dudka and Adriano, 1997; van Green et al., 1999). Pyrite bearing mine tailings disposed of at neutral or slightly alkaline conditions can weather and continue to leach metals through acid mine drainage (AMD) for decades or even centuries after the mining activity has ceased, ultimately contaminating the surface and subsurface environment, not only in the adjacent areas, but often over much more extended areas. At many historical smelting sites, slag wastes often containing high percentages of lead and zinc, have been weathering slowly and thereby releasing metals into the surrounding soil and potentially into groundwater. The chemical and physical properties of the wastes and the prevailing environmental conditions affect the rate of weathering and therefore the rate of metal release.

The reactions of acid and metal sulfides may be illustrated by the oxidation of pyrite.

$$2\text{FeS}_2(s) + 2\text{H}_2\text{O} + 7\text{O}_2 \rightarrow 4\text{H}^+ + 4\text{SO}_4^{2-} + 2\text{Fe}^{2+}$$  \hspace{1cm} (i)

$S_2^{2-}$ is oxidized to form hydrogen ions and sulphate, the dissolution products of sulphuric acid in solution. Soluble $\text{Fe}^{2+}$ is also free to react further. Oxidation of ferrous ion to ferric ions occurs more slowly at lower pH values:

$$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$$  \hspace{1cm} (ii)

At pH levels between 3.5 and 4.5, iron oxidation is catalyzed by a variety of metallogenium, a filamentous bacterium. Below a pH of 3.5 the same reaction is catalyzed by the iron bacterium *Thiobacillus ferrooxidans*. Other bacteria capable of catalyzing the reaction are presented in Table 1. Ferric iron may precipitate as iron hydroxides ($\text{Fe(OH)}_3$), producing acid, or being a catalyst for further oxidation of pyrites:

$$2\text{FeS}_2(s) + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$  \hspace{1cm} (iii)
\[ \text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 3\text{H}^+ \quad (iv) \]

The dissolution of pyrite by ferric iron (Fe\(^{3+}\)), in conjunction with the oxidation of ferrous ion constitutes a cycle of dissolution of pyrite. Fe(OH)\(_3\) precipitates and is identifiable as deposits of amorphous, yellow, orange or red deposits on stream bottoms ("Yellow Boy"). Either way, due to intermediate rate determining reactions and very effective bacterial catalysis, the production of acid mine drainage is a rapid and self-perpetuating process, which continues as long as air, water and pyrite are available (USEPA, 1994). Similar and more or less simultaneous reactions will also release high amounts of metals such as Cu, Co, As, Ni, Mo and Sb to the aquatic environment.

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>pH</th>
<th>Temp. °C</th>
<th>Aerobic</th>
<th>Nutrition</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Thiobacillus thioparus</em></td>
<td>4.5-10</td>
<td>10-37</td>
<td>+</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>T. ferrooxidans</em></td>
<td>0.5-6.0</td>
<td>15-25</td>
<td>+</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>T. thiooxidans</em></td>
<td>0.5-6.0</td>
<td>10-37</td>
<td>+</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>T. neapolitanus</em></td>
<td>3.0-8.5</td>
<td>3-37</td>
<td>+</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>T. denitrificans</em></td>
<td>4.0-9.5</td>
<td>10-37</td>
<td>+/-</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>T. novellas</em></td>
<td>5.0-9.2</td>
<td>25-35</td>
<td>+</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>T. intermedius</em></td>
<td>1.9-7.0</td>
<td>25-35</td>
<td>+</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>T. perometabolis</em></td>
<td>2.8-6.8</td>
<td>25-35</td>
<td>+</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>Sulpholobus acidocaldarius</em></td>
<td>2.0-5.0</td>
<td>55-85</td>
<td>+</td>
<td>Autotrophic</td>
</tr>
<tr>
<td><em>Desulfovibrio desulfuricans</em></td>
<td>5.0-9.0</td>
<td>10-45</td>
<td>-</td>
<td>Heterotrophic</td>
</tr>
</tbody>
</table>

The heavy metal soil contamination from mining and smelting create a wide spectrum of hazards under an equally wide spectrum of contexts. Adverse environmental impacts from contaminated mining sites include risk to human health, phytotoxicity, contamination of water and soil and ecotoxicity. The elemental contamination and acidification destroys physico-chemical properties of the soils, resulting in a permanent reduction in soil fertility. Soils barren of vegetation are particularly susceptible to erosion (Fig.1.1). Briefly, the most serious and usually irreversible effects of mining and smelting activities can be categorized as:
Fig. 1.1 Schematic diagram of the potential environmental impacts of mining / smelting activities (Dudka and Adriano, 1997)
- Changes in hydro-geological systems
- Hydrological transformations of soils and surficial flows
- Contamination of soils and surficial water reservoirs
- Pollution of the atmosphere

