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# HEAVY METALS SPECIATION IN THE SOILS OF THE CAUVERY CATCHMENT AREA

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By

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Certificate

The research work embodied in this thesis entitled “**Heavy Metals Speciation in the soils of the Cauvery Catchment Area**” has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. This work is original and has not been submitted in part or full for any other degree or diploma of any other University.

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# Chapter-1

## Introduction

Soils are our major natural resource because most of our food and clothing comes directly or indirectly from them. After centuries of use and misuse, the importance of soil in the environment is realized. Since, most soils take thousands or millions of years to form they cannot be replaced if they are washed away by erosion. It is therefore of paramount importance that our soil mantle be carefully nurtured so that it is preserved in a healthy and fertile state for generation after generation (Fitzpatrick, 1986).

As soils consist of heterogeneous mixtures of different organic and organo-mineral substances, clay minerals, oxides of Fe, Al and Mn, and other solid components as well as a variety of soluble substances, the binding mechanisms for heavy metals in soils are manifold and vary with the composition of the soils, the soil reaction, and redox conditions. Thus, a metal may form different species according to whether it is bound to various soil compounds, reacting surfaces, or to external or internal binding sites with different bonding surfaces.

The composition of soils changes with depth from surface to subsurface horizons. Under humid climatic conditions precipitation percolates through soils and transports soluble heavy metals with the soil solution. The concentration of heavy metals in the solution phase is of major importance for all ecological considerations because plants take up the available metals from the soil solution (Brummer, 1986). The processes affecting the concentration of a metal in the soil include changes in soil water content, departure from equilibrium or steady state to non equilibrium conditions, changes in the activity of microorganisms which influence redox conditions, contents of soluble chelating agents and the contents of soil atmosphere. These processes moderate the reactions of heavy metals such as precipitation-dissolution, adsorption-desorption, and complex and ion pair formation in relation to the pH and thus influence the distribution of the various metal species in the solid phases in the soil and in the soil solution (Brummer, 1986).

Heavy metals in various forms, possess different mobilities and phyto-availabilities (Alloway, 1990; Kuo *et al.*, 1983). Generally, there is a poor correlation between the abundance of an element in the soils and its uptake by plants; however better correlation has been observed between the concentration in the exchangeable form and plant uptake. Thus, metal availability for plant uptake in soil depends upon the chemical form in which that particular element is present (Gupta *et al.*, 1975; Xian, 1989).

To characterize availability of nutrients three factors are considered: the total amount of potentially available elements (quantity factor), the concentration or activity as well as ionic ratios of elements in the soil solution (intensity factor), and the rate of element transfer from solid to liquid phases and to plant roots (rate factor or reaction kinetics) (Salomons and Forstner, 1984).

Functionally defined speciation is exemplified by the 'plant available species', that is, 'biologically active' or mobile forms. In operationally defined speciation the physical or chemical fractionation process applied to the sample defines the fraction obtained. Sequential extraction procedures are commonly used to isolate, separately, metals associated with 'water/acid soluble', 'exchangeable', 'reducible', 'oxidizable' and 'residual' fractions of a sediment. The reducible, oxidizable and residual fractions are often equated with Fe-Mn oxide, organic matter / sulfides and silicates respectively.

Plants take in nutrients from the soil mostly in the form of ions. There are sixteen essential elements needed by the plants which can be categorized as macronutrients (C, H, O, P, K, N, S and Ca) and micronutrients (Fe, Mg, B, Mn, Cu, Zn, Mo and Cl) (Donahue *et al.*, 1971; Brady, 1996).

The total metal concentration is not the true total value available to the plants. Plants are exposed to the nutrients via the soil solution, therefore, total metal concentrations do not necessarily reflect levels of metals in the soil solution (Rieuwerts *et al.*, 1998). Total concentrations of elements in soils are dependent on a number of factors. Background concentrations, influenced by local bedrock geochemistry, may be supplemented to differing degrees by anthropogenic input. Regional differences in geology and in anthropogenic source, give rise to spatial



variation in total metal concentrations (McGrath and Loveland, 1992; Webb *et al.*, 1978).

Element bioavailability in soils is largely dependent on the partition of the elements between the solid and solution phases. The importance of the element content of the soil solution as a major controlling factor in the bioavailability of elements is widely acknowledged (Alloway *et al.*, 1988; Boekhold *et al.*, 1993; Kabata-Pendias, 1993; Lee *et al.*, 1996). Sequential extraction procedure therefore, provides some idea on the bioavailable fraction of an element.

Rock weathering, soil formation and nutrient release for bioavailability are all inter-related surface geochemical processes. Soil formation comprises of two processes-weathering, the changes from consolidated mass not capable of growing plants to the development of an unconsolidated layer of material that can support plants and soil development, the changes occurring within the loose material as time passes (Miller and Donahue, 1995). River basin sediments deposited in the flood plains and deltas and soils derived from them are very fertile and ideal for agriculture. This may be because the sediments have been derived from uplifted upland which have undergone only physical weathering and erosion and have not seen much chemical weathering. As sediments are transported, they undergo weathering and transformation resulting in loosening of elements trapped in the minerals and therefore being made available to plants. Farmlands also receive water from upland, which is rich in nutrient elements. Farmlands have good water holding capacity that is sustained throughout the year keeping them fertile.

A weathering profile developed on granitic bedrock, near the village Magadi in Karnataka was studied as a part of the on-going studies of the Cauvery river basin in Southern India. Magadi is about 80 km west of Bangalore City, where Archean gneisses and granitic rocks occur. This region was thought to have been uplifted episodically since the time of the collision of Indian continent with the Asian continent (Radhakrishna, 1991 and Valdiya, 1998). The granitic rocks here seem to have suffered only mild chemical weathering (Sharma and Rajamani, 2000). In order to understand the process and mechanism of release of various nutrient elements during this incipient chemical weathering, the present study was undertaken as a part of an integrated project.

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## Chapter-2

### Review of Literature

#### **2.1 Nutrient elements and their role**

Green plants synthesize their food from simple substances taken out of the air and the soil. Plants need large quantities of C, O, H, N, P and S for building tissues, and smaller quantities of Fe, Mn, Zn, Cu, B and Mo and sometimes Co for building up its enzymes and electrolytes like K, Mg, Ca, Na and Cl to carry out the process (Russel and Russel, 1973). There are at present 16 elements known to be essential for the growth and reproduction of the plants. These elements, on the basis of amount required by plants, can be categorized as 1) Macronutrients: Chemical elements necessary in large amounts (usually 50 mg/kg in the plant) for the growth of plants and they include C, H, O, P, K, N, S and Ca and 2) Micronutrients: Chemical elements necessary in only extremely small amounts (< 50 mg/kg in the plants) for the growth of plants. They include, Fe, Mg, B, Mn, Cu, Zn, Mo and Cl ( Brady, 1996).

#### **2.2 Uptake of nutrients by plants**

Plants take in nutrients from the soil mostly in the form of ions. The sixteen essential elements move into the plant primarily in the following form ( Donahue *et al.*, 1971).

C CO<sub>2</sub>  
H H<sup>+</sup>, HOH  
O O<sup>-</sup>, OH<sup>-</sup>, SO<sub>4</sub><sup>-</sup>, CO<sub>2</sub>  
P H<sub>2</sub>PO<sub>4</sub>  
K K<sup>+</sup>  
N NH<sub>4</sub><sup>+</sup> NO<sub>3</sub><sup>-</sup>  
S SO<sub>4</sub><sup>-</sup>  
Ca Ca<sup>++</sup>  
Fe Fe<sup>++</sup>, Fe<sup>+++</sup>  
Mg Mg<sup>++</sup>  
B BO<sub>3</sub><sup>-</sup>  
Mn Mn<sup>++</sup>  
Cu Cu<sup>++</sup>

Zn  $Zn^{++}$

Mo  $MoO_4^-$

Cl  $Cl^-$

Almost all nutrients are absorbed by plants in an inorganic form; organic forms of nutrients in the soil solution are usually mineralized to the inorganic form before absorption. Ion absorption is one of the principle functions of plant roots, and the kinetics of ion-absorption affects nutrient supply and plant growth (Barber, 1984). Roots possess an appreciable cation exchange property and even a small anion-exchange property. The measured cation exchange properties are located within the apoplasm (Haynes, 1980). The origin of the cation-exchange properties is believed to be mainly due to the presence of carboxyl groups. Roots cation exchange properties are theorized to vary with density of charge (Lauchli, 1976). Divalent and trivalent cations dissociate much less from exchange sites than monovalent cations. With higher valency ions on the exchange sites, there is a larger solution volume in the apoplasmic pathway through which ions can diffuse to the plasma membrane. This may allow an increase in monovalent ion uptake rate and for increased uptake in the presence of Ca and other polyvalent cations (Haynes, 1980).

Heavy metals have been found to accumulate in the apoplasm, where they would tend to reduce charge on the cell wall aiding in increasing the relative absorption of monovalent nutrients (Barber, 1984).

Various factors affect the transfer rates of nutrient elements from soil to the plants. Soil pH has a direct relationship to the availability of metals as it affects their solubility and their capacity to form chelates in the soil. Other factors affecting the transfer rate include exposure period; competition and synergism of metals and cation exchange capacity of soil (Norvell and Lindsay, 1972; Takijima and Katsumi, 1973; Brar and Sekhon, 1976; Miller *et al.* 1977).

The cation exchange is dependent on the density of negative charges on the surfaces of soil colloids and the relative charges of the metal species in solution and on the soil surface. The surface negative charges may be pH dependent or permanent, where isomorphous substitution, of  $Si^{4+}$  by  $Al^{3+}$ , has occurred in clay minerals (Evans, 1989). In order to maintain electroneutrality, the surface negative charge is balanced by an equal quantity of cations from the soil solution, and this cation exchange, between the balance and solution cations, is reversible (Alloway, 1995; Gast, 1979). The cations form weak, electrostatic bonds with the soil surface and are

easily exchanged with other, similarly adsorbed cations, preference being proportional to the valency and inversely proportional to the hydrated radii (larger in cations with smaller ionic radii due to their increased polarizing power. Therefore, the strength with which cations of equal charge are held by ion exchange is generally proportional to the unhydrated ionic radii (Elliott *et al.*, 1986).

### **2.3 Distribution of nutrient elements in soil**

Another adsorption process, specific adsorption, involves the exchange of metal cations with surface ligands to form partly covalent bonds with charged mineral surfaces. Metals are specifically adsorbed in the preferential order Cd<Zn<Cu<Pb (Alloway, 1995). Specific adsorption is pH dependent, involves both organic and inorganic colloids and often occurs when concentrations of metals are low (Jarvis and Jones, 1980; Evans, 1989). Highly selective adsorption sites specifically adsorb metal cations which have affinities for particular sites (Forbes *et al.*, 1976; Jarvis and Jones, 1980; Tiller *et al.*, 1984; Basta and Tabatabai, 1992). For this reason, adsorption of metals may not always be affected by competition from other cations. With increasing metal concentrations and increasing saturation of surface sites, the affinity of adsorbing surfaces for particular metals decreases (Tiller *et al.*, 1984). Soil organic matter has an essential function in the accumulation and transport of metals as well as in delaying their circulation in the soil. Metal complexation involves a centrally located metal ion in solution being surrounded by one or more organic or inorganic ligands (Hill and Holman, 1983). Berrow and Mitchell, 1980, state that up to 99% of the metal content of the soil solution may be present in complexed forms. Complexation may be in the form of chelation, where the complex forming ligands form two or more coordination bonds with the metal ions (Lindsay, 1979). Complexant Organic Ligands include citric, oxalic or gallic acids or more structurally complex acids such as those contained in the soluble or more structurally complex acids such as those contained in the soluble fulvic and humic acid fractions (Evans, 1989). The most important inorganic ligands with regard to metal binding in solution appear to be the hydroxide and chloride ions (Garcia-Miragaya and Page, 1976; Sposito, 1983). Complexation of metal cation has important consequences for metal binding, depending on the affinity of the complexing ligand for the soil surface. Metals may also complex directly with solid phase components such as humic substances (Mc Laren *et al.*, 1981). Complexation is important in the soil chemistry of

Cu and models predict that all but a small fraction of Cu in soil solution is in complexed form (organic form) (Jones and Jarvis, 1981; Behel *et al.*, 1983; Temminghoff *et al.*, 1997).

Throughout the world, soil is the principle supply source of essential elements for plant growth. Soil is the source of 13 of the 16 elements essential for plant growth. Twelve of the 13 elements originated in the parent rock from which the soil developed, N being present in very small quantities.

The nutrient supplying power of sand and silt is very low because these are composed of relatively undecomposed primary mineral. By contrast, clay has a greater power to supply nutrients to plants because it is composed of secondary weathered minerals (Kaolinite, Montmorillonite and Illite), and hydrous oxides of Fe and Al. Clay are normally low in available P and are high in available K and Mg. Loam tests low to medium in available P, medium in K and high in Mg. Sands are shown as low to medium in available P and K and low to high in Mg. (Shickluna, 1962).

The N, P and S in soils are constituents of organic matter. Approximately 95% of the total soil N, 5-60 % of total soil phosphorus and 10-80% of the total soil S are present in the organic matter being available to plants only after biological decomposition. K occurs in the soil mostly as a constituent of primary minerals that exist in sand and silt particle and that released by decomposition of minerals remain in soil solution and be available to plants and some adsorbed on the surfaces of clay and humus particles in readily exchangeable and available form. Ca and Mg in soils occur in both slowly and readily soluble minerals and rocks and are available like K (Donahue, 1971).

Three 'distributive' types of elements in minerals have been distinguished (1) Camouflaged elements, which exhibit the same ionic radius, but similar or different charges and replace the elements in the structure (2) Autonomous elements, are located outside the structure of the essential minerals, but incorporate into accessory ones (3) Fissural elements are linked to the lattice surface, retained in an adsorbed form on intercrystalline surfaces inside the physical discontinuities of the crystals or inside the fissures (Goldshmidt, 1954; Lelong *et al.*, 1976).

