DETERMINATION OF TRACE METALS IN DIFFERENT PHASES OF SEDIMENTS BY SEQUENTIAL EXTRACTION METHOD

Project submitted to the Central University of Punjab

For the award of

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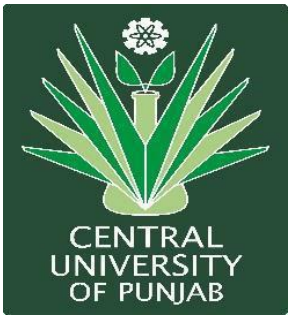
Geology

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Certificate

I declare that the project entitled **Determination of trace metals in different phases of sediments by sequential extraction method** been prepared by me under the guidance of Dr. Jitendra Kumar Pattanaik, Assistant Professor, Department of Geography and Geology, Central University of Punjab. No part of the project has formed the basis for the award of any degree or fellowship previously.

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Certificate

This is to certify that the work incorporated in this M.sc thesis entitled **"Determination of trace metals in different phases of sediments by sequential extraction method"** submitted by **Subhransu Swain** to the Central University of Punjab in fulfilment of the requirements for the award of the Degree of **M.Sc.** Earth and Geological Science, under my guidance. I further certify that this work has not been submitted to any other University or Institution in part or full for the award of any degree or diploma. Research material obtained from other sources has been duly acknowledged in the thesis. Any text, illustration, table etc., used in the thesis from other sources, has been duly cited and acknowledged.

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ABSTRACT

Determinations of trace metals in different phases fromsediments by sequential extraction method

Elements are distributed in different phase based on their affinity to different complexes present in the sediment phases. Some phases are rich in certain element due to geochemical behaviour of that element.Sediments from weathering profile and river bedload carries information about the chemical weathering intensity, neoformations, type of clay minerals formed due to alteration ofprimary mineral phase. XRD analysis gives us information about the distribution of different minerals presents in weathering profile and bedload deposits. Change in mineral assemblage from weathering profile to bedload deposits by different surficial process can be obtained from mineralogical and geochemical analysis of sediments. Semi-quantification and mineral phase identification from XRD analysis shows mineral distribution and indicate the clay mineral percentage is high in the weathering profile sediments.An analytical procedure involving sequential extraction have been developed for understanding partitioning of particulate trace metals into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residuals.Sequential leaching of weathering profile sediments indicate that the partitioning of trace elements like Pb, Ni, Cu, Zn, Tl and Thin organic phase is high and it contains 50-70% of the total. Whereas, element like Co, Cd, U is in lower concentration which is varies between 0 – 20 %.Except As, U Tl all other element shows higher (> 50%) partitioning in the organic phase of the Bed load sediments.

Key words: Sequential leaching, trace metals, weathering profile, sediment phases, XRD

(Name and signature of student) (Name and signature of supervisor)

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Chapter-1
Introduction

1.1Distribution of Element

Elements are distributed in different phases of sediment due to a) what are the different phases present in the sediment like oxide phase,carbonate,exchangeable phase which exchanges their character in different phases; b) how they are formed; and c) type of elemental distribution in different phases of sediments (Shaw,1961). Distribution of elements in the different phases of sediment helps us to understand processes like sediments formation history,environmental and depositional condition, and the weathering pattern (Shaw,1961). Therefore it is important to understand the distribution of elements in the various phases of the sediments.

1.2 Importance of sequential extraction

Several studies explained presence of particulate metals (total metal concentration)in natural water system where metals are associated with suspended matter or bottom sediments. Few attempts have beenmade to estimate the speciation of particulate trace metals that elucidate the partitioning among the various forms in which they exist. Procedure such as i) methods designed to understand the separation between residual and non-residual metals only, and ii) more elaborate methods making use of sequential extractions can be taken up for the study(Tessier et al., 1979). The former method normally involves a single extraction and provides clues between anomalous and background samples than does the determination of the total metal concentration (Gibbs, 1973). This method is simple and rapid but it is difficult to find a suitable reagent to extract non-residual metals without influencing detritus present in the sediments. Sequential extractions procedure is a time consuming process but it provides information about the origin, mode of occurrence, biological and physicochemical availability, mobilization, and transport of trace metals (Tessier et al., 1979). The purpose of this study was to examine the advantages of this method of sequential "selective" extractions for understanding partitioning of trace metals indifferent phases of sediments formed from basalt. Here releases of particulate trace metals into different chemical forms in solution under various physio-chemical conditions were studied.