1.2 Fate of metal ions in the soil environment

Soils are the heterogeneous systems which serve as the sources and sinks for nutrients and toxic chemicals, and where chemicals are distributed between complex, intimately interacting compartments (biotic, liquid, solid and gaseous phases) (Fig.1.2). Additionally, for centuries, soil has been the repository for heavy metals and can act as the memory of an ecosystem, providing a good picture of its evolution over time, recording the date of environmental impact episodes and accumulating the chemicals employed or produced by human activities, thus modifying its quality and fate. Trace metals can be retained in soils by both sorption and precipitation reactions. However, the fate of metals in the soil environment is element-specific and dependent on both soil properties and environmental factors. Geochemically, an element introduced into soil may interact with the soil minerals and organic phases (Fig. 1.2) and end up in one or more of the following physicochemical forms:

- Free or complexed ions or colloids in soil solution,
- Sorbed to the surfaces of clays, Fe and manganese oxyhydroxides, or organic matter that are easily exchangeable,
- Present in the lattices of secondary minerals such as, phosphates, sulphates or carbonates,
- Occluded in amorphous materials such as Fe and Mn oxyhydroxids Fe sulphides or organic matter; and
- Present in the crystal lattices of primary minerals.

It is essential to identify which physicochemical forms are actually present in soils, as the mobility and bioavailability of these metals in the complex and dynamic soil-plant-water systems changes with time and shifting environmental conditions. Because of soil heterogeneity and inherent variability in chemical, mineralogical, and physical properties of the soil, it is extremely difficult to predict the fate and behavior of trace elements in soils without understanding the factors.
Both soil properties and soil solution composition determine the dynamic equilibrium between metals in solution and soil solid phase. The lower the metal solution concentration and the more sites available for sorption, the more likely that sorption/desorption processes will determine the soil solution concentration (Brummer et al., 1983). However, the distribution of an element between soil solution and solid phases at equilibrium is governed by:

- the density of surface binding sites for each component (e.g. clay mineral, hydrous iron oxides)
- the binding intensity of metal ion to each component
- the abundance of each component
- the chemical characteristics (e.g. pH, ligands and their concentration) of the solution phase and
- the concentration of other ions, major or trace, competing for binding sites.

The soil liquid phase – soil solution – contains the dissolved chemical in free and complex forms as well as chemicals associated with colloidal particulates and is considered the hub around which the other interacting compartments of the soil revolve. The soil solution is of considerable importance in the soil-plant-man pathway for the potentially hazardous trace metals, as most of the metal ions taken up by the plants reach the root in solution. Consequently, the mechanisms affecting the concentration of metals in soil solution, and the chemical forms in which these metals occur are critical for assessing their bioavailability. The principle factor governing soluble and plant available concentration of metals is pH. Metal sorption is always greater under neutral or alkaline conditions. The term sorption includes adsorption, insoluble complex formation and precipitation. Other factors such as the organic matter content, cation exchange capacity and the contents of hydrous (or “free”) oxides of iron and manganese and calcium carbonate are also important in controlling the sorption of metals and hence their soluble concentrations. Metals such as lead and copper are more strongly sorbed by both organic and mineral soil constituents than either cadmium or zinc and are consequently present at lower concentrations in soil solution.

The soil-plant system is the fundamental and constructive unit of the geosphere and biosphere. Therefore, heavy metal pollution of the soil has an
important influence not only on the yield and quality of crops, but also on the quality of atmospheric and aquatic environment, and even on the health of human beings via food chains, as in the classic example of ‘Itai-Itai’ disease in Japan, which was traced to the consumption mostly of rice and soybean grown in an environment heavily polluted with Cd from a nearby mine and smelter.