## 2.4 Factors affecting Bioavailability of elements

The total metal concentration, however, is not the true total value available to the plants. Receptors such as plants and microbiota are exposed to Cd, Cu, Pb, Zn etc. via the soil solution, therefore, total metal concentrations do not necessarily reflect levels of metals in the soil solution (Rieuwerts *et al.*, 1998). Total concentrations of elements in soils are dependent on a number of factors. Background concentrations, influenced by local bedrock geochemistry, may be supplemented to differing degrees by anthropogenic input. Regional

Differences in geology and in anthropogenic source, give rise to spatial variation in total metal concentrations (McGrath and Loveland, 1992; Webb *et al.*, 1978).

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## 2.5 Distribution of elements in different phases in soil

Metals are continuously supplied to the soil solution by weathering of the soil. Ram and Verloo (1985) define the mobile fraction of an element as “the sum of the soluble amount in the liquid phase and the amount retained by the solid phase that can be transferred to the liquid phase of the soil”. McAllen and Crawford (1973) and Minutia *et al.*, (1987) both report the importance of the solid phase in providing a constant supply of elements for uptake via solution. Elements exist in soil in several compartments. For example, relatively available form, such as those held on cation exchange sites. Elements in soils may be contained in several forms that are largely unavailable to plants and animals. These include metals occluded in the lattices of secondary minerals and precipitated oxides of Fe and Mn, present as carbonates or bound with insoluble organic species (Thornton, 1995). Therefore, metals may be present in one of the following forms a) as ions or inorganic/organic compounds in solution b) as exchangeable ions in organic or inorganic exchange complexes (e.g. humic materials and clay particles) c) as complexes or chelates with organic materials d) as precipitated insoluble compounds and coprecipitate on solids e) incorporated on solid biological materials f) incorporated in the crystalline structures of primary and/or secondary minerals. Among these various forms, the first two are the available

ones to the living beings. Those complexed in organic materials are less available. Those precipitated on solids are available only after altered chemical conditions. Those incorporated on solid biological materials are available only after decomposition and those trapped in crystalline structures are available only after weathering (Baudo, 1982). The movement of metals from one compartment to the other, from unavailable forms to available forms, for example, is controlled by chemical conditions and time (Rieuwerts *et al.*, 1998).

## **2.6 Mode of release of elements from the reservoir**

From the parent rock materials, metals are released through weathering processes. The transport rate of metals depend significantly on their occurrence in igneous, metamorphic and sedimentary rocks and on the intensity of weathering processes and the mode of transport (Salomons and Forstner, 1984).

Weathering includes all physical, chemical and biologic actions, which abrade or dissolve rocks. The main agent of chemical weathering is water, especially when it contains a small amount of dissolved CO<sub>2</sub> which makes it more acidic. Na is readily leached from rocks, while Ca, Mg and K are dissolved somewhat more slowly; the other common rock constituents Al, Fe and Si are much less soluble (Bowen, 1979).

Sesqui-oxides of Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> are least mobile and SiO<sub>2</sub> moderately, whereas the basic cations of K<sub>2</sub>O, MgO, Na<sub>2</sub>O and CaO can be readily removed (Perel'man, 1967). The susceptibility of the minerals therefore, to chemical weathering generally shows a sequence reverse to the reaction series of Bowen. The weathering stability for soil minerals has been found higher for most clay minerals- especially for aluminous, chlorites and kaolinite than for quartz, on the other hand, calcite and particularly gypsum are much less resistant than the least resistant silicates (Jackson, 1968).

The element mobility depends on their solubility limits, which are mainly a function of pH and, for elements such as Fe and Mn, of the Eh (Telong *et al.*, 1976). Redox conditions evoke a significant migration contrast for some elements (Perel'man, 1967) e.g.: migrational intensity for U and Zn in oxidizing environments in strong but is strongly reducing environments it is "weak". Cu, Ni, Co pass from a moderate migrational intensity in an oxidizing milieu to near immobility in strongly reducing environments.

A further mechanism for migration intensity during weathering is the “entrapment of elements in secondary mineral products” (Lelong *et al.*, 1976). Chiefly the Fe and Mn phases in crusts and their deposition on clay minerals (mainly montmorillonite) are significant carrier substances for many trace metals. Also important are the amorphous weathering products in the selective entrapment of some elements: Si-Mg gets from experimental weathering of peridot contain high concentration of Mn, Fe, Co, Ni, Zn and Cu (Lelong *et al.*, 1976).

The products of weathering as classified by Goldschmidt, 1954; Degens, 1967 and Bowen, 1976 are:

- Resistates, or unchanged minerals from primary rocks;
- Hydrolysates, mostly clay from weathering of aluminosilicates minerals;
- Oxidates, precipitates of  $\text{Fe}(\text{OH})_3$ , e.g. as “coatings” on detrital grains;
- Carbonate precipitates, mostly calcite, eg as skeletons of marine plankton;
- Evaporates, mostly salt or gypsum from drying salt lakes.

## 2.7 World soil types (FitzPatrick, 1986)

- 1) **Acrisols:** Tropical and sub-tropical soils, have monsoon climate and are extremely weathered and leached. Generally of low fertility because of both micro and macronutrient deficiencies coupled with Al toxicity. Highly susceptible to erosion if used for arable cultivation. Therefore, best reserved for forestry and grazing.
- 2) **Andosols:** Developed in volcanic ash, natural fertility of these soils is high when formed in basic ash but many have low fertility mainly because of their great capacity to fix P.
- 3) **Aerenosols:** Developed from coarse-textured unconsolidated material except recent alluvium. Generally have very low natural fertility but sometimes can give good crop yields when they occur in humid areas and supplied with fertilizers. When exposed they erode very rapidly especially by wind.
- 4) **Cambisols:** They show early stages of development. Some cambisols of the tropics show a considerable degree of weathering and are very close to acrisols and Ferralsols. The relatively unweathered Cambisols of cooler regions have a very high inherent fertility and usually carry a deciduous forest. But they can be adapted to agriculture.



- 5) **Chernozems:** These are the dark colored soils of the steppe and prairie grassland areas. These soils have a high nutrient status, excellent structure and high water holding capacity, which together impart a high natural fertility. But since these soils occur in low rainfall areas drought is a hazard.
- 6) **Ferralsols:** These are the deep, red, brown and yellow, highly weathered soils of the tropics. They tend to have moderate to high contents of clay, a well-developed granular structure and a labyrinth of passages produced by termites. The clay mineralogy is dominated by kaolinite, goethite, hematite and gibbsite. As they are strongly weathered they occur under high rainfall conditions and are extremely nutrient deficient. Have high capacity for fixing P. The exchange capacity of the organic matter in these soils are very important because of the low CEC of the clay; however the organic matter is rapidly mineralized under hot tropical conditions. Poor for agriculture, they can carry natural forests sustained by natural cycling.
- 7) **Fluvisols:** Young soils of recent alluvial deposits, deltas, estuaries and coastal situations. They have a wide range of natural plant communities and occur in all parts of world. Some fluvisols are extremely fertile such as the Alluvium of the Nile and many other large rivers.
- 8) **Gleysols:** These are wet mineral soils common in humid climates and are poorly drained.
- 9) **Greyzems:** Soil of cool continental areas, having high natural fertility.
- 10) **Histosols:** Wet organic soils, occurring mainly in the cold temperate areas.
- 11) **Kastanozems:** Soils of cool semi arid areas with grassy vegetation. Have high inherent fertility but dry conditions impose severe limitations.
- 12) **Lithosols:** These are the shallow soils of mountainous areas.
- 13) **Luvisols:** Occur mainly in temperate regions where they form some of the major agricultural soils. They also occur in the tropics and subtropics where they are agriculturally good soils.
- 14) **Nitosols:** These are clayey red soils of the tropics and are among the most fertile soils, extensively used for a wide range of crops.
- 15) **Phaeozems:** Principal soils of the prairies of N.America and have a very high inherent fertility.
- 16) **Planosols:** Soils of flat continental areas with marked seasonality and are poor in agriculture.

**17) Podzols:** Principal soils of the northern coniferous forest and have low potential for agriculture.

**18) Podsoluvisols:** These soils are common beneath the moist deciduous forests of the cool temperate areas and show slow permeability.

## **2.8 Sequential Extraction Procedure for the extraction of elements present in secondary phases**

Use of total concentration as a criterion to assess the potential effects of sediment contamination implies that all forms of a given metal have an equal impact on the environment; such assumption is untenable. Generally there is a poor correlation between total metal content in the soil and plant uptake, whereas better correlation have been observed for extractable forms of metals (Gupta *et al.*, 1975; Xian, 1989). An analytical procedure involving sequential chemical extractions was developed for the partitioning of particulate trace metals, into five fractions, by Tessier *et al.* (1979). Several schemes have come up with different modifications but Tessiers scheme is the most thorough researched scheme.

In determining the amount of exchangeable metal ions, an extractant is used which contains cations more strongly bound to the exchange positions as compared with the metals; common extractants in use are  $\text{BaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{NH}_4\text{Oac}$  etc. (Salomans and Forstner, 1980). To release metal ions weakly bound to specific inorganic sites (e.g. on carbonates) extraction with 0.4MHOAc, HOAc / NaOAc (pH-5), or complexing agents (of moderate ligand strength) has been recommended (Pickering, 1981). A single extraction method for the determination of trace metals associated with carbonates makes use of an acidic ion exchanger (Deurer *et al.*, 1978). Dissolution of the amorphous (or 'poorly ordered') inorganic phases can be promoted by reducing the Fe and Mn to lower valency states e.g. through reactions with hydroxylamine, oxalate or dithionate ions. Oxalate treatment did not appear to attack crystalline material, but it has shown that the degree of interaction varies with illumination (Schwertmann, 1964; Eaton, 1979; Pickering, 1981). The metal fraction associated with organic matter has been extracted through oxidation of this component with NaOCl or  $\text{H}_2\text{O}_2$ .

By dissolving the sediment using  $\text{Na}_4\text{P}_2\text{O}_7$ , through proton displacement (with 0.5M HCl) or by chemical competition (using 0.05N EDTA); the apparent ability of

both EDTA and HCl to release metal ions associated with both organic and oxide phases has led to these being used as extractants for the evaluation of total non-detrital fraction (Pickering, 1981). For the dissolution of detrital or lattice bound components, a combination of acids has generally been used. Nitric acid promotes destruction of organic matter, but when used alone or in conjunction with HCl or HClO<sub>4</sub>, the procedure doesn't completely dissolve some type of silicate minerals.

The use of sequential extractions, although time taking; furnishes detailed information about the origin, mode of occurrence, biological and physiochemical availability, mobilization and transport of trace metals (Tessier *et al.*, 1979; Novozamski, *et al.*, 1993; Forstner, 1993, Orisini and Bermond, 1993; Lelester and Probst, 1998).

## **2.9 Sequential extraction experiments worldwide**

Heavy metals are not permanently fixed on sediments and can be released back by changes in environmental conditions, such as pH, redox potential and the presence of organic chelators. It is generally believed that metals are generally associated with smaller grain size (Forstner, 1984). The concentration of various elements in the secondary phase can be determined by using sequential extraction methods. The sequential extraction procedure has found many applications such as by agriculturists, geochemists, chemists, environmentalists etc.

Zn, Mn and Cu in various soil fractions were studied by Shuman (1978). The Zn, Mn and Cu contents were higher in fine textured, higher organic matter soils than in coarse textured, low CEC soils. The fine textured soils had a large proportion of their Zn and Cu in the clay fraction, but the coarse textured soils had relatively higher percentages in the organic matter fractions. Percentage Cu was highest in the organic matter and clay fraction. McKenzie (1980) found that the adsorption of Pb by MnO was upto 40 times greater than that by FeO, and Pb was adsorbed more strongly than any of the other ions studied, by all of the oxides other than Goethite. That is the reason why Pb is accumulated in the MnO in soil. Gedde and Laitinen (1974) found adsorption in the order Pb > Zn > Cd on amorphous hydrous oxides of Fe and Mn, and Forbes *et al.* (1976) found that adsorption on Goethite decreased in the order Cu > Pb > Zn > Co > Cd. Studies by Brummer (1986), indicate that the adsorption of heavy metals on soil particles is not only restricted to the formation of surface complexes but can also take place in the structure of minerals.

Chlopecka (1994) found that the mobility of Cd, Cu, Pb and Zn in soil is strongly dependent upon soil pH. The chemical forms of metals are affected by pH, Eh, organic matter and other factors. Increase in pH results in higher adsorption of Cd, Zn and Cu by soils (Massey, 1972; Cavallaro and McBride, 1978; Kuo and Baker, 1980; Soon, 1981; Xian *et al.*, 1989) promotes the formation of metal hydroxides and reduces plant uptake of Cd, Zn and Pb (Street *et al.*, 1978; Kuo *et al.*, 1985). Oxides of Fe and Mn in soils are capable of sorbing large amounts of trace metal ions and can therefore be important in controlling trace metals concentration in soil solution, and hence trace metal bioavailability in soils. The concentrations of Cd and Co specifically sorbed by the oxides at pH 6.0 were greater for the Mn oxides than for the Fe oxides. The metals were also much less readily desorbed from the Mn than Fe oxides and Cd was more readily desorbed than Co (Backes *et al.*, 1995).

Ma and Rao (1997) found that residual fraction is the most abundant pool for all metals. Significant amount of Zn is present in potentially available fraction. A major portion of Cu is associated with the organic, Fe-Mn oxides and carbonate fractions in most soils. They found that decrease in the order of sequential extraction, the apparent mobility and potential bioavailability were Zn > Cu > Cd > Ni. Luo and Christie (1998) found large portion of extractable Cu in organic matter and exchangeable fraction which may be attributed to the formation of organic Cu-complexes while the predominance of extractable Zn in the Fe-Mn oxides and carbonate fractions suggest that inorganic sorption and precipitation are important factors. Controlling Zn solubility in the sludge materials and amended soils. Among Zn, Cd and Cu, Walter and Cuevas (1999), found only Cu in exchangeable fraction. Pb and Cr were found mainly in residue. Ni was found in inorganic and organic matter fraction. Zn was found in carbonate and organic matter. The toxicity of trace metal is also studied by Kumaresan and Riyassudin (1999) and similar results were reported.