1.3. Basalt rock-

Basalt rock is an igneous rock, also known as the volcanic equivalent of Gabbro. It is an ultrabasic in composition and contains essential minerals such as augite, calcic-plagioclase, iron-oxidesand olivine. Labradorite is the chief constituent of groundmass whereas the calcic plagioclase may occur as the phenocrysts.Augite frequently occurred as phenocryst and groundmass,but olivine as phenocrysts.The texture of the rock is mainly fine grained to glassy,porphyritic type texture are common and abundant gas cavities may occur near the top of basalt flows to make the rock vesicular.

1.4. Soil formation on Basalt rock-

Basalt releases much calcium and will produce only clay and silt when it weathers to soil. It is one of the most common rocks in the area, so that the black clay soils, uniform texture, coarse structure and grey clay soils which develop on the basalt, or the alluvium from it, are widespread. The grey clay

soils tend to be found on lower slopes, swales and low-lying alluvial terraces, where longer periods of water logging compared with the higher slopes, have caused the soil to develop a grey colour.Lateral seepage and runoff from higher lying areas are probably responsible for the enrichment of their subsoils with sodium and, no doubt, also with lime (Asio, 2007).

The black clay soils, uniform texture, coarse structure occur pre-dominantly on the better drained slopes of the undulating basalt plains. A small amount of sand occurs in these fine textured soils. This sand must have originated elsewhere and been blown or washed onto the basaltic soils(Asio, 2007).

Although the black and grey clay soils are widespread, duplex soils are most common soils on the basalt plains. Their subsoils can be red, red-brown, or yellow-brown in colour, and they can be calcareous or both calcareous and sodic. Several processes in the formation of soils can lead to the development of a lighter textured topsoil (A horizon) which abruptly overlies a heavy textured subsoil (B horizon), of these, the addition of some silt and fine sand to the top soil as a surface wash from different geological material on higher ground or as a windblown dust accession, is probably the most important in the development of a duplex soil on the basalt. Obviously, a long time is required before pronounced duplex characteristics can develop in the soil profile(Asio, 2007).

In some smaller areas on basalt, soils can be found which differ markedly from the black or grey clay soils and the duplex soils. In Romsey land system the typical soil is a red soil which becomes gradually heavier textured with depth and which has a weakly developed structure. Weak structure and earthy fabric - especially in the subsoil - generally occur when the soil loses its active clay minerals either through their continued weathering, to a more inert type or through their removal by leaching. These red gradational soils are the result of intense leaching and weathering of the basalt during an era of warm, humid conditions (Asio, 2007).

1.5 Basaltic terrain in India-

In India basalt out crops are found in Deccan trap, Himalayan sequence, Shyllet near Shillong and Rajmahal trap.

I.Deccan Basalt-

The Deccan Traps are one of the largest volcanic provinces in the world. It consists of more than 6,500 feet of flat-lying basalt lava flows and covers an area of nearly 200,000 square miles. Estimates of the original area covered by the lava flows are as high as 600,000 square miles (1.5 million square km).The Deccan Traps are flood basalts similar to the Columbia River basalts of the northwestern United States. The Deccan basalts may have played a role in the extinction of the dinosaurs. Most of the basalt was erupted between 65 and 60 million years ago. Gases released by the eruption may have changed the global climate and lead to the demise of the dinosaurs 65 million years ago (Gupta and Singh, 1994).

II.Himalayan Basalt-

The intrusive continental basalts of the Tethyan Himalaya are not necessarily co-magmatic feeder dykes or the hypabyssal equivalents of the middle Permian Panjal Traps flows associated with the Permo-Mesozoic rifting of the Tethys, as is generally considered. A comparative study of basic rocks