**Fig. 1.2 Fate of pollutants and nutrients in soil ecosystem (Naidu et al., 2001)**

1.3 Metal speciation

It is increasingly realized that the distribution, mobility and biological availability of chemical elements depends not simply on their concentrations but, critically on the chemical and physical associations which they undergo in natural systems. Changes in environmental conditions, whether natural or anthropogenic, can strongly influence the behavior of both toxic and essential elements by altering the forms in which they occur. In order to comprehend the environmental chemistry of an element, it would be necessary to characterize in full the proportions and chemistries of all its various forms under the diverse range of conditions possible in natural systems. Whilst, this is clearly impracticable, speciation science seeks to characterize, at least some of, the most important forms
of an element, in order to understand the transformations between forms which can occur, and to infer from such informations the likely environmental consequences.

To assess the environmental impact of polluted soil, the determination of the total metal content is not sufficient, because it is the chemical form of the metal in the soil that determines its behavior in the environment (mobility, pathways, and bioavailability) and its mobilization capacity. The behaviour and fate of metals are governed by a range of different physico-chemical processes, which dictate their availability and mobility in the soil system.

The need to determine different species of trace elements in environmental and biological materials is beyond question, since the effects or toxicity of an element and its behavior depend to a great extent on its chemical forms, as well as, amounts present (Kot and Namiesnik, 2000). The paradigm shift from simple determination of total metal concentration to a more sophisticated fractionation based approach indicates about the general recognition that information about the physiochemical forms of elements is required for understanding their environmental behaviour, including mobility, pathways and bioavailability.

The IUPAC defines speciation as "the analytical activity of identifying and measuring the quantity of one or more individual chemical species in a sample" and the speciation of an element as "the distribution of defined chemical species of an element in a system" (Templeton et al., 2000). Although no generally accepted definition of the term exists, speciation is taken to mean firstly, the active process of the identification and quantification of the different defined species, forms or phases in which an element occurs in a material. Secondly the term "speciation" can also mean the description of the amounts and kinds of species, forms or phases present in the material. The different defined species can be broadly specified, in the context of soils,

i. Functionally, i.e. by their role

ii. Operationally, i.e. the reagents or procedure used to isolate and quantify them

iii. Classical speciation, where specific chemical compounds or oxidation states are defined (Ure, 1991).

Whilst classical speciation is always preferred, it is possible only in exceptional cases for solid samples. The determination of species concentrations tends to be more challenging than determination of total elemental contents due to:
i. difficulties associated with isolating the compound of interest from complex matrices 
ii. most of the speciation techniques disturb (to some extent) the equilibria existing between the various chemical species present in the system under study 
iii. for species present in ultra-trace levels, few analytical procedures possess the degree of sensitivity required, and 
iv. suitable standard reference materials are often unavailable (Pickering, 2002).

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

Direct surface analysis, such as EXAFS (Enhanced X-ray Absorption Fine Structure Spectroscopy), SEM/EDX and XRD give interesting information on association of metals on the solid, but these methods are relatively expensive and very specialized. Trace element speciation in soils is thus often accomplished by a variety of different empirical single as well as sequential extractions. These extraction tests are commonly used to study the mobility of metals in soils and sediments by mimicking different environmental conditions or dramatic changes on them (Rauret, 1998). In single extractions a large spectra of extractants have been used to extract the "mobile" or "bioavailable" forms of metals, viz.

- Very strong acids such as aqua regia, nitric acid
- Chelating agents like EDTA, DTPA
- Buffered salt solutions e.g. ammonium acetate (pH 7)
- Unbuffered salt solutions e.g. CaCl₂, NaNO₃, BaCl₂ etc.

These extractants are hypothesized to extract exchangeable or weakly bound "available" metals in the soils, which are believed to be available for uptake by soil organisms. The term "fractionation" is frequently used intermittently with speciation but emphasizes the concept of subdividing a "total content". To elucidate the fractionation of heavy metals between different forms a plethora of sequential extraction or fractionation schemes have been proposed, many of which
are derived from the work of Tessier et al. (1979). The philosophy behind SEP is that a solid sample (soil, sediment, dust, wastes etc.) is subjected to successive attacks with a series of progressively harsher reagents to dissolve increasingly refractory forms. These methods do not provide a direct characterization of metal speciation, but are intended to simulate the chemical reactivity of metals under various possible natural and anthropogenic modifications of environmental conditions. The most commonly isolated phases in different sequential extraction schemes are: Exchangeable, Carbonate bound, Fe-Mn oxide bound (Reducible), Organic (Oxidisable) and Residual. Assessment of metal mobility and bioavailability in soils and sediments using SEP’s assumes that mobility and bioavailability decrease in the order of extraction, implying that metals in the exchangeable fractions are most mobile and bioavailable, whereas metals in residual fraction are tightly bound and are least mobile under natural environmental conditions. The speciation of trace metals in soils and sediments helps in understanding geochemical processes and also allows one to assess:

- The distribution pattern of metals according to their affinity to soil components and the strengths with which they are bound to the matrix,
- The potential of remobilization with changes in surrounding chemistry (especially pH or Eh),
- The bioavailability of an element and toxicity to plants, animals and man,
- The significance of multiple sources,
- The efficiency of soil as a sink for metals.