## **2.10 Sequential extraction experiments in India**

Experiments on this aspect have also been carried out in India. Jha *et al.* (1990) found that Fe, Mn and Pb show a preference for the oxide fraction, whereas Cu and Zn are predominant in organic and carbonate fractions of sediments. They found that 80% Mn, 78% Fe, 9% Pb, 67% Cu and 55% Zn are present in chemically mobile phases of the sediments. Vaithyanathan *et al.* (1992) worked on heavy metal

transport in Cauvery River, which chiefly takes place in particulate form. They found that the elements Fe, Mn, Pb, Cu, Zn, Ni, Co and As are dominantly present in the < 20 µm fraction of the river sediments. Speciation study showed that Fe-Mn oxide fraction held the largest share of heavy metals in the sediments. Chakrapani and Subramanian (1993) worked on suspended and bed sediments showed that Fe, Zn, Cu and Pb are associated with the residual fraction and Mn with the exchangeable fraction. Panda *et al.* (1995) worked on the geochemistry of Chilka Lake. They reported that exchangeable fraction is not Geochemically significant (<2 %) and reducible and organic matter bound fractions are the significant phases in the non lithogenous fraction phenomenon being attributed to the scavenging affinity for sorption into organic matter of the lagoon sediments. Grain size and geochemical partitioning of heavy metals in sediments of the Damodar rivers were studied by Singh *et al.* (1998). The chemical fractionation study showed that lithogenic is the major chemical phase for the heavy metals. Fe-Mn oxides and organic bound fractions are significant phases in the non lithogenic fraction and that the carbonate fraction is less significant for heavy metal scavenging.

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## **Chapter-3**

### **Field Details**

Samples for this study have been collected from Magadi, located about 50km south-south-west of Bangalore on the catchment area of the river Cauvery (Fig 3.1). The site is situated on the Mysore Plateau. The profile is 3m thick and is developed on granitic bedrock.

#### **3.1 Location and origin**

Cauvery is one of the major river systems in southern India. The Cauvery River basin covers a large area of 87,900 km<sup>2</sup> over the states of Kerala (2,930 km<sup>2</sup>), Karnataka (36,240 km<sup>2</sup>) and Tamilnadu (48,310 km<sup>2</sup>). It extends from 75°28'E to 79°52'E and 10°7'N to 13°28'N. The River originates at Talacauvery in the western edge of Shyadri range of the Western Ghats (1350m above MSL) and takes easterly course over the Mysore Plateau and Tamilnadu plains and drains at Bay of Bengal (Fig.). The general easterly course becomes southward between Hogenekal and Bhavani in Tamilnadu.

#### **3.2 Climate**

This region experiences semi-arid to sub-humid tropical climate and receives an average of 1090mm rainfall. It rains mainly through the southwest monsoon, over a period of about three months. It has an elevation of 630m. The mean annual temperature of the Cauvery basin is 25°C although in summer (March to May) the maximum temperature reaches 43°C. The region has only sparse vegetation cover, except in the peneplained areas, which are under cultivation.

#### **3.3 Description**

The river is approximately 800 kms long. Rivers Bhavani and Amaravati, also originating from Western Ghats, join Cauvery and make it a major river in the Tamilnadu plains. This river has build floodplain deposits on either side, providing fertile farmland in Tamilnadu plains. Between the time Cauvery leaves the Mysore plateau and reaches the plains of Tamilnadu, it flows through a series of block mountains thought to have been formed by the reactivation of Archean faults and

shears as a consequence of collision of the Indian landmass with the Asian subcontinent (Radhakrishna, 1993 and Valdiya, 1998). The drainage pattern of the river, therefore becomes trellis resulting in an overall southerly flow for the main channel.

As the river Cauvery nears the Stanley reservoir at Mettur, it winds its way through deep valleys and gorges with almost vertical cliffs, and the river becomes antecedent. As Cauvery flows south from Mettur, it widens gradually, as the bordering hills move away. About 20km downstream, the hills appear on both sides, allowing the river to widen and start forming a floodplain. The gradient also reduces and thus flow rate decreases.

Downstream from the confluence of Cauvery and Bhiwani, the river has formed a vast floodplain. River Amaravati joins it at Karur from where the main channel takes an eastward turn towards Tiruchirappalli. At the widest point (~4 km), near Mohanur, the floodplain extends to a few kilometers on both sides of the riverbank. Farmlands exist right on the riverbank and on levee deposits, supporting intensive agriculture.

### **3.4 Lithology**

These floodplains have been dated to be between 800-5000 years old. Along the eastern margin of the Mysore plateau the river was subjected to rejuvenation by late Cenozoic tectonic activities (Radhakrishna, 1993). Major lithologies of the catchment area of the river include middle to late Archean gneisses and charnockites with small amounts of Archean supracrustal rocks and Proterozoic granitoids. All along the river course, charnockitic rocks stand out like hills, while the granites and gneisses have weathered away. Whereas the peneplained regions of the uplift plateau are made predominantly of Archean gneisses and schists in the catchment area, those constituting high mountains ( upto 2700m) are commonly made of charnockites. This mode of occurrence of gneisses and charnockites had lead early geologists to suggest a denudational origin for the charnockitic hills. Field evidences and mineralogical observations in the upper reaches of Cauvery catchment area reveal that the gneisses are more susceptible to weathering compared to massive granites or charnockites, which stand out relatively fresh in the profiles. The present day sediments are, therefore, mostly supplied by these charnockites (Singh, 1999).

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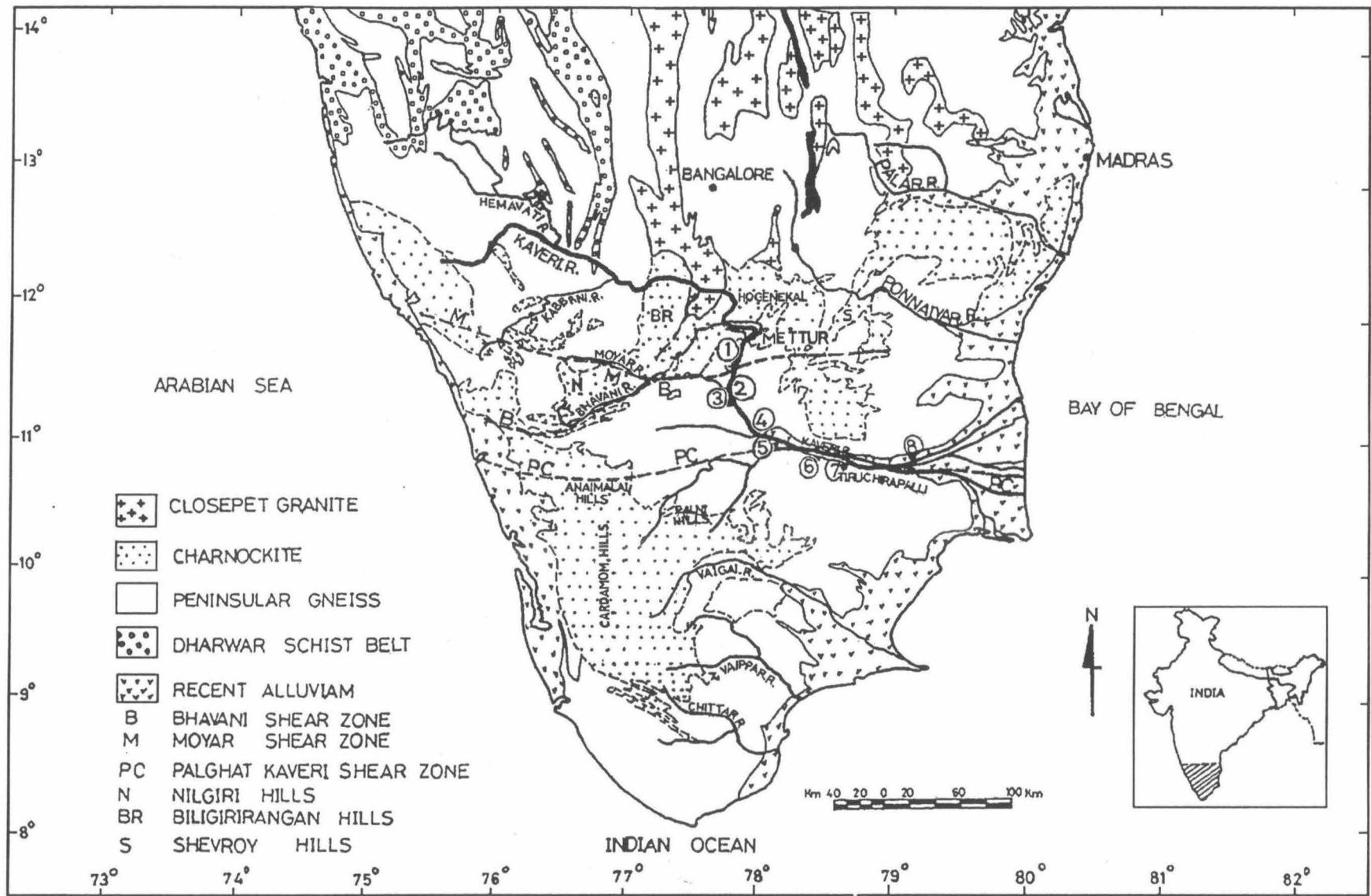


Fig: 3.1.1 Map of southern India showing the course of Cauvery river and the sampling site.



## Chapter-3

### Methodology

This study was carried out with utmost care to maintain the quality of data. Keeping in view that the quality of data is of paramount importance materials, methods and instruments used for generating the data have been chosen meticulously.

The research methodology adopted in this work can be divided into four parts viz. (1) Sample Processing (2) Mineralogical Studies (3) Chemical Speciation and (4) Analytical methodology.

#### **3.1 Sample processing:**

About 1 Kg of fresh rock samples were collected from the profile to characterize them geochemically so that the variation in the weathered samples can be made. The rock samples were reduced to small chips and crushed in hardened steel mortar to -60 mesh size. These crushed samples were homogenized thoroughly by coning and quartering, ground to -200 mesh size in an agate mortar and stored in plastic vials. After processing each sample, sieves and the mortar were washed with soap solution, dried up with the help of air blower and cleaned with acetone before proceeding to next sample to prevent contamination.

#### **3.2.1 Mineralogical studies:**

The mineralogical study involves the preparation of thin sections of all fresh and weathered rock types which include gneisses, granite, amphibolite, charnockite and pyroxene granulite and observing them under transmitted light microscope mainly to decipher the texture, mineralogy, type of alteration and grade of metamorphism. This study also involves preparation of bulk sample slides of all rocks and sediments from the profile for the observation of different minerals present under XRD studies. The mineralogical observations were used to substantiate the second part of the work i.e., geochemical study. The geochemical study involves processing of samples including fresh rock, saprolith, saprolite and soil/sediment for geochemical analysis

and quantitative determination of major and trace-elements including rare earth-elements by various wet chemical procedures adopted for the determination of different elements. These are described in the following paragraphs.

### **3.2.2 Mineralogical analysis:**

Thin sections were prepared for the petrographical studies of different rock types, whereas mineralogical study of weathered rocks (saprolith and saprolite) and soil was done by X-ray diffractometry. For XRD analysis, the specification opted during the scan were as follows -

Target:  $\text{CuK}\alpha$ ; Filter: Ni; Range 400cps for clay fractions and 100cps for bulk mineralogical analysis; Goniometer speed:  $1^\circ$  of  $2\theta$  angle per minute; Scan angle:  $2^\circ$  to  $35^\circ$  for clays, and  $2^\circ$  to  $45^\circ$  for bulk samples. The clay fractions were separated by Atterberg Cylinders (Muller, 1967), and separately run on X-ray diffractometer as untreated, glycol treated (12 hours at  $50^\circ\text{C}$ ) and heat treated ( $550^\circ\text{C}$  for 1 hour) (Carrol, 1974). The minerals and their proportions were determined from the diffractograms after Griffin (1971) and Carrol (1974).

### **3.3 Sequential extraction procedure:**

After a critical evaluation of the available literature, the following chemical extraction method was used for the study. The quantity indicated below refer to 1g sample (dry weight). After each step the leachate was separated from the sample by centrifugation (8000 r.p.m.), collected in plastic bottles and stored in the refrigerator. Centrifugation is preferred over filtration to prevent sample loss. The samples were washed with distilled water and dried completely at  $40^\circ\text{C}$  each time before proceeding for the next step (Leleyter and Probst, 1998).

- (1) **Water soluble:** The sample was extracted at  $20^\circ\text{C}$  for 30 min. with distilled water with continuous agitation.
- (2) **Exchangeable:** The residue from (1) was leached at  $20^\circ\text{C}$  for 2 hrs with 10 ml of 1M magnesium nitrate.

- (3) **Bound to carbonates:** The residue from (2) was leached at 20°C for 5 hrs with 10 ml 1M Sodium Acetate (pH=4.5).
- (4) **Bound to manganese oxides:** The residue from (3) was leached at 20°C for 30 min. with 10 ml 0.1 M hydroxylammonium chloride.
- (5) **Bound to amorphous iron oxides:** Residue from (4) was leached at 20°C for 4 hrs in the dark with 10 ml [0.2 M ammonium oxalate-0.2 M oxalic acid].
- (6) **Bound to crystalline iron oxides:** Residue from (5) was leached at 80°C for 30 min. with 10 ml [0.2 M ammonium oxalate- 0.2 M oxalic acid- 0.1 M ascorbic acid].
- (7) **Bound to organic matter:** 3 ml 0.02M HNO<sub>3</sub> and 8ml of 35% H<sub>2</sub>O<sub>2</sub> was added to the residue from (6) and was kept at 85°C for 5hrs and agitated continuously. 5 ml 3.2M ammonium acetate (20% (v/v) HNO<sub>3</sub> ) was then added and kept at 85°C for 30 min.