from SE Zanskar, NW Spiti and Upper Lahul shows the coexistence of geochemically different basalts in this region. The Panjal Traps of SE Zanskar and NW Spiti are tholeiitic continental flood basalts (CFB). They originated from an 'enriched' P-MORB-type magma which underwent a limited evolution by fractional crystallization and probable crustal contamination. In the adjacent Upper Lahul area, the Baralacha La Dyke Swarm shows a close spatial association with Lower Carboniferous trans-tensional syn-sedimentary faults. These dykes consist of tholeiitic to alkalic basalts, belonging to a co-magmatic suite that evolved mainly by fractional crystallization. Geochemical data indicate that the Panjal Traps and the dykes are not co-magmatically related. These characteristics imply either the coexistence, in the studied area, of contemporaneous but chemically different magmas or temporally unrelated magmatic events. The Baralacha La Dyke Swarm could be associated with a Lower Carboniferous trans-tensional tectonic event, related to an early phase of Permian rifting of Neo-Tethys (Vanny, 1993).

III. Shyllet Basalt-

Basaltic andesites of Precambrian age are reported and described for the first time from Garo Hills, Meghalaya. These volcanic occur as xenoliths within Proterozoic granitoids. Petromineralogical and petrochemical characters of the volcanics revealed them to be basaltic andesite. The basaltic andesite are observed both as porphyritic and aphyric types. The basaltic andesite xenoliths exposed due north of Chiwathegir are aphyric, fine grained, hypocrystalline, inequigranular and hyalopilitic. Microlites of plagioclase occur in a cryptocrystalline matrix composed of mafics. The basaltic andesite of Garo Hills exhibit similar petrographic characteristics to those of Archaean greenstone belts. Volcanic rocks from Garo Hills plot in the field of basaltic andesite. The basaltic andesite of Garo Hills exhibit similar petrographic characteristics to those of Archaean greenstone belts. Volcanic rocks from Garo Hills plot in the field of basaltic andesite(Rao and Sharma, 1997).

IV.Rajmahal Basalt-

Rajmahal Basalt is the provenance of Rajmahal Trap mainly from eastern India source covering part of Jharkhand,West-Bengal,Meghalaya. The Rajmahal Traps, at the junction of the Singhbhum craton towards the west and the Bengal basin towards the east, are one of the most conspicuous features on the geological map of the eastern Indian shield. It appears that around 117 Ma ago the earth opened along the palaeo-continental margin of eastern India and a huge amount of molten rock poured on to the land blanketing an area of about 4100 km^2. When identified subsurface correlative basalt in seismic and drilling results is considered, the Rajmahal Traps extend southward below the surface for at least 100 km, beneath the Tertiary sediments of the Bengal basin covering an area of about 200000 km^2. The central part, with not less than 28 lava flows of 20 to 70 m, is about 0.6 km thick. Evidently, the event, which produced such a large amount of basaltic magma on the continental surface, must have had a profound influence on the crustal evolution including present day configuration of the continental lithosphere. It has been suggested that igneous intrusion at the base of the crust may underlie all shallow flood basalts (Valdiya, 2010).

In this work sediment samples were collected from the weathering profile developed over the Rajmahal basalt and bed load from stream draining primarily Rajmahal basalt. Therefore detail description of Rajmahal basalt is given below.

Lithology:

The Rajmahal volcanic are predominantly tholeiitic basalt, quartz tholeiite, olivine tholeiite and alkali basalt. The Intertrappean Beds are composed of sedimentary rock like siltstone, claystone and shale. The Rajmahal Traps of upper Jurassic to lower Cretaceous basalts with sandstone and shale as Intertrappeans occupy the contact zone of the eastern Indian shield and the Bengal basin (Sengupta, 1988).

Geological setting:

Tectonically, the western boundary of the Rajmahal Traps is faulted one with down-throw towards the east. The eastern boundary of the Rajmahal Traps is characterized by N-S trending fault controlled basement depression that connects the Purnea basin of the Ganga valley with the Bengal basin (Tiwari and Jassal, 2003). These faulted contacts together with the Damodar Gondwana graben, represent a triple junction at the mouth of the Bengal basin, whose one arm failedas a rift (Burke and Dewey, 1973). The common pattern of structural style, Gondwana sedimentation, and Cretaceous volcanism, suggest that the Rajmahal Traps evolved through decompressional melting of mantle material along the then eastern continental margin of India following rifting of Gondwanaland (Mukhopadhyay et al., 1986; Mukhopadhyay, 2000). The rising hot and buoyant molten mantle material stretched the crust and entire lithosphere. The upper part of the crust deformed in a cold, brittle fashion separated by down-dropped valleys/grabens. The garbens may fill with up to 8 km of sediments and volcanic strata as they subside while forming basins. These volcanic rocks were formed from the eruptions of the Kerguelen hotspot in the early Cretaceous. The similarity between the geochemical data of Rajmahal volcanic and lavas of the Kerguelen Plateau confirms this. According to the plate tectonics, the Indian subcontinent was over this hot spot during the Cretaceous age.