A variety of sequential extraction procedures cited in literature, use a variety of reagents with a wide range of experimental conditions including: sample storage, sample preparation, temperature, size fractionation, reagent concentration, sequence of extractants, solid to solution ratio, treatment time, pH control, shaking time, and filtration vs. centrifugation.

Initially developed to examine trace metal fractionation in soils and sediments, SEP’s are being applied to an ever-widening spectrum of environmental matrices. Despite the expanding applications, the integrity of methods and meaningfulness of the results are increasingly being questioned. Foremost among the criticisms are conceptual problems related to the specificity of the techniques used, operational problems like sample handling, reagent selectivity and
specificity, interferences. The lack of uniformity in the procedures used did not allow the results to be compared worldwide nor the methods to be validated. Because it is uncertain if the proposed binding forms or metal species really exist, the methods used, indeed, are mainly "Operationally defined". This type of determination is often referred to as 'speciation' although strictly speaking, this term should not be applied and the measurements performed by single and sequential extractions correspond to "fractionation" studies (Quevaouviller, 2002). Considering the experimental uncertainty associated with all presently available methods of solid phase metal speciation, Quevaouviller (2000) has emphasized the need of method standardization and validation.

The most important factors defining metal speciation at a particular point in space and time are: pH, composition and amount of organic matter, clay minerals, the presence and nature of Fe/Mn/Al oxides and hydroxides, redox potential, concentrations of salts and complexing agents, anion and cation content of soil solution. Metal ion speciation depends strongly on the composition of soil system. Soil conditions that promote precipitation or sorption tend to reduce metal ion mobility, while those that promote dissolution or desorption enhance mobility. Metals that tend to be the most mobile and biavailable are those that form weak outer-sphere associations with solid soil phases and are not sorbed. On the other hand, metals those form inner-sphere complexes with soil solids are much less likely to desorb and are, hence, not expected generally to be mobile or bioavailable.

Mobility is a concept frequently used in soil science to estimate the risk of contamination of other environmental compartments by toxins, and especially by heavy metals. However, some difference exists over the definition of mobility, originating from the fact that this term is used in different fields. Trace element mobility within soils differs for native and anthropogenic sources (Karczewska, 1996) as well as type of anthropogenic source (Davis et al., 1994). The lability and mobility of metals in soils are related to their physico-chemical forms in soils. Their bioavailability and toxicity to plants, hence to animals and human beings through the food chain, and their mobility in the ecosystems highly depend upon their forms and the pathways of transformation in soils.

Many concerns are raised about the validity and appropriate use of speciation techniques, and caution is always advocated. However, we should not
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disregard evidence from any method. Applied in an appropriate manner, information is always gained; it is the relative weight we apply to the information and its role in the subsequent interpretation that should be the driving factor. The factors defining and influencing the speciation and the change with both time and environmental conditions provide the greatest challenge and opportunity for environmental science and technology.

Unlike organic pollutants, metals cannot be degraded into harmless forms such as carbon dioxide, but persist indefinitely in the environment. The only approach available for remediating heavy metal polluted soils is to remove the metals or to convert the metals into less bioavailable forms.

As metal contaminated soils often present an unacceptable risk to human and ecological health, the remediation of soils contaminated with heavy metals is an important problem for many countries and concentrates the efforts of many authorities and scientists. If the remediation measures are taken, the "Ecodisasters" such as Minamata methylmercury incident, Itai-Itai - the cadmium poisoning (Jintsu valley, Japan), will not find a place in the world history. The contamination of the surface of earth by human interventions is a relatively old phenomenon; the evaluation, assessment and remediation of negative impacts are relatively recent. The identification of a contamination problem is only a small part of the contamination scenario. The decision to remediate implies that the ownership of the contamination problem has been accepted. Evaluation of the comprehensive risk of a contaminated site and designing an effective remedial action requires site-specific knowledge of the behaviour and fate of the individual contaminants. The metal speciation is fundamental to the response of metals to remediation techniques. Because of the above discussed pollution potential of sulfidic ore mining and beneficiation, and a paucity of information on them in our country, there is need to obtain information on relevant environmental parameters.