### **3.3 Analytical methodology:**

#### **3.3.1 Preparation of "B-solution" by acid digestion:**

Majority of the major and trace elements were analyzed by the "B" solution prepared by the acid digestion method, which is a modified procedure of Shapiro and Brannock (1962). In this method 0.5 g of sample powder (-200 mesh size) is taken in a cleaned Teflon crucible and to this 10 ml of conc. HF, 5 ml conc. HNO<sub>3</sub> and 1 ml HClO<sub>4</sub> are added and heated at a temperature of about 85-90 °C for about 5-6 hours in covered condition. After 5-6 hours, the lid is removed and the solution is dried completely. In the second step, 5-ml conc. HF, 10-ml conc. HNO<sub>3</sub> and 1 ml HClO<sub>4</sub> are added and dried completely. In the third step, 10 ml of HNO<sub>3</sub> is added to remove the traces of HF and the solution dried completely. Finally, 25 ml of 2N HCl is added and heated to about 100 °C to bring the digested sample into solution. After regular swirling, the solution is transferred to a volumetric flask and diluted to 200x. This solution is directly used for the determination of trace elements such as Ni, Cr, Ba, Sr and Y. An aliquot of this solution was diluted 20 times (4000X) was used for major

element analyses except silica. Silica was determined by calorimetric method using a Bausch & Lomb spectrophotometer.

### 3.3.2 Preparation of "A-solution" for determination of SiO<sub>2</sub>.

The dissolution of the sample was done by 'A-solution' method as suggested by Shapiro and Brannock (1962).

In Ni crucibles, 10 ml of 15% NaOH was taken and dried under IR lamp. To these, 0.05 gm of -200 mesh samples were added and fused over Bunsen burner for 10 minutes. The crucibles were cooled to room temp, filled with water and kept covered overnight. The contents of crucibles with washings were transferred to 500ml plastic beakers containing 300ml water and 10ml of 12N HCl. The solutions in beakers were quantitatively transferred to a series of 1000ml flasks and were warmed up till the solution becomes clear. The solution is made up to 1000ml on cooling and 100ml of each was further transferred to plastic bottles and preserved for SiO<sub>2</sub> determination. The whole process was followed with no time-lag in between to avoid much contact of solution with glassware.

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#### Reagents:

Reagents used were ammonium molybdate solution of 7.5%, tartaric acid solution of 8% strength and reducing agent. Ammonium molybdate solution of 7.5% was prepared by dissolving 7.5 gms of reagent grade (NH<sub>4</sub>)<sub>6</sub> Mo<sub>7</sub> O<sub>24</sub> · H<sub>2</sub>O in 75-ml of water in 100-ml volumetric flask with gentle heating and a subsequent addition of 10-ml of 1:1 H<sub>2</sub>SO<sub>4</sub> on cooling. The volume was made up to the mark and stored in plastic bottle. Reducing solution was prepared by dissolving 40 gms of reagent grade anhydrous sodium sulphate in 10-ml water with subsequent addition of 0.15 gm of 1-amino-2-naphthol-4-sulphonic acid and stirred till complete dissolution. Solution of 9 gms of reagent grade sodium bisulphite in 90-ml water was added to the first solution and mixed thoroughly and was then stored in plastic bottle in dark place.

#### Procedure:

10-ml of 'A' solution of each sample, standard and blank were pipetted out and transferred to 100-ml volumetric flasks to which 1-ml of ammonium molybdate



solution (7.5%) was added and stirred. This was allowed to stand for 10 minutes. To this solution, 5 ml of tartaric acid solution was added and stirred followed by addition of 1-ml reducing solution. The volume was made up to 100-ml and then allowed to stand for 30 minutes. Then the absorbance of each solution was measured at 650 nm by spectrophotometer using blank solution A used as reference. This was compared with the absorbance of solution A of rock standards by plotting graph and SiO<sub>2</sub> % was calculated. To calculate it numerically, factor for each of the two standards was computed and average is taken.

$$\text{Factor} = \frac{\% \text{ SiO}_2 \text{ of standard}}{\text{absorbance of standard}}$$

Now % of SiO<sub>2</sub> of each sample was calculated using the formula:

$$\text{SiO}_2 = \text{Average factor} \times \text{absorbance of sample solution}$$

### **3.3.3 Rare Earth Elements Separation of the leachate:**

The rare earth element concentration in the different fractions separated by sequential extraction was determined using GBC-Labtam 8440 ICP-AES. Different fractions were separated using the Lelyster and Probst scheme. 20gm sample was taken and after each step the leachate was separated and stored at 4°C for the separation of REE. The REE separation from the matrix and preconcentration was done by cation exchange chromatography. Since the abundance of these elements was very low, they have to be separated as a group from the rest of the matrix elements so that the spectral interference from the matrix elements can be avoided.

The leachate was dried completely and residue dissolved in 30 ml of 1N HNO<sub>3</sub> and loaded on to the HNO<sub>3</sub> quartz columns packed with cation-exchange resin AG50W-X8 (100-200 mesh in Hydrogen form). The loaded solution was eluted with 50 ml of 1.8N HNO<sub>3</sub> to get rid of most of the matrix elements and the rare earths along with ferric iron remaining in the columns were collected with 180 ml of 6N HNO<sub>3</sub> and dried on a hot plate. The residue obtained was dissolved in 30 ml of 1N

HCl and loaded in to the HCl quartz columns packed with the same cation exchange resin. To get rid of iron, elution was done with a predetermined quantity of 70 ml 1.7N HCl and the REEs were collected with 240 ml of 6N HCl and dried. The residue was dissolved in 5 ml of 2:1 2N HNO<sub>3</sub> and 2N HCl and analyzed by a polychromator in the GBC-Labtam 8440 ICP- AES. Standardization for REEs were done with metal standards obtained from Johnson and Matthey Inc., London and in-house rock standards 90-57 and VM-9 which were run as unknowns.

### **3.3.4 Rare Earth Elements Separation of the residue:**

Sample (0.5gm) was fused with 1gm NaOH (10ml of 15% NaOH solution dried under infra-red lamp) and 1.25gm of Na<sub>2</sub>O<sub>2</sub> (sample: NaOH: Na<sub>2</sub>O<sub>2</sub> = 1: 2: 2.5) in a Ni crucible over a meker burner for about 20 min. and was kept in water for 8 hrs. The sample was washed by 6N HCl into a 500 ml beaker. The solution was heated gently on a hot plate (90-100°C) to evaporate until the viscous gel of silica is formed. It was filtered through Whatman-42 and 41 filter paper and the filtrate was dried completely. The dried material was picked with 30ml of 1N HCl and transferred to a centrifuge bottle. 10-12 drops of phenol red indicator was added to this solution. Then NH<sub>4</sub>OH was added drop by drop until the colour changed to pink and all trivalent cations got precipitated. This solution was then centrifuged at 6000rpm for 30min. at 4°C. The supernatant liquid was filtered and discarded. The precipitate in the centrifuge bottle was transferred to a teflon beaker using 6N HCl and was completely dried on the hot plate. This residue was passed through HNO<sub>3</sub> and HCl columns in the similar manner as stated above for the REE separation of leachate and dried. Then it was dissolved in 5 ml of 2:1 2N HNO<sub>3</sub> and 2N HCl and analyzed by a polychromator in the GBC-Labtam 8440 ICP- AES.

### **3.3.4 Instrumentation:**

Major and trace elements were analysed by Inductively Coupled Plasma - Atomic Emission Spectrophotometer (ICP-AES). Potassium was analyzed by a flame photometer since this alkali metal is readily ionized at lower temperatures and the high temperature of the plasma is not suitable for the analysis of these elements since

it leads to excessive ionization of these elements. SiO<sub>2</sub> was determined by using a Spectronic-20 Bausch & Lomb Spectrophotometer.

Similar sample processing and dissolution procedures were followed for both standards and sample solutions for any particular set of analysis. Samples were thoroughly homogenized before weighing. Only high quality analytical reagents and acid supplied by reputed companies such as Merck and BDH were used in the present study. Tripple distilled water was used for cleaning the glass wares and for solution preparation, the last two distillations being done in a pure quartz distillation unit. The unit was operated only to fifty percent of its efficiency to reduce the quantity of ions going in to the final stage.

During the major and trace element analyses, International Rock Standards (IRS) and in-house rock standards were run as unknown after the calibration of the instrument, thereby checking precision of the given set of analysis.

### **3.3.5 ICP – AES for analysis:**

Several authors have noted the excellent analytical sensitivities that were obtained for most of the major and trace elements including rare earth elements in the Inductively Coupled Plasma - Atomic Emission Spectrophotometer (Fassel, 1978; Floyd et al., 1980). Unlike the relatively low temperature flame used in the atomic absorption spectrophotometer, the high temperature in ICP - AES gives excellent analytical signals for most of the elements except alkali metals. Optimizing the operating parameters of the instrument for both sequential (monochromator) and simultaneous (polychromator) mode of analysis is important. Many of the operating parameters such as observation height above the coil (torch height), sample gas flow, and coolant gas flow pressures, selection of appropriate wavelength and PMT voltage in the case of monochromator analysis have to be optimized before any given set of analysis. Observation height refers to the part of the plasma that is used for generating the light signal. Certain refractory elements such as Zr, Ti etc. require a higher temperature portion of the plasma, which means an increase in torch height. On the other hand for the analysis of sodium (Na) which is readily ionizable element, cooler portion of the plasma is needed which means a reduction in the torch height and a

considerable increase in the auxiliary and coolant gas flow supplies to the plasma is required.

Another important aspect of major and trace element determination by the sequential ICP (monochromator) analysis is the selection of a suitable wavelength with minimal spectral interference. Although elements have several sensitive wavelengths, we selected relatively sensitive wavelengths devoid of spectral interference from other elements in the analyte solution. During the initial period of data generation, the spectral interference problem was checked using the top 4-5 sensitive emission lines and the most suitable wavelength found out. The above exercises, to find out the optimum instrument settings and wavelength selection in the monochromator ICP analysis were done mainly by keeping an eye on the optimum peak/background ratio, for any particular element of interest. Higher the peak/background ratio for any particular element, the better it was in terms of quality of the data. This was particularly important for trace element analysis, because a higher peak/background (P/B) ratio means that spurt in the detection limit, which means even at very low levels good quality data, can be obtained.

Before a given set of analyses, in both the sequential ICP analysis and the simultaneous analysis, the instrument was checked for its performance by looking at the peak/background ratio for the most sensitive elements in both types. In monochromator analysis Cu at 324.754 nm was used and for rare earth element analysis in polychromator, ytterbium (Yb) was used. Generally, a P/B ratio of about 120 was obtained for Cu in the monochromator and a P/B of ~1000 was obtained for Yb in the polychromator. Other, instrumental parameters such as proper aspiration of solution, proper nebulization, optimum torch height and optimum sample gas pressure etc. were taken care off. Proper nebulization without any pulsation in the aerosol spray produced was checked by looking at the RSD% of the counts for 10-ppm Cu before calibration of the instrument for analysis. Usually, the REE analysis by the polychromator was performed after 2-3 hours of the ignition of the plasma and after performing some major and trace element analysis in the monochromator set up. This was because of the fact that a stable plasma was essential for rare earth element determination since they were present in very low concentration levels. While most of



the major and trace element analyses in the monochromator was performed without changing most of the instrument settings such as sample gas flow, coolant and auxiliary gas flows, torch height etc., the instrument settings were optimized with respect to Ce whenever the machine was operated for rare earth element analysis in the polychromator. Yb being highly sensitive, optimization with respect to Ce did not detort the data quality. Whereas it improved the sensitivity of Ce (peak/background ratio) significantly, thereby improved the data quality of LREE. Since the rare earth element determination requires a pre concentration procedure and involves enormous amount of time, labor and consumption of chemicals etc. and therefore extra care was taken before REE analysis.

### **3.3.6 Determination of Loss on Ignition (LOI):**

LOI was determined as suggested by Maxwell (1968). 1 g of each sample ( - 200 mesh) was taken into pre-weighed quartz crucibles (50ml volume). It was kept in muffle furnace, uncovered, and temperature was raised to 500 °C, increasing by 100°C each time. Once the temperature was attained the lids were kept on the crucibles and the temperature was increased in successive steps to 1000 °C, at which it was kept for one hour. It was allowed to cool to room temperature and the samples were weighed. To determine the LOI, difference in the weight before and after heating was calculated in percentage.

### **3.3.7 Determination of Chemical Index of Alteration(CIA) :**

Nesbitt and Young (1984) suggested a parameter called Chemical Index of Alteration (CIA) to be calculated from the chemical analyses of rocks and sediments. In the calculation the molar proportions of the oxides of Al, Ca, Na and K were taken. This index was defined as -

$$CIA = Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O) \times 100$$

CaO\* represents the Ca in silicate form only. For the determination of CIA of the sediments, where Ca was present as carbonates the CaO\* has been determined by leaching the samples with cold diluted HCl (Gale and Hoare, 1991; Tripathy and Rajamani, 1999), and corrected for P<sub>2</sub>O<sub>5</sub>. The other elements were recalculated to

100% accordingly and have been used for the calculation. For fresh rock and slightly weathered samples, the CaO\* values were taken as equal to CaO minus Ca for apatite. The molar proportions of Al<sub>2</sub>O<sub>3</sub>, CaO+Na<sub>2</sub>O and K<sub>2</sub>O were plotted on triangular plot (Nesbitt and Young, 1984, 1989). Which was called as A-CN-K diagram.

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## Chapter-5

### Results and Discussion

#### **5.1 Mineralogy of the profile samples**

Samples (Mg-1 to Mg-8) from different horizons with distinct characteristics were sampled from freshly exposed profile. The bedrock (Mg-1) is overlain by weathered saprolite (Mg-2) which is overlain by Mg-8 to Mg-3, Mg-3 being at the top of the profile. The mineralogy of the different samples of Magadi weathering profile was determined by X-Ray diffraction technique. Dominantly Quartz, Feldspar and Mica are present in the samples. The differentiation amongst Kaolinite and Chlorite is difficult because both minerals have nearly similar peaks ( $7^{\circ}$  and  $14^{\circ}$ ). Only after giving heat/acid treatment kaolinite and Chlorite can be differentiated. The bedrock samples and the saprolithic material show similar mineralogy and there is not much variation in different horizons of the profile. This may be because of very small amount (<5%) of weathering products formed due to chemical weathering. Similarly, not much change is seen in the mineralogy after the different secondary phases are leached out by the chemical speciation. Barely any change in the mineralogy indicates that the profile has undergone only incipient chemical weathering.