Stratigraphy:

Rajmahal formation:- It is situated above the Dubrajpur formation and coincide the Barakar onto the crystalline basement along the western margin. It has maximum thickness 330m and thins 100m towards near the eastern of the Raniganj basin. The inter-trappean beds of the Rajmahal group contain sandstone, carbonaceous shale, grey shale and tuff.

The Rajmahal formation may be divided into four major successive zones such as:

a) Basalt lower trap flows with unfossiliferous intertrappean beds

b) Successive lava flows with highly fossiliferous intertrappean beds

c) Overlying lava flows with scarcely fossiliferous intertrappean beds

d) Lava flows with no intertrappean beds

Table-1.Lithostratigraphy of Rajmahal formations (simplified from Sengupta,1988).

FORMATION	LITHOLOGY	AGE
Rajmahal formation	Soil, Alluvium	Cretaceous Lower cretaceous Middle Jurassic
	Laterite	
	D. Upper trap flows with and without intertrappean scarcely fossiliferous	
	C. Upper trap flows with fossiliferous intertrappean bed 8 with Taeniopterisspatulata – Brachyphyllumrhombicum. Assemblage zone 3	
	B. Lower trap flows(4 to 6) with fossiliferous intertrappean beds(4 to 7) with Cladophlebisindica – Dictyozamitesindicus assemblage zone 2	
	A. Lower trap flows (1 to 3)with unfossiliferous intertrappean beds(1 to 2)	
IGNEOUS CONTACT		
Dubrajpur formation	Baked sandstone, siltstone	Lower Jurassic Triassic
	Fossiliferous siltstone with Ptylophyllumacutifolium and Gleichenitesgleichenoides Assembly zone-1	
	Pebbly sandstone	
	Coarse sandstone, shale and clay beds	

1.6. Literature Review-

For this project work following scientific papersrelated to the proposed work was referred to get background information. It helped to design the work plan and to correlate this work with the existing literature.Some of reviews are discussed below:

Teissier et al., (1979) made an analytical procedure for extraction of particulate trace metals by sequential leaching method.The experiment carried out mainly by taking fluvial river sediment and the accuracy evaluated by comparing total metal concentration with the sum of five individualfractions.The distribution of metal between various fractions does not reflect the discrete sediment phases for a given moment.Sequential extraction procedures simulate to a certain extent of various environmental conditions to which sediments may be subjected. Though this method requires more time but itprovides information about the origin,biological and physicochemical availability,mode of occurrence,mobilization and transports of trace metals.

Rauret et al., (1998) made an improvement of the BCR by the standards. Measurements and testing programme of European Commission for three steps sequential extraction procedure prior to the certification of the new sediments and soil reference materials.This method used to certify the extractable trace elements contents of sediment reference materials.This procedure ensures the comparability of data in this field.The objective of this project was to describe new sediments and soil reference materials for their extractable contents of trace metals.This procedure validates the analysis of soils and sediments, and it will also facilitate comparability of data in European Union.

Rao et al., (2007) review different methods applied for the single and sequential extraction schemes for metal fractionation in environmental samples such as soil and industrially contaminated soils, sewage sludge ,road dust and run-off, waste and other miscellaneous materials. Selective extraction

have been used to target elements species in soils, elements bound to ,associated with particulate soil phases.Radionuclide is another important area where single and sequential extraction methods are employed.

Alleyne (2004) studied soil sample from Cuba and determined elements like Ni, Cd, Cu, Zn. He modified theTessier et al. (1979) procedure, by taking the extracted fractions into HCl medium and the final measurement by flame atomic absorption spectrometry with a non-conventional nebulisation system.