Long term effectiveness, permanence, reduction of toxicity, mobility, implementation costs, compliance with standards and guidelines, and community acceptance should be the important criteria for detailed evaluation of a soil remedial action. The particular issues of concern in the remediation are the laboratory to field scale evaluation of contaminant behaviour and the approach used to assess the reliability of remediation options.
Contaminated soils can be remediated by chemical, physical, thermal and biological techniques. The available techniques may be grouped into two categories: (1) *ex situ* techniques, which require removal of contaminated soil for treatment on- or off-site (e.g. solidification, soil washing, soil excavation etc.), and (2) *in situ* methods, which remediate without excavation of soil (chemical immobilization, phytoremediation, encapsulation, electroremediation etc.). *in situ* techniques are favored over *ex situ* techniques due to their lower costs and reduced impact on the ecosystem.

1.4 Description of the Study Area

1.4.1 Heritage

The study area investigated, Zawar, is an historical Zn-Pb mining community in Rajasthan. Zawar mines are the "earliest dated lead-zinc mines in the world". The world's oldest zinc mining district is littered throughout with ancient mines (old workings), slag heaps and countless earthen retorts strewn all over the area; mute remnants of ancient mining and smelting activities, indicates the presence of thriving zinc smelting industry in the past, which dates back to 14\textsuperscript{th} century (Erskine, 1908). At Zawar, zinc production may have commenced as early as 2000 B.C., but certainly flourished between the 14\textsuperscript{th} and early 19\textsuperscript{th} centuries. This is supported by the inscriptions on temples, carbon dating of wood and charcoal specimens retrieved from old workings, coupled with the findings of old furnaces and silver coins in the course of excavation in this area. Zinc was extracted by the distillation process, the system consisting of retorts with external condensers within banks of brick-lined furnaces. The retorts were cylindrical with one end open, approximately 30cm long and 1cm thick with an internal diameter of 10cm. A batch of 36 sealed retorts (charged with previously roasted ore together with charcoal and other ingredients) were then placed in the furnace to rest on a perforated clay plate with their necks protruding through the larger holes into a cooler chamber below the main furnace. The high temperatures in the furnaces induced the retorts to fuse together and these were later reused as a building material to make walls. This sophisticated technology of distillation and condensation is certainly ancestral to all such operations to use today. The technological skill and ingenuity typified in the once flourishing industry decayed
into oblivion following a series of feudal wars and famines in the early 19th century. The modern mining commenced in 1942 when the Mewar Mineral Co. attempted to reopen some of the old workings, and the Geological Survey of India started intensive exploration (Mookherjee, 1964).

1.4.2 Geology and Mineralization

Zawar is situated 44 km south of Udaipur in Aravali hills of Rajasthan, in a terrain of undulating topography, the low lying flat valleys regularly interspersed with small hillocks, at about 380 MSL. Temperature of this place varies from 5°C to 40°C. Average rainfall is around 650 mm mainly in monsoon season. The predominating wind direction in this area is south-west (IMD, 1988).

These soils are hilly soils. These are lithosols and regosols of the hilly ranges of Aravalli. These soils are shallow, gravelly, light in texture and reddish brown to grayish brown in colour (Pareek and Seth, 1972).

The rocks in Zawar belt constitute part of the Pre-Cambrian Aravali system and include an assemblage of low grade metamorphosed sediments comprising mainly greywackes, phyllites, dolomites and quartzites. The rocks overlie unconformably the Pre-Cambrian basement complex of gneisses, schists and intrusive granites (Fig 1.3).

Zawar area has witnessed at least two major periods of tectonic activity. The post-Aravali activity folded the rocks into the Zawar anticlinorium plunging north whereas the subsequent post-Delhi orogeny modified the geometry of the anticlinorium giving rise to a cross folded structure with an east-west trending and westerly plunging overturned anticline. The Bowa-Mochia-Balaria complex represents the later structure with Mochia and Balaria mines occurring on the northern limb by Zawarmala and Baroi-Haran magra. The stratigraphic sequence in ascending order is basically greywacke, lower phyllite, dolomite, quartzite and upper phyllite.