#### **5.2 Geochemistry**

The concentration of various major and trace elements in the various horizons of the profile has been given in table 5.1. Silica values show no systematic variation excepting some depletion during weathering (maximum depletion is in Mg-5). The values lie between 55.9% (Mg-1) to 72.3% (Mg-8). The average alumina concentration varies between 16.8% (Mg-1) and 23.9% (Mg-6), the top surface consisting of 20.3% (Mg-3). Alumina is slightly enriched in the middle horizons (Mg-6). This increase of Al is not due to loss of mobile elements. The greater increase in the middle horizons may be because of illuviation (Drever, 1988). There is depletion in the concentration of FeO in the middle horizons. This is likely because of the mobility of Fe during weathering. Because ferric ions ( $Fe^{3+}$ ) is commonly immobile

the mobility of Fe implies a significant part of Fe was kept as Fe<sup>2+</sup> for it to be mobile. This is made possible probably by soil microbes as they could locally control the redox potential of the soil and soil solution (Drever, 1988). Ca and Na are regarded as the most mobile elements and are the first ones to move when weathering takes place. In our samples also Ca reduces in the upper horizons by almost 50%. Na shows a progressive decrease in lower horizons but it is increasing again in the upper horizons. Sr is getting depleted in the saprolithic material but increases in the upper horizons. The increase in Na and Sr in upper horizons may be caused due to local mixing. Potassium doesn't show any systematic variation; it remains more or less constant in different horizons though a drop in concentration is seen in Mg-5 (3.7%). Ba, like K, is retained in the profile. This behaviour of elements may be due to their adsorption onto weathered products.

Chemical index of alteration, CIA, is a measure of chemical weathering based on the mobilities of Ca, Na, K and Al. A CIA of 50 or below indicates little chemical weathering of the rocks whereas, a value of 100 means complete weathering, provided the source has a predominance of granitic rocks (Nesbitt and Young, 1989). The CIA value calculated for the fresh rock is 55.9; and that for the saprolite sample Mg-8 is 72.3; the top soil horizon has a value of 67.6 (Table 5.1 and Fig.5.1.1). CIA is increasing from unweathered rock 55.9 (Mg-1) to weathered rock material (72.3) Mg-8. In the weathered profile it doesn't show much variation (Mg-8 has 72.3 and Mg-5 has 70.6) showing that the profile has not undergone much chemical differentiation due to weathering. However, it shows a decline in the topmost horizon (67.6) that may be because of local mixing of the weathered eroded material with the material transported from some other site.

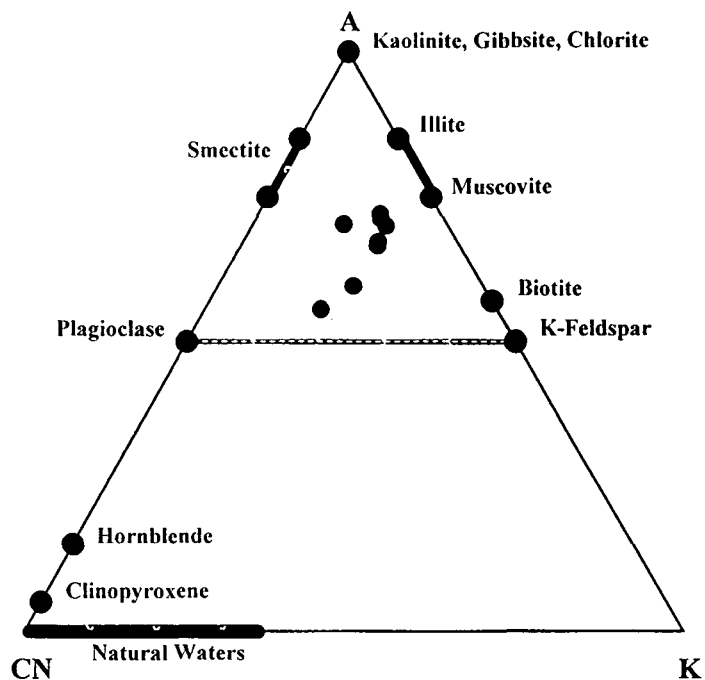
C-14 dating of Cauvery flood plain sediments suggest that the age of the profile should vary between 800-5000 years (Singh, 1999). Therefore, less weathering of profiles situated in catchment area of Cauvery River can be attributed to the less age of the profile. Rainfall received by the area is also less (**1090mm**) and can be suggested as one of the reasons as to why weathering in the profile is less. It is further supported by sparse vegetation and hence no bio-weathering, which can be one of the reasons why the profile has seen only modest chemical action and didn't succumb to intense weathering.

	Mg-3*	Mg-4	Mg-5* ‡	Mg-6	Mg-7*	Mg-8	Mg-2*	Mg-1
	Top soil	Top soil	Zone of illuviation	Zone of illuviation	Zone of illuviation	Zone of illuviation	Weathered-rock	Bed-rock
<b>Major oxides (in wt. %)</b>								
SiO <sub>2</sub>	68.5	64.5	60.5	67.5	62.1	64.0	66.3	69.3
TiO <sub>2</sub>	0.43	0.37	0.24	0.23	0.16	0.16	0.20	0.49
Al <sub>2</sub> O <sub>3</sub>	20.3	22.1	20.4	23.9	22.0	20.9	17.8	16.8
FeO	3.4	2.9	2.1	1.9	1.8	1.8	2.5	3.1
MnO	0.04	0.04	0.02	0.02	0.02	0.02	0.03	0.05
MgO	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.7
CaO	0.3	0.4	0.5	0.7	0.6	0.7	0.6	1.4
Na <sub>2</sub> O	1.85	2.05	2.20	1.17	1.13	0.85	2.88	3.30
K <sub>2</sub> O	5.65	6.30	3.65	5.80	5.84	4.90	5.60	4.85
P <sub>2</sub> O <sub>5</sub>	0.05	0.06	0.06	0.06	0.06	0.07	0.06	0.17
LOI	4.94	5.06	6.70	5.85	7.81	7.89	4.33	1.61
<b>Trace elements (in ppm)</b>								
Ni	16	17	16	15	25	30	41	16
Cr	8	7	9	23	22	29	33	6
Ba	687	700	663	664	791	693	633	486
Sr	213	201	191	153	163	150	201	232
<b>CIA</b>	67.6	66.9	70.6	71.6	70.3	72.3	60.0	55.9
<b>pH</b>	8.6	8.6	8.8	8.2	8.5	8.2		

**Table: 5.1** Concentration of major (%) and trace (ppm) elements in the Magadi profile.

\* Samples chosen for sequential extraction

‡ Sample chosen for REE



**Fig, 5.1.1:** Ternary plot of A-CN-K. A, CN and K denote molecular proportions of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}+\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  respectively. Samples plot in the regions of relatively unweathered material. Plots are of sediment samples Mg-1, Mg-2, Mg-3, Mg-4, Mg-5, Mg-6, Mg-7 and Mg-8

### 5.3 Behaviour of different elements in various phases

Heavy metals in soils occur in various forms, each possessing different mobilities and phytoavailabilities (Alloway, 1990; Kuo *et al.*, 1983). Generally there is a poor correlation between total metal content in the soil and plant uptake, whereas better correlation have been observed for extractable forms of metal (Gupta et al, 1975; Xian, 1989).

Behaviour of ten elements Fe, Mn, Al, Ca, Ni, Cu, V, Co and Zn was studied in the seven phases 1-water soluble, 2-exchangeable, 3-carbonate, 4-Mn oxide, 5-amorphous Fe oxide, 6-crystalline Fe oxide and 7-organic fraction. Four samples, Mg-3, Mg-5, Mg-7 and Mg-2 were chosen from the profile based on extent of weathering. The concentration of various elements in secondary phases is given in table 5.2. The behaviour of these elements is shown in fig.5.1.2.

The concentration of Fe in the bulk sample varies from 1.8-3.4 % of which very small quantity is present in the available form. Fe is very high in both amorphous as well as crystalline FeO phases. It is as high as 8822 ppm in Mg-5 in crystalline FeO phase. Organic phase also consists of quite a considerable amount of Fe. It is observed that bulk Fe is slightly enriched in the upper horizons of the profile due to oxidation of  $Fe^{++}$  to  $Fe^{+++}$  and formation of immobile phases. In the organic fraction it is enriched in the lower horizon (9097 ppm in MG-7). This may be because Fe is getting complexed by organic acids in the eluvial horizons and translocated downwards as soluble complexes (Drever, 1988).

Mn is often present associated with Fe. High concentration of it is present in both crystalline and amorphous FeO phases. It is present in much higher concentration in crystalline FeO fraction in Mg-2 (189.7 ppm). It may be present in higher concentration in crystalline fraction because Mg-2 has not undergone much weathering. Divalent Mn also gets complexed with soil organic compounds. It is present in all horizons except Mg-3. Like Fe, Mn also seems to be getting enriched in the lower horizons in organic fraction. This can be attributed to the complexation associated with organic acids. Amorphous Fe oxide phase is also high in the lower horizons compared to the upper ones.

Very high concentrations of Al are present in both the FeO phases (829.3 ppm in amorphous FeO and 555.8 ppm in crystalline phase in Mg-3). Al is also present in the water soluble and exchangeable fractions though not in very high concentration. Considerable amount is present in organic fraction. The distribution of Al in organic phases seems to be complimentary as the upper horizons (Mg-3 and Mg-5) are depleted in Al while the lower ones (Mg-7 and Mg-2) are enriched. Al might be getting enriched in the lower horizons complexed and transported by organic acids and getting precipitated in the lower horizons due to metal saturation (Drever, 1988). Small concentration is also present in Mn oxide fraction (30.4 ppm in Mg-3 and 67.2 ppm in Mg-2).

Ca is one of the most mobile cation and is the dominant exchangeable cation in many soils. Highest concentration of Ca has been found to be present in the exchangeable phase (909 ppm in Mg-3 and 1268 ppm in Mg-7). Ca is also present in considerable concentration in the carbonate phase that occurs only in the soils above pH-7.0. Small concentrations are present in water-soluble, oxide fractions and organic fractions. Not much change is seen in the concentration of Ca in various weathered horizons (Mg-2-Mg-7) as they seem to get reprecipitated in the alkaline condition.

Ni is chiefly present in the exchangeable and carbonate phases. Small concentrations of Ni are also present in the three oxide fractions, organic fraction and the water-soluble fraction. The higher concentration of Ni in exchangeable phase in Mg-2 is not clear and needs to be understood.

Cr is present mainly in the exchangeable and the FeO fractions. Higher concentration associated with Fe oxide fraction may be caused by adsorption of Cr by Fe colloids (Jenne, 1968). While in exchangeable form Cr concentration increases downwards, it is decreasing in the crystalline FeO fraction. Cr is also present in the amorphous FeO fraction and organic fraction though in small quantity.

Cu in soil can occur in soil solution, both ionic and complexed; as an exchangeable cation on the exchange complex; as specifically adsorbed ion; in organic matter; in occluded oxides and in minerals (Donahue *et al.*, 1971). Gupta and Chen (1975) found very little Cu in the exchangeable form, and McLaren and Crawford (1973) and Rauret *et al.*, 1988 indicated that the bulk of "available" Cu reserves in the organic fraction. In our samples, however, Cu was traced in very small



quantities. Although it shows its presence in both the Fe oxide fractions it is difficult to say much about its behaviour in secondary phases because of the low concentration traced.

V and Co are also present in very small quantities and it is difficult to say with much surety about the trend followed by them in the various secondary phases.

Zn was found in high concentration in carbonate and organic phases. The proportion of the Zn complexed in solution increases as soil pH increases (4.3 ppm in carbonate and 6.8 ppm in organic phase in Mg-3). It is reported that Carbonate and exchangeable forms are especially susceptible to pH change (Chao, 1984; Dudka *et al.*, 1990; Tessier *et al.*, 1979). The preferential carbonate bonding of Zn can be attributed to the relatively high stability of Zn carbonates under certain pH-Eh conditions as well as to the characteristic precipitation of these compounds with Ca carbonate (Deurer *et al.*, 1978). This can also be the result of a similarity of the ionic radii of Zn to that of Ca (Pederson and Price, 1982; Zhang *et al.*, 1988). Considerable amount is present in both the FeO fractions (3.2 ppm in amorphous and 1.8 ppm in crystalline FeO in Mg-3). Shuman (1976, 1977) showed that Fe oxides adsorb considerable quantities of Zn. Traces of Zn have been found to be present in MnO fraction (0.4 ppm in Mg-5). Zn seems to be retained in the upper horizons of the profile. Mg-2 (parent material) is rich in Zn complexed with organic matter (7.8 ppm). Himes and Barber (1957) showed that organic matter chelates Zn in soils.