Nakamaru (2005) took agricultural soils from Japan and determined the new elements Se. He applied a new sequential extraction procedure to 12 soil samples in order to quantify the effect of soil components on Se adsorption. The sequential extraction results showed that 80–100% of the adsorbed Se was recovered as Al-bound Se and Fe bound Se.

Ndzangou(2006) took podzolic soil near Quebec in Canada and determined Pb, Cr elements by complete sequential extraction procedure which has been applied for understanding the complex chemical speciation of Pb in forest soils. The distribution of Pb and Cr in the studied forest soils mainly reflectsprogressive contamination of the watershed byanthropogenic sources.

Julian and Collado (2002) said that the sequential chemical extraction (SCE) of heavy metals mention that the major problems in sequential chemical extraction are- reagent selectivity, operative definition of methods,elemental redistribution or read sorption, variable experimental conditions, scarcity of certified reference materials, major difficulty to validate the existing methods and the evaluation of its precision. In spite of all the above methodological problems, they indicate that,at the present time sequential extraction protocols constitute the better approach to describe the geochemical association of trace elements with different fractions of solid materials.

Gal(2006) take mining site soils and determined the elements like As,Sb etc. and remarked that a non-specific sequential extraction test showed As to be strongly associated with Fe and Al ox hydroxides. In the case of Sb,in addition to the crystalline Fe oxides bound Sb the Al silicate phase also appeared to be significant. At both the sites Sb appears to be chemicals more accessible than As with consistent availability despite the varied origin and host soil properties.

Hagarova(2005) worked on soil samples from Slovakia,he followed five steps of sequential extraction procedure with KH_2PO_4 + H_2PO_4(Ph 7.0,P-buffer).He remarked the sequential extraction procedure used allowed differentiation of five forms of selenium bound in the soils.Solution adsorbed ligand exchangeable and plant protein-bound.Application of the p-buffer to soils resulted in a row recovery of selenium, when compared to the total selenium contents of the respective soils.

1.7. Research Problem-

Elements are distributed in different phase based on their affinity to different complexes present in the sediment phases. Some phases are rich in certain element due to geochemical behaviour of that element.By studying the distribution of elements in different phases;it will help us to understand the process of sediments formation; environmental and depositional condition; and extent of chemical weathering in the source region.Climate, vegetation cover, microbial activity and topography controls

the chemical weathering and sediment production, hence it may affect the distribution of element in the different phases which is still debatable.

1.8. **Objective-**

In this study following objectives were taken up to answer the above research problem.

- To determine the mineral phase present in the sediment samples using XRD analysis.
- To estimate distribution of trace and heavy metals in the different phases of sediments using sequential leaching followed by ICP-MS analysis.
- To compare elemental distribution in the sediments of river bed load and weathering profile.

Chapter-2
Material and Methods

2.1 Sampling and analytical method-

The study area is in the Sahebganj district of the Jharkhand state. This district is surrounded by small part of Bhagalpur in the north and Kathiar district of Bihar state and the east by West-Bengal. Topography of this area is mainly covered with basaltic flows of Rajmahal traps. Major soil typesare black in colour and originated from basaltic lava and other types of soils such as red soil, eroded soil, foothill soil, tal soil and alluvial soil are present.For this work,total eight numbers of samples were collected out of which five samples were from weathering profile and three from bed loads of Ghumani River draining Rajmahal basalt. Weathering profile samples are collected from various elevations showing different degree of weathering and Bed loads are collected form middle of the river to avoid local contaminations. For sample collection PP/plastic scoop were used to avoid metal contamination from metallic scoop.

Lab Work: The samples brought to lab and then dried at 51°C in a hot air oven.After dried,the samples are first grinded by agate mortar / hand only to disintegrate large agglomerates and then coarser size fraction >2mm was separated by sieving.After that the samples were homogenized by cone and quadratic method,half of the samples were kept for future work and half taken for grinding by Restch RS 200 cup mill using agate cup and discand stored at room temperature.

2.2. XRDAnalysis:

X-ray diffraction (XRD) is a popular analytical technique, which has been used for the analysis of both molecular and crystal structures, qualitative identification of various compounds, quantitative resolution of chemical species, measuring the degree of crystallinity, isomorphous substitutions, stacking faults, polymorphisms, phase transitions, particle sizes etc. (Baron,2016). When X-ray light reflects on any crystal, it leads to form many diffraction patters and the patterns reflect the physico-chemical characteristics of the crystal structures. In powder specimen, diffracted beams are typically come from the sample that reflects its structural physico-chemical features. Thus XRD technique can analyze structural features with other ambiguities of a wide range of materials such as inorganic catalysts, superconductors, bio molecules, glasses, polymers and so on(Baron,2016).