Mineralization is confined to the main dolomite horizon and occupies shears, faults and fracture planes. Ore horizon comprises of stringers and veins of variable widths ranging from a few mm to several meters with intervening barren partings, or as fine grain dissemination, which are most noticeable in Baroi. The ore bodies are of lensoidal nature, the lenses overlap each other and interconnected by link veins, as in the wider portions of central Mochia and Zawrmala, but more
commonly as small, narrow discrete lenses averaging 100-200m in strike length. Ore bodies along strike and dip exhibit both concordant (Baroi, Zawarmala) and discordant (Balaria, Mochia) relationship with the host rock but have conformable plunge/pitch.

1.4.3 Mining

Zawar group of mines comprises of three operating underground mines viz. Mochia, Balaria, Zawarmala, and one closed mine viz. Baroi. The lead zinc ore mineralization, extending over a strike length of 20 km, is hosted by sheared metamorphosed dolomite in country rocks of greywackes, shales and quartzies of Proterozoic age. These mines have a combined ore production of 4000 tonnes per day (tpd) employing sub-level top slicing and shrinkage stopping methods with matching state-of-the-art beneficiation and infrastructural facilities. Sphalerite (ZnS) is the predominant sulphide mineral in the ore, the second most abundant being pyrite. Galena is more locally concentrated but the main mineral at Baroi. Native silver, chalcopyrite, arsenopyrite and pyrrhotite are also known to occur. Cadmium and silver values are present in solid solution with sphalerite and galena respectively. The metal content (Zn+Pb) ranges from 3% to 24% in various intersections, while silver is usually in the range of 30-40 ppm.

The ore used for beneficiation is composed of galena, sphalerite and pyrite in a gangue of dolomite and quartz. The conventional froth-flotation technology is adopted to produce separate lead and zinc concentrates. On an average the ore contains 5% metal (both Pb and Zn) and 95% of the total mined ore is pumped out as tailings.

Beneficiation plant rejects, known as tailings, are impounded separately in a valley (natural topographic depression between areas of higher ground) by constructing a dam (New Tailing Dam). The water contained in the tailing slurry is reclaimed through percolation and collection techniques at the tailing dam and recycled into process.
Fig. 1.3 Surface geological map of Zawar area
1.5 Objectives

The mining and smelting of the metals is a worldwide activity and indeed may be regarded as “global” – defined by the U.K. Inter-Agency Committee on Global Environmental Research to include matters of local or regional nature that are repeated with sufficient frequency to give them global significance. Investigations into environmental impact have to date been largely limited to those in industrialized wealthy countries of the west. Priority in the future should be given to the investigations in developing countries where environmental considerations usually take second place to economic growth.

Numerous studies have been undertaken into trace element contamination derived from mining activities, in soils, plants, waters and sediments in various countries. However, only a few studies have been carried out in India.

For the present study Zn-Pb mining area of Zawar (Rajasthan) has been selected. Over the years these mining activities are liable to have contaminated the soil and biotic community with heavy metals, typically zinc, lead and cadmium.

Due to mining history which spans two millennia, and to the complex mineralogical and geochemical composition of the ore deposit, a great variety of waste materials occur in the area of Zawar, which include dumpings with ore fragments, tailings from beneficiation plant and historical smelting slags. The mobilization of toxic elements from these sources differs and therefore, a detailed geochemical study is necessary before deciding on specific remediation technique. In view of the above, a general aim of this study was to examine the geochemical composition of soils, mining wastes, tailings and slag material and to compare their potential for releasing toxic elements into the environment, under changing environmental conditions. More precisely, the objectives were:

- To study the physico-chemical characteristics (viz. pH, EC, TOC, PS, carbonate content) of different solid matrices (viz. soils, tailings, mining waste and smelting slag) sampled from the study area.
- To ascertain the level and extent of contamination by Pb, Cd, Zn and Mn as well as to establish the spatial variability for different kind of solid matrices in Zawar area.
Introduction

- To estimate the mobility and potential bioavailability of these metals in the different solid matrices by using single extraction method.
- To elucidate the fractionation of Cd, Pb and Zn in solid matrices and also to determine, if the speciation of these metals exhibits variability in different solid matrices sampled from the area.
- To compare the efficiency of two well known sequential extraction schemes (Tessier's and modified BCR Scheme) on mine tailings.
- To evaluate the extraction selectivity and efficiency of two sequential extraction procedures in order to assess the metal associations in the tailings of the above-mentioned area.

Sampling and analytical procedures, adopted towards the above objectives are described in the following chapters.