#### **5.4 Distribution of rare earth elements in various secondary phases**

The leachates obtained by sequential extraction were dried and picked in acid and were passed through the columns and REE was determined in the various secondary phases. Rare earth elements in five secondary phases (carbonate, Mn oxide, amorphous Fe oxide, crystalline Fe oxide and organic fractions) were determined in sample Mg-5. The results are given in table 5.3. REE from 20gm sample was extracted into 5 ml acid solution. 70.5 ppm Ce is present in the bulk solution of which 24.7 ppm is present in the residue. Ce is mainly concentrated in amorphous FeO and organic phases where concentrations of 13.2 and 13.8 ppm respectively are observed. Crystalline FeO also has significant amount (8.6 ppm). Nd, in bulk was found to be 14.8 ppm of which 6.1 ppm is present in the residue. Highest concentration is found to

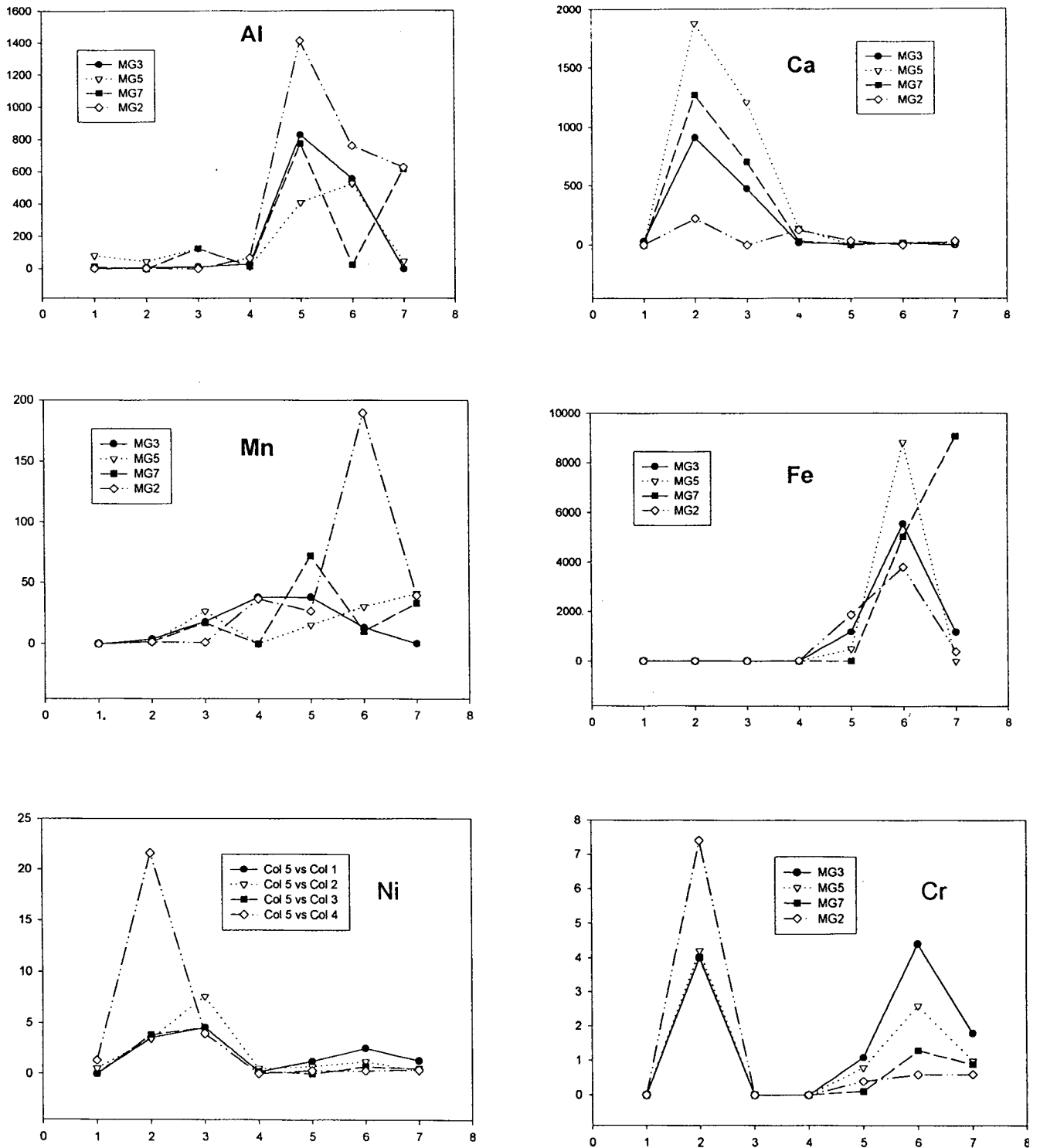
**TABLE: 5.2** Concentration of elements in the seven phases **a.** water soluble **b.** exchangeable **c.** bound to carbonate **d.** bound to MnO **e.** bound to amorphous FeO **f.** bound to crystalline FeO **g.** bound to organic matter **R.** residual

Samples	Behaviour of Fe in all the phases							
	a	b	c	d	e	f	g	R
MG-3	0.0	0.0	0.0	0.87	1193.2	5557.8	1175.3	8705.8
MG-5	33.5	0.0	0.0	0.0	489.7	8822.5	0.0	5752.0
MG-7	0.0	0.0	0.0	0.0	0.0	5052.5	9079	5752.0
MG-2	0.0	0.0	0.0	20.2	1881.1	3812.7	382.4	5130.2
Samples	Behaviour of Mn in all the phases							
	a	b	c	d	e	f	g	R
MG-3	0.0	3.9	18.2	38.1	38.3	13.6	0.2	94.85
MG-5	0.0	1.5	26.7	0.0	15.5	30.6	41.5	94.85
MG-7	0.0	2	17	0.0	72	10.5	33.5	94.85
MG-2	0.0	1.5	1.2	36.8	26.9	189.7	40	94.85
Samples	Behaviour of Al in all the phases							
	a	b	c	d	e	f	g	R
MG-3	3.1	8	12.4	30.4	829.3	555.8	0.0	4221.01
MG-5	80.2	43.4	124.9	13.5	408.8	524.4	46.1	4154.0
MG-7	12.1	0.0	124.4	16.1	775.3	24.9	616	3721.0
MG-2	2.5	2.6	0.0	67.2	1413	759.4	626.6	3386.87
Samples	Behaviour of Ca in all the phases							
	a	b	c	d	e	f	g	R
MG-3	33.73	909.1	475.3	18.01	12	14.8	0.0	90.24
MG-5	3.3	1879.7	1207.8	140.8	0.0	15.33	5.26	87.27
MG-7	0.36	1268.6	700.4	34.1	0.0	21.8	20.8	101.2
MG-2	0.0	223.3	0.0	126.5	36.81	0.0	34.6	84.36
Samples	Behaviour of Ni in all the phases							
	a	b	c	d	e	f	g	R
MG-3	0.0	3.5	4.5	0.2	1.2	2.5	1.3	12.72
MG-5	0.5	3.4	7.6	0.5	0.7	1.2	0.3	12.25
MG-7	0.0	3.8	4.5	0.2	0.0	0.7	0.5	15.45
MG-2	1.3	21.6	3.9	0.0	0.3	0.3	0.4	14.77

Continued

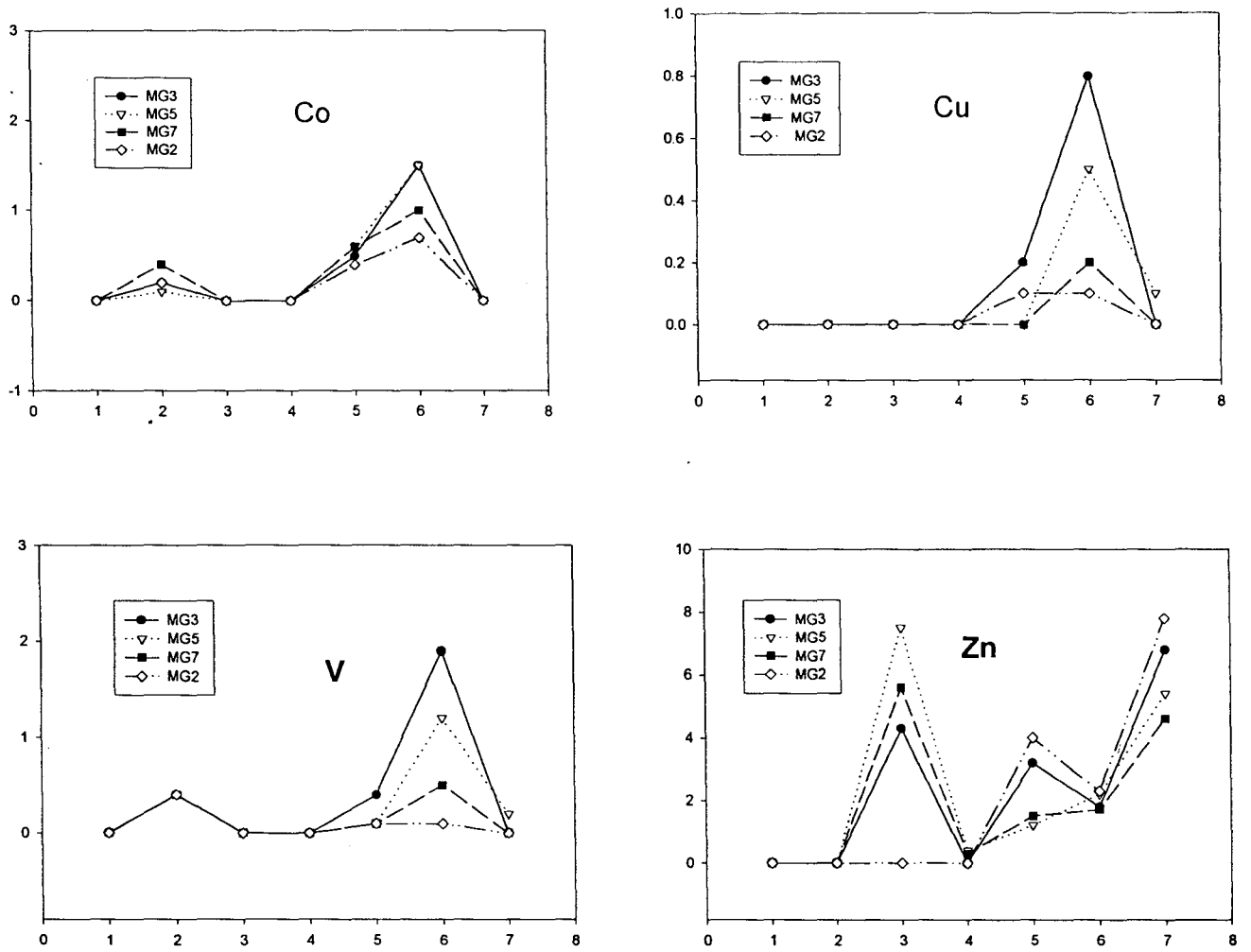
TABLE Contin.....

Samples	Behaviour of Cr in all the phases							
	a	b	c	d	e	f	g	R
MG-3	0.0	4	0.0	0.0	1.1	4.4	1.8	5.5
MG-5	0.0	4.2	0.0	0.0	0.8	2.6	1	5.7
MG-7	0.0	4	0.0	0.0	0.1	1.3	0.9	12.97
MG-2	0.0	7.4	0.0	0.0	0.4	0.6	0.6	17.02
Samples	Behaviour of Cu in all the phases							
	a	b	c	d	e	f	g	R
MG-3	0.0	0.0	0.0	0.0	0.2	0.8	0.0	1.2
MG-5	0.0	0.0	0.0	0.0	0.0	0.5	0.1	0.7
MG-7	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.5
MG-2	0.0	0.0	0.0	0.0	0.1	0.1	0.0	1.4
Samples	Behaviour of V in all the phases							
	a	b	c	d	e	f	g	R
MG-3	0.0	0.4	0.0	0.0	0.4	1.9	0.0	2.3
MG-5	0.0	0.4	0.0	0.0	0.1	1.2	0.2	1.7
MG-7	0.0	0.4	0.0	0.0	0.1	0.5	0.0	1.6
MG-2	0.0	0.4	0.0	0.0	0.1	0.1	0.0	2.1
Samples	Behaviour of Co in all the phases							
	a	b	c	d	e	f	g	R
MG-3	0.0	0.2	0.0	0.0	0.5	1.5	0.0	1.0
MG-5	0.0	0.1	0.0	0.0	0.6	1.5	0.0	1.3
MG-7	0.0	0.4	0.0	0.0	0.6	1	0.0	0.9
MG-2	0.0	0.2	0.0	0.0	0.4	0.7	0.0	1.5
Samples	Behaviour of Zn in all the phases							
	a	b	c	d	e	f	g	R
MG-3	0.0	0.0	4.3	0.0	3.2	1.8	6.8	3.9
MG-5	0.0	0.0	7.5	0.4	1.2	2.2	5.4	4.7
MG-7	0.0	0.0	5.6	0.3	1.5	1.7	4.6	3.5
MG-2	0.0	0.0	0.0	0.0	4	2.3	7.8	4.1



**Fig: 5.1.2** Behaviour of various elements in the secondary phases (1. Water soluble 2. Exchangeable 3. Bound to carbonates 4. Bound to Mn oxides 5. Bound to amorphous Fe oxides 6. Bound to crystalline Fe oxides 7. Bound to organic matter).

Contd.....



**Fig: 5.1.2** Behaviour of various elements in secondary phases (1. Water soluble 2. Exchangeable 3. Bound to carbonates 4. Bound to Mn oxides 5. Bound to amorphous Fe oxides 6. Bound to crystalline Fe oxides 6.bound to organic matter).

be in the carbonate (2.6 ppm) followed by the FeO phases (1.6 ppm in amorphous and 1.3 ppm in crystalline). MnO fraction seems to contain very less quantity of both Ce and Nd. Sm is 2.8 ppm in the bulk, of which 1.3 ppm is left in the residue. All the phases except the MnO fraction seem to contribute almost the same quantity to the bulk. Eu is 0.7 ppm in the bulk and 0.3 ppm of it is left in the residue. It is in high concentration in carbonate and organic fraction, which is 0.1 and 0.1 ppm respectively. The relative enrichment of Eu with respect to the neighbour elements (Sm and Gd) may be due to the affinity of  $\text{Eu}^{++}$  to Ca. The FeO fractions also seem to contribute substantial quantity though MnO fraction is again contributing only traces of it (0.01 ppm). Gd 2.5 ppm in the bulk of which 1.1 ppm is in the residue. Gd is present in almost the same concentration in the carbonate, the two FeO fractions and the organic phase (0.34 ppm, 0.31 ppm, 0.30 ppm and 0.31 ppm respectively). MnO fraction consists of only 0.03 ppm. Dy in bulk is 0.9 ppm, 0.5 ppm being present in the residue. Amorphous FeO fraction consists of 0.3 ppm of it. The carbonate, crystalline FeO fraction and the organic fraction also contribute to the bulk. Concentration of Er in bulk is 0.9 ppm, 0.5 ppm of which is present in the residue. It is mainly present in the FeO fraction (0.2 ppm in amorphous and 0.1 ppm in crystalline). Carbonate and organic fractions also have some concentration of Er. The concentration of Yb in the bulk sample is 0.4 ppm of which 0.3 ppm is present in the residue. Amorphous FeO is the main contributor to it (0.1 ppm). It is also present in carbonate, crystalline FeO and the organic phases.