XRD fundamental principle

InXRD, a monochromatic X-raybeam is focused on sample material to resolve structural information in the crystal lattice. Usually, the materials are composed of repeating uniform atomic planes which make up their crystal. Typically, polychromatic X-rays are produced in a special tube called cathode-ray tube. Filtering polychromatic X-rays through a monochromator produces monochromatic radiation which hits onto the material atomic planes, separating the diffracted, transmitted and absorbed rays (Baron, 2016).

X-rays are produced within a closed tube under vacuum atmosphere. Application of 15-60 kilo- volts current within the tube gives electrons which hit a Cr, Fe, Co, Cu, Mo or Ag anode from which X-ray beams are generated. Thus, produced X-rays are then collimated and directed onto the powder

sample. Interactions of incident X-rays with the sample atomic planes create diffracted, transmitted, refracted, scattered and absorbed beams according to Braggs law which given below-

$$n\lambda = 2d \sin \theta$$

Where n is an integer defining order of diffracted beam, λ represents wavelength of the incident X-ray beam, d marks the distance between near atomic planes or d-spacings, and represents the angle of the incidence X-ray. The degree of diffracted X-rays depends on arranging the materials atomic planes on crystal lattice. The law recounts diffraction angle and lattice atomic planes spacing at specific wavelength of electromagnetic radiation. A detector is used to detect diffracted X-rays followed by processing and counting of the diffracted rays to give rise diffracted or pattern beams. Changeover of diffracted patterns into d-spacings allows recognition of the unknown sample. Typically materials are identified by comparing the diffracted pattern beams with many reference patterns stored in the JCPDS library (Guinier, 1963).



Figure 1. Photograph of XRD machine used for sample analysis and installed at Inter University Accelerator Centre, New Delhi.

2.3. XRF

XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays (“a fingerprint”) that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition*(www.thermofisher.co/xrf analysis).*XRF (X-ray fluorescence) is a non-destructive analytical technique used to determine the elemental composition of materials. XRF analyzers determine the chemistry of a sample by measuring the fluorescent (or secondary) X-ray emitted from a sample when it is excited by a primary X-ray source. Each of the elements present in a sample produces a set of characteristic fluorescent X-rays ("a fingerprint") that is unique for that specific element, which is why XRF spectroscopy is an excellent technology for qualitative and quantitative analysis of material composition *(www.thermofisher.co/xrf analysis).*

The X-ray fluorescence process*(www.thermofisher.co/xrf analysis)*:

1. A solid or a liquid sample is irradiated with high energy X-rays from a controlled X-ray tube.
2. When an atom in the sample is struck with an X-ray of sufficient energy (greater than the atom's K or L shell binding energy), an electron from one of the atom's inner orbital shells is dislodged.
3. The atom regains stability, filling the vacancy left in the inner orbital shell with an electron from one of the atom's higher energy orbital shells.
4. The electron drops to the lower energy state by releasing a fluorescent X-ray. The energy of this X-ray is equal to the specific difference in energy between two quantum states of the electron. The measurement of this energy is the basis of XRF analysis.

Most atoms have several electrons orbital (K shell, L shell, M shell, for example). When x-ray energy causes electrons to transfer in and out of these shell levels, XRF peaks with varying intensities are created and will be present in the spectrum, a graphical representation of X-ray intensity peaks as a function of energy peaks. The peak energy identifies the element, and the peak height/intensity is generally indicative of its concentration (www.thermofisher.com/elements spectroscopy).

2.4. Sequential Leaching: Before going for extraction procedure main objective is the selection of fraction, whichis described below.

Fraction 1: Exchangeable- Numerous studies performed on sediments or on their major constituents (clays,hydrated oxides of iron and manganese, humic acids) have demonstrated the adsorption of trace metals; changes in water ionic composition (e.g., in estuarine waters) are likely to affect adsorption-desorption processes (Teissier et al., 1979).