### **5.5 Contribution to the total REE by each secondary phase**

The contribution of total rare earth elements (Ce, Nd, Sm, Eu, Gd, Dy, Er and Yb) in the various secondary phases to the bulk is shown in Fig 5.1.3 The total REE in the bulk is 93.4ppm (100%). The residue obtained by extracting all the secondary phases is found to contain 34.7 ppm of the REE. It, therefore, contributes to 37.2% to the bulk. Similarly, contribution of each secondary phase to the bulk was calculated. In this study, it was found that the organic fraction is contributing a maximum of 17.5 ppm to the bulk, which comes to 18.7%. The other major contribution is by the amorphous Fe Oxide phase. It contributes 16.1 ppm (17.3%). Also contributing significantly are the carbonate and the crystalline Fe Oxide phases. Carbonate phase consists of 9.2 ppm (9.9%) and the Crystalline Fe Oxide phase consists of 10.9 ppm

(11.7%). Mn Oxide fraction seems to be devoid of REE contributing only a small concentration of 1.04 ppm (1.1%) to the bulk.

Organic, FeO phases and the carbonate phase, therefore, are the main secondary phases contributing REE. The order of contribution of different secondary phases to the bulk is:

**Organic fraction > amorphous FeO fraction > crystalline FeO fraction > carbonate fraction > MnO fraction**

Leleyeter and Probst (1999) also reported that the rare earth elements are mainly linked to the carbonates, organic matter and organic oxides.

### **5.6 Concentration of REE in secondary phases**

The weight of secondary phases in the sample is calculated by the difference between the weight of the sample before and after sequential extraction.

Weight of sample = 20 gm

Weight of sample after sequential extraction = 18.63 gm

Weight of secondary phases = 1.37 gm

% contribution of secondary phases and the residue (by weight) can be calculated from the above information. It is found that secondary phases and residue constitute 6.85 % and 93.15 % respectively to the bulk. These secondary phases mainly occur as coating on the grains.

The secondary phases were found to consist 54.8 ppm of REE while only 34.7 ppm is present in the residue. Since only 6.9 % (by weight) of secondary phases consist of 54.8 ppm REE, REE seems to be getting concentrated in the secondary phases. The REE are therefore, getting 800 folds concentrated in the secondary phases.

### **5.7 Explanation of weathering trend observed in A-CN-K diagram using elemental behaviour in different fractions**

Ni, Cr, V, Zn, Co, Al, Ca are present in the exchangeable fraction in all the horizons. The presence of exchangeable elements in all the horizons (CIA = 55.9 to

Elements	Mg-5-c	Mg-5-d	Mg-5-e	Mg-5-f	Mg-5-g	Mg-5-R	Mg-5-B	Sum of exchangeable
Ce	4.67	0.69	13.23	8.64	13.80	24.71	70.49	41.03
Nd	3.32	0.23	1.59	1.31	2.63	6.08	14.81	9.09
Sm	0.47	0.04	0.32	0.25	0.45	1.29	2.78	1.53
Eu	0.11	0.01	0.07	0.05	0.09	0.31	0.70	0.32
Gd	0.34	0.03	0.31	0.30	0.31	1.09	2.47	1.29
Dy	0.18	0.01	0.30	0.18	0.13	0.46	0.91	0.79
Er	0.09	0.02	0.18	0.14	0.06	0.54	0.86	0.49
Yb	0.05	0.01	0.14	0.05	0.04	0.26	0.41	0.28

**Table: 5.3** The concentration of REE (in ppm) in various secondary phases of sample Mg-5 (c. carbonate d. bound to Mn oxide e. bound to amorphous FeO f. bound to crystalline FeO g. Bound to organic matter R. residue B. bulk)



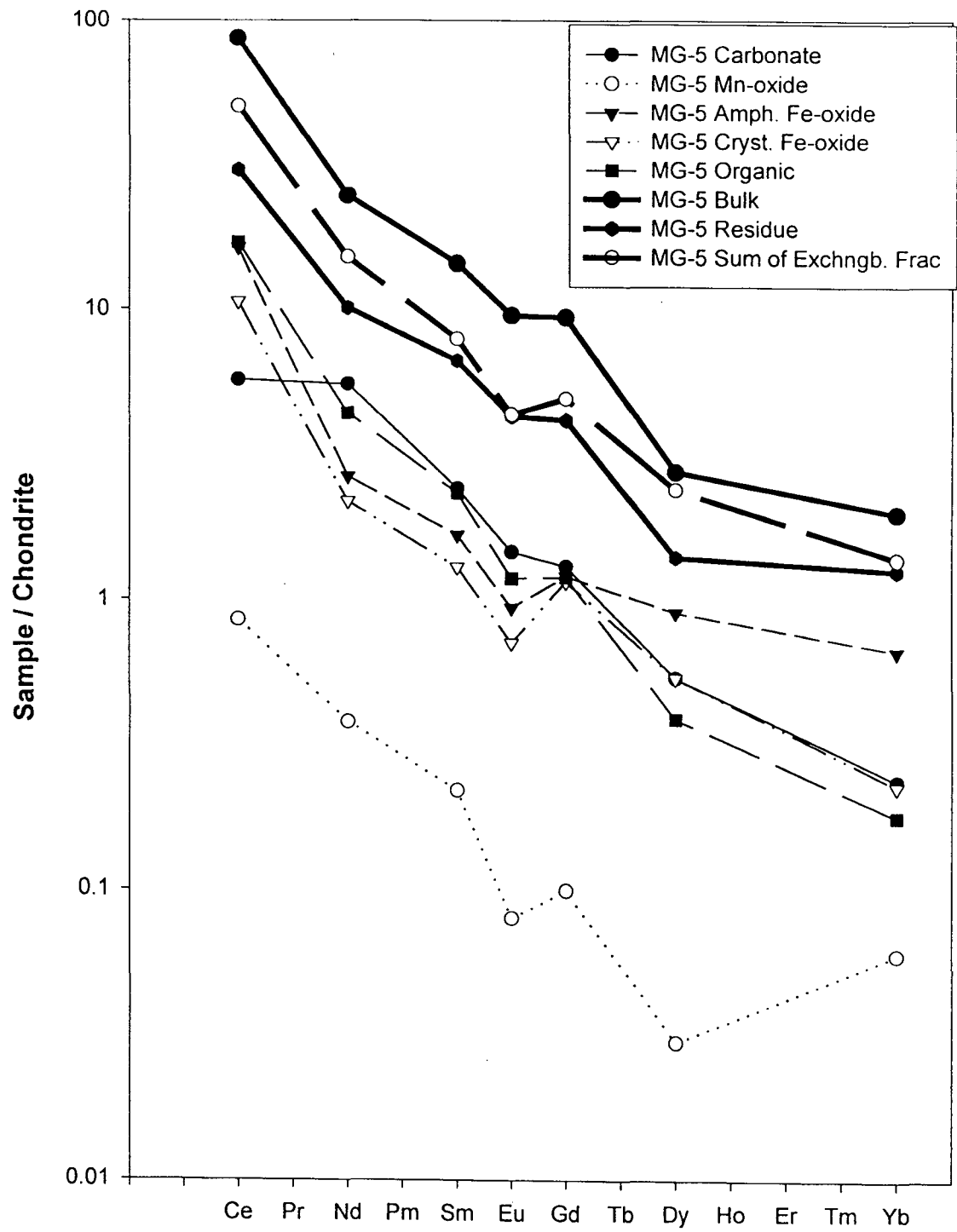


Fig: 5.1.3 REE pattern of different fractions of weathered granodiorite (Mg-5) in Magadi.

72.3) may not be due to in situ chemical weathering but either due to import through percolating solutions or biological activities. The presence of higher amount of Al, Fe, Zn, Cr and REE in organic fraction supports that the biological activity plays an important role in the transport of these elements viz. Illuviation. Whereas, Cr, V, Zn, Co and Al are also substantially present in the both Fe oxide phases. Mn and Fe are mainly present in crystalline Fe oxide phases. This shows that these elements have not been subjected to much mobilization due to less weathering. As such no generalization can be given on the trend followed by the different elements.

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## Chapter-6

### Summary

The quantification of chemical weathering in terms of CIA of the weathered granitic rock of Magadi has been used to understand element distribution in different phases. CIA values of 56 and 60 were obtained for the fresh rock samples, whereas, for the saprolite material CIA varied from 68 to 72. From CIA values, it can be inferred that chemical weathering is only in its preliminary stages although due to physical weathering the fresh rock has been converted to saprolite. The physical disintegration of the rock with little chemical changes points to a very recent neotectonic activity (Sharma and Rajamani, 2000).

This region experiences a semi-arid climatic condition with an average annual temperature of 25<sup>0</sup>C and annual rainfall of 1090 mm (mainly during monsoon period). This climatic condition, under which a very large part of the year passes without rain does not favour chemical mobilization of the elements due to weathering. Microorganisms however, seem to be playing an important role although vegetation in this region is sparse. The mobilization of even the otherwise supposedly immobile REE by organic matter indicates the significant role organisms play in mobilizing nutrient elements. The illuviation of Fe and Al in the middle part of the profile in association with organic matter is a further confirmation to the microbial activity in the region.

The presence of the elements Ni, Cr, V, Zn, Co, Al and Ca in the exchangeable fractions is, therefore, not because of *in situ* chemical weathering but probably due to biogeochemical activities. These elements are probably sequestered from the rocks through percolating water and released due to highly alkaline conditions in the profile.

With time, the elements released during biogeochemical weathering pass into different chemical phases (water soluble, exchangeable, bound to carbonates, bound to Fe-Mn oxides and bound to organics). These phases formed in different physico-chemical conditions can be fractionated. The prevailing conditions in the soil determine the re-dissolution and bioavailability of the elements.

In our study area, though negligible amounts of elements are present in water-soluble form, exchangeable elements are present in considerable amount. Plants absorb elements from the soil in the ionic form, and the water-soluble and exchangeable forms are therefore, readily available to the plants. The sampling profile in Magadi is alkaline in nature and so the carbonates present hold substantial quantity of trace elements in them (Al, Mn, Ca, Ni, Cr, V, Co and Zn). Fe-Mn oxides exist as nodules, concretions, cement between particles, or simply as coatings; these are excellent scavengers for trace metals. Elements bound to crystalline FeO are trapped, however, in primary minerals and are therefore unavailable to the plants. The organic fraction plays a significant role in the profile and consists of Zn, Cr, Fe, Mn, Al, Ca and Ni. The chemistry of soil organic matter has marked influence on bioavailability. In Magadi, due to alkaline condition, carbonates exist in the soil and they harbour trace metals in them. Harboring of trace metals by carbonates is also been reported by Stover et al., 1976 and Chester and Hughes, 1967. Carbonates get dissolved in the water to neutralize the acidic condition posed by organic acid and the elements bound to both carbonates and organic matter get released and become available to the plants. Therefore, the release of elements from carbonates and organic matter is chiefly governed by a change in pH.

Organic phase, FeO phases and the carbonate phase are the main secondary phases consisting REE, amongst which organic fraction plays the most important role. This has also been reported by Leleyeter and Probst, 1999. Compared to the primary phases, REE gets more concentrated in the secondary phases. As much as 800 folds concentration of REE in the secondary phases was seen in this work. Because secondary phases are variably mobilisable, REE can also be mobilised in the weathering profile. However, our observation suggests that at least under the conditions of mild chemical weathering, REE are not fractionated in the profile.

Unlike our findings, Prusty *et al.*, (1994) found in the polluted Tiri river sediments that organic fraction does not play any significant role in harbouring heavy metals but the carbonate and Fe-Mn oxide fractions are the more important scavengers. It is seen that the concentration of a metal in a particular fraction depends upon the concentration of that particular fraction in the sediments which, on the other hand, depends upon the physical conditions and the geological setup of the site.

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## References

- Alloway, B. J. (1995). Soil processes and the behaviour of metals. In: Alloway (ed.) Heavy metals in soils, Glasgow, Blackie.
- Backes, C. A., McLaren, R. G. Rate, A. W. and Swift, R. S. (1995). Kinetics of Cd and Cu desorption from Fe and Mn oxides. *Soil Sci. Soc. Am. J.* **59**: 778-785.
- Barber, S. A. (1984). Nutrient absorption by plant roots, In: Soil nutrient bioavailability. A Wiley-Interscience Publication, John Wiley and sons. Pp55-89.
- Basta, N.T. and Tabatabai, M. A. (1992). Effect of cropping systems on adsorption of metals by soil: 2.Effect of pH. *Soil Science*, **153**: 195-204.
- Baudo, R. (1982). The role of speciation in the transfer of heavy metals along the aquatic food web. In: Ravera, O. (ed.) Ecological Effects on heavy metals speciation in aquatic ecosystems. Ispra-courses, Ispra-Itali, 31pp.
- Behel Jr., D., Nelson, D. W. and Sommers, L. E. (1983). Assessment of heavy metal equilibria in sewage sludge treated soil. *J. Env. Qua.* **12**: 181-186.
- Boekhold, A. E., Temminghoff, E. J. M. and Vanderzee, S. E. A. T. M. (1993). Influence of electrolyte composition and pH on Cd sorption by an acid sandy soil. *J. Soil Science.* **44**: 85-96.
- Bowen, H. J. M. (1979). Environmental Chemistry of the Elements. Academic Press, London. New York. Toronto. 333pp.
- Brar, M. S. and Sekhon, G. S. (1976). Interaction of Zinc with other micronutrient cations I.effect of Cu on Zn adsorption by wheat seedlings and its translocation within the plant. *Plant Soil.* **45**: 137-143.
- Brummer, G. W. (1986). The importance of chemical speciation in Environmental Processes. Eds. Bernhard, M., Brinckman, F. E. and Sadler, P. J. Springer-Verlag Berlin. Pp-169-192.
- Carrol, D. (1970). Clay minerals; A guide to their X-ray identification. Special Paper 126. Geol. Soc. America. Boulder, Colorado. 80p.
- Cavallaro, N. and McBride, M. B. (1978). *Soil Sci. Soc. Am. J.* **42**: 550.
- Chakrapani, G. J. and Subramanian, V. (1993). Heavy metals distribution and fractionation in the sediments of the Mahanadi River basin, India. *Env. Geol.*, **22**: 80-87.
- Chao, T. T. (1984). *Geochem. Explor.* **20**: 101.

- Donahue, R. L., Shickluna, J. C. and Robertson, L. S. (1971). Soils and plant nutrition, In: An introduction to soils and plant growth. Prentice-hall, inc., New Jersey. Pp. 222-223.
- Drever, J. I. The effect of land plants on weathering rates of silicate minerals. *Geochim. Et Cosmochim. Acta*, **58(10)**, 2325-2332.
- Dudka, S., Piotrowska, M. Chlopecka, Alopatek, J. (1990). Speciation, mobility and phytoavailability of trace metals in a sewage sludge mended soil IUNG R(270), Pulawy.
- Duerer, R. Forstner, U. and Schmoll, G. (1978). Selective chemical extraction of carbonate associated trace metals in recent Lacustrine sediments. *Geochim. Cosmochim. Acta*. **42**: 425-427.
- Eaton, A. (1979). Observations in the Geochemistry of soluble Cu, Fe, Ni and Zn in the San Francisco Bay Estuary. *Environ. Science. Technol.* **13**: 25-432.
- Elliott, H. A., Liberatii, M. R. and Huang, C. P. (1986). Competitive adsorption of heavy metals. *J. Env. Qua.* **15**: 214-219.
- Evans, L. J. (1989). Chemistry of metal retention by soils. *Env Sci and Tech.* **23**: 1046-1056.
- Fassel, V. A. (1978). Quantitative elemental analysis by Plasma Emission spectrometry. *Science* **202**: 183-191.
- Floyd, M. A., Fassel, V. A. and D'silva, A. P. (1980). Computer controlled scanning monochromator for the determination of 50 elements in geochemical and environmental samples by ICP-AES. *Anal. Chem.* **52**: 2168-2172.
- Forbes, E. A., Posner, A. M. and Quirk, J. P. (1976). The specific adsorption of divalent Cd, Co, Cu, Pb and Zn on Goethite. *J. Soil Science*, **27**, 154-166.
- Forstner, U. (1993). Metal speciation: General concepts and applications. *International J. Environ. Anal. Chem.* **51**: 5-23.
- Gale, S. J. and Hoare, P. G. (1991). Quaternary sediments-Petrographic methods for the study of unlithified rocks. Wiley, New York, pp. 69-127.
- Garcia-Miragaya, J. and Page, A. L. (1976). Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. *Soil Sci. Soc. Am. Journal.* **40**: 658-663.
- Gast, R. G. (1979). Encyclopedia of soil science. R. W. Fairbridge and C. W. Finkl (eds.) Stroudsburg Pa., Dowden, Hutchinson and Ross.
- Goldschmidt, V. M. (1954). Geochemistry. Clarendon, Oxford. 730pp.

- Griffin, G. M. (1971). Interpretation of X-ray diffractograms data. In Procedures. In: mR. E. Carver (ed.), sedimentary petrology. Wiley, New York, pp. 541-569.
- Gupta, S. K. and Chen, K. Y. (1975). *Environ. Lett.* **10**: 129.
- Haynes, R. J. (1980). Ion exchange properties of roots and ionic interactions within the root apoplasm: Their role in ion accumulation by plants. *Bot. Rev.* **46**:75-99.
- Hill, G. C. and Holman, J. S. (1983). Chemistry in context, 2<sup>nd</sup> edn. Thomas Nelson and Sons Ltd., Walton-on-Thames.
- Himes, F. L. and Barber, S. A. (1957). Chelating ability of soil organic matter. *Soil Sci. Soc. Am Proc.* **21**: 368-373.
- Jackson, M. L. (1968). Weathering of Primary and Secondary minerals. *Tyrans 9<sup>th</sup> Int. Congr. Soil science. Adelaide.* **4**: 281-292.
- Jarvis, S. C. and Jones, L. H. P. (1980). The contents and sorption of Cd in some agricultural soils of England and Wales. *J. Soil Science.* **31**: 469-479.
- Jenne, F. A. (1968). Controls of Mn, Fe, Co, Ni, Cu and Zn concentrations in soil and water; the significance of Fe and Mn oxides. *Am. Chem. Soc. Adv. Chem. Ser.* **73**: 337-387.
- Jha, P. K., Subramanian, V., Sitasawad, R. and Grieken, R. V. (1990). Heavy metals in the sediments of the Yamuna River (a tributary of River Ganges, India). *Sci. Total Env.* **95**: 7-21.
- Kabata-Pendias, A. and Pendias, H. (1992). Trace elements in soils and plants. CRC Press Boca Raton.
- Kumaresan, M. and Riyazuddin, P. (1999). Chemical speciation of trace metals. *Res. J. Chem. Environ.* **3**(4).
- Kuo, S. and Baker, A. S. (1980). *Soil Sci.Soc. Am. J.* **44**: 969.
- Kuo, S., Lellum, E.J. and Baker, A.S. (1985). *Soil Science.* **139**: 122.
- Lauchli, A. (1976). Apoplasmic transport in tissues, In U. Luttge and M. G. Pitman, Eds. Transport in plants. Springer –Verlag, New York. pp22-29.
- Lee, S. Z., Allen, H. E., Huang C. P. Sparks, D. L., Sanders, P. F. and Peijnenburg, W. J. G. M. (1996). Predicting soil-water partition coefficients for Cd. *Env Sci and Tech.* **30**: 3418-3424.

- Lelong, F., Tardry, Y., Grandin, G., Trescases, H. and Boulange, B. (1976). Pedogenesis, chemical weathering and processes of formation of some supergene ore deposits. In: Wolf, K. H. (eds.) Handbook of stratabound and stratiform ore deposits. Elsevier, Amsterdam. **3**: 93-173.
- Lelyeter, L and Probst, J. L. (1998). A new sequential extraction procedure for the speciation of particulate trace elements in river sediments. *International J. Environ. Anal. Chem.* **51**: 97-108.
- Lindsay, W. L. (1979). Chemical equilibria in soils, John-Wiley and sons, New York.
- Luo, Y. M. and Christie, P. (1998). Bioavailability of Cu and Zn in soils treated with alkaline stabilized sewage sludges. *J. Env. Qua.* **27**: 335-342.
- Ma, L. Q. and Rao, G. N. (1997). Chemical fractionation of Cd, Cu, Zn and Ni in contaminated soils. *J. Env. Qua.* **26**: 259-264.
- Massey, H. F. (1972). *Soil Science*. **114**: 17.
- Maxwell, A. J. (1968). Rock and mineral analysis. In: P. J. Elving and I. A. Koltoff (eds.), Chemical Analysis (vol. 27), Interscience Publishers, New York, 559 p.
- McGrath, S. P. and Loveland, P. J. (1992). The soil Geochemical Atlas of England and Wales. Blackie, Glasgow.
- McKenzie, R. M. (1980). The adsorption of Pb and other heavy metals on oxides of Fe and Mn. *Aust. J. Soil Res.* **18**: 61-73.
- McLaren, R. G. and Crawford, D. V. (1973). Studies in soil Cu I: The fractionation of Cu in soils. *J Soil Science.* **24**: 172-181.
- McLaren, R. G., Swift, R. S. and Williams, J. G. (1981). The adsorption of Cu by soil materials at low equilibrium solution concentrations. *J. of Soil Science*, **32**: 247-256.
- Miller, J. E. Hassett, J. J. and Koeppel, D.E. (1977). Interactions of Pb and Cd on metal uptake and growth of corn plants. *J. Environ Qual.* **6**:18-26.
- Minnich, M. M., McBride, M. B. and Chaney R. L. (1998). Cu activity in soil solution: Relation to Cu accumulation in young snapbeans. *J. Soil. Sci. Soc. Am.* **51**: 573-578.
- Muller, G. (1967). Sedimentary Petrology, I. Methods in sedimentary petrology. Hafner Publishing Company, New York, 183p.
- Nesbitt, H. W. and Young G. M. (1984). Prediction of some weathering trends of plutonic and volcanic rocks based on thermodynamic and kinetic considerations. *Geochim. Cosmochim. Acta* **54**: 1523-1534.



- Nesbitt, H. W. and Young G. M. (1989). Formation and Diagenesis of weathering profiles. *Jour. Geol.* **97**: 129-147.
- Norwell, W. A. and Lindsay, W. L. (1972). Reactions of DTPA chelates of Fe, Zn, Cu and Mn with soils. *Soil Sci. Soc. Am. Proc.* **36**: 778-789.
- Novozamski, I. Lexmond, T. M. and Houba V. J. G. (1993). A single exposure procedure of soil for evaluation of uptake of some heavy metals by plants.
- Orsini, L and Bermond, A. (1993). Application of a sequential extraction procedure to calcareous soil samples: Preliminary studies. *International J. Environ. Anal. Chem.* **51**: 97-108.
- Panda, D., Subramanian, V. and Panigrahy, R. C. (1995). Geochemical fractionation of heavy metals in Chilka Lake (East Coast of India) - a tropical coastal lagoon. *Environmental Geology*. Pp: 199-210.
- Pederson, P. F. and Price, N. B. (1982). The Geochemistry of Mn carbonate in Panama basin sediments. *Geochim. cosmochim. acta.* **46**: 59-69.
- Perel'man, A. L. (1967). Geochemistry of epigenesis. Plenum, New York. 266pp.
- Pickering, W. F. (1981). Selective chemical extraction of soil components and bound metal species. *CRC Critical Rev. Anal. Chem.* **Nov**: 233-266.
- Prusty, B. G., Godgil G. and Sahu K. C. (1994). Partitioning of heavy metals in polluted Tiri river sediments due to tailing discharges from Zawar mines, Rajasthan. *Earth Sciences in Environment*. Pp: 215-229.
- Radhakrishna, B. P. (1993). Neogene uplift and geomorphic rejuvenation of the Indian peninsula. *Curr. Sci.* **64**: 787-793.
- Ram, N. and Verloo, M. (1985). Effect of various organic materials on the mobility of heavy metals in soil. *Env Pollu.* **B10**: 241-248.
- Rieuwerts, J. S., Thornton, I., Farago, M. E. and Ashmore M.R. (1998). Factors influencing metal bioavailability in soils: Preliminary investigations for the development of a critical loads approach for metals. *Chemical Speciation and bioavailability.* 10(2).
- Russell, E. W. and Russell E. J. (1973). The food of Plants In: Soil conditions and plant growth. William Clowes and sons. Ltd. London. Pp23.
- Salomans, W. and Forstner, U. (1984). Metals in continental water. In: Metals in hydrocycle. Springer-Verlag New York. Pp. 349.
- Salomons, W. and Forstner, U. (1980). Trace metal analysis on polluted sediments-2 Evaluation of environmental impact. *Environ. Technol. Lett.* **1**: 506-517.

- Schwertmann, U. (1964). Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammonium oxalat-Lösung. *Z Pflanzenernähr dung Bodenkd.* **105**: 194-202.
- Shapiro, L. and Brannock, W. W. (1962). Rapid analyses of silicate, carbonate and phosphate a rock. *U. S. Geol. Surv. Bull.* **48**: 49-55.
- Shickluna, J. C. (1962). The relationship of pH, available P, K and Mg to soil management groups. *Michigan State University Quarterly Bulletin*, **45**: 136-147.
- Shuman, L. M. (1976). Zn adsorption isotherms for soil clays with and without iron oxides removed. *Soil Sci. Soc. Am. J.* **40**: 349-352.
- Shuman, L. M. (1977). Adsorption of Zn by Fe and Al hydrous oxides as influenced by aging and pH. *Soil Sci. Soc. Am. J.* **41**: 703-706.
- Singh, A. K, Husnain, S. L and Banerjee, D. K. (1998). Grain size and geochemical partitioning of heavy metals in the sediments of the Damodar River - a tributary of the lower Ganga, India. *Env. Geol.* **680**: 1-9.
- Singh, P. (1999). Geochemistry of the alluvial sediments of the Kaveri Floodplain, south India. Ph.D. Thesis, School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, India, 134p.
- Soon, Y. K. (1981). *J. Soil Sci.* **32**: 85.
- Sposito, G. (1983). The chemical forms of trace metals in soils In: Applied Environmental Geochemistry. Academic press, London.
- Street, J. J., Sabey, B. R. and Lindsay, W. L. (1978). *J. Env. Qua.* **7**: 286.
- Takijima, Y. and Katsumi, F. C. (1973). Cd contamination of soils and rice plants caused by Zn mining. *Soil Sci Plant Nutr.* **19**: 173-180.
- Temminghoff, E. J. M., Vander Zee, S. E. A. T. M. and deHaan, F. A. M. (1997). Cu mobility in a Cu contaminated sandy soil as affected by pH and solid and dissolved organic matter. *Env. Sci. and Technology*, **31**: 1109-1115.
- Tessier, A., Campbell, P. G. C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*. **51** (7): 844-850.
- Thornton, I. (1995). Metals in the global environment: Facts and misconceptions. International council on metals and the environment, Ottawa.
- Tiller, K. G., Gerth, J. and Brummer, G. (1984). The sorption of Cd, Zn and Ni by soil clay fractions: Procedures for partition of bound forms and their interpretation. *Geoderma*. **34**: 1-16.

- Tripathi, J. K. and Rajamani, V. (1999). Geochemistry of the loessic sediments on Delhi Ridge, Eastern Thar Desert, Rajasthan: Its implications to exogenic processes. *Chem. Geol.* **47**: 159-174.
- Vaithyanathan, P., Ramanathan, A. and Subramanian, V. (1992). Transport and Distribution of heavy metals in Cauvery River. *Water, Air and Soil Pollution.* **71**: 13-28.
- Valdiya, K. S. (1998). Late quaternary movements and landscape rejuvenation in south Karnataka and adjoining Tamilnadu in southern India shield. *Jour. Geol. Soc. India.* **51**: 139-166.
- Walter, I. and Cuevas, G. (1999). Chemical fractionation of heavy metals in a soil amended with repeated sewage sludge application. *Sci. Tot. Env.* **226**: 113-119.
- Webb, J. S., Thornton, I., Thompson, M. Howarth, R. J. and Lowenstein, P. L. (1978). The Wolfson Geochemical Atlas of England and Wales. Clarendon Press, Oxford.
- Xian, X. (1989). *Plant and Soil.* **113**: 257.
- Xian, X. and Shokohifard, G. (1989). *Water, Air and Soil Poll.* **45**: 265.
- Zhang, J., Huang, W. W. and Martin, J. M. (1988). Trace metal distribution in Huanghe. *East Coast Shelf Sci.* **26**: 499-516.

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