Fraction 2: Bound to Carbonates-Several workers have shown that significant trace metal concentrations can be associated with sediment carbonates; this fraction would be susceptible to changes of pH (Teissier et al., 1979).

Fraction 3:Bound to Iron and Manganese Oxides- It is well established that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic(i.e., low Eh)conditions (Teissier et al., 1979).

Fraction 4:Bound to Organic Matter-Trace metals may be bound to various forms of organic matter: living organisms, detritus, coatings on mineral particles, etc. The complexation and peptization properties of natural organic matter (notably humic and fulvic acids) are well recognized, as is the phenomenon of bioaccumulation in certain living organisms. Under oxidizing conditions in natural waters, organic matter can be degraded, leading to a release of soluble trace metals (Teissier et al., 1979).

Fraction 5:Residual- Once the first four fractions have been removed, the residual solid should contain mainly primary and secondary minerals, which may hold trace metals within their crystal structure. These metals are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature (Teissier et al., 1979).

Leaching Procedure–After a critical evaluation of the available literature, the following chemical extraction methods were retained for the further study, the quantities indicated below refer to 1 gram sediment samples i.e the dry weight of original sample used for the initial extraction. The "selective" extractions were conducted in centrifuge tubes (polypropylene, 50 ml) to minimize losses of solid material. Between each successive extraction, separation was effected by centrifuging at 7000 rpm for 15 min. The supernatant was removed with a pipette and analyzed for trace metals, whereas the residue was washed with 5 ml of deionised water; after centrifugation for 10 min, this second supernatant was discarded and again another wash done by deionises water for same time as above. The volume of rinse water used was kept to a minimum to avoid excessive solubilisation of solid material, particularly organic matter. Deionised water used in preparing stock solutions.The extraction procedure described above is differentiated by the action of different chemicals,which are different for different phase of extraction (Teissier et al., 1979).

a.**Exchangeable** – The sediments are extracted at room temperature for 1 hour with 8 ml of magnesium chloride solution (1M $MgCl_2$,pH 7.0) with continuous agitation (Teissier et al., 1979).There are also many reagents including ammonium acetate,sodium acetate and magnesium chloride has been liberating exchangeable metals.From the above,earlier ammonium acetate has been widely used but some worker said it attacked the carbonate.Except this,whenever the other two reagents are treated lesser amount of calcium fraction found when sodium acetate used rather than $MgCl_2$ in the preliminary extraction (Teissier et al., 1979).That effect described the complexing ability of acetate.For this reason it has recently been found to be an effecting reagent for describing specific adsorbed trace metals, MgCl2, was finally selected as an initial reagents for the sequential extraction procedure.

b.**Bound to Carbonate** – The residue from (a) was leached at room temperature with 8 ml of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation 5 hour in temperature 25^oc was maintained and the time necessary for complete extraction was evaluated (Teissier et al., 1979).Some workers have demonstrated that the lower pH values leads to a partial attack of Fe and Mn oxides.The timerequired for carbonate dissolution will depends upon such factor as particle size,percentage and type of carbonates present.The extraction time is likely to be sufficient for more samples of finely divided suspended solids.However, for coarse bottom sediments with high carbonate contents,longer leaching times and frequent pH adjustment necessary.

c.**Bound to Fe-Mn Oxides**– The residue from (b) was extracted with 20 mlof 0.04 M $NH_2OH.HCl$ in 25% (v/v) HOAc (Teissier et al., 1979). The latter experiments were performed by heating sample 96 ± 3 °C for 6 hour with occasional agitation and the time needed for complete dissolution of the free iron oxides was evaluated (Teissier et al., 1979).For this work most often used both Hydroxylamine hydrochloride-acetic acid and sodium dithionite-citrate.Gupta and Chen, (1975),who employed both the combination in parallel experiments,reveals the trace metals concentrations were, are consistently lower in the leachates obtained with dithionite citrate than in those obtained by another one.The difference was greatest for those trace metals which forms the most insoluble sulphide salts. several additional problems are raised by the utilization of the dithionite-citrate couple: (i) dithionite is highly contaminated with zinc and its purification by a chelation-extraction procedure proves difficult (ii) frequent clogging of the burner is observed upon analysis of the aqueous extracts by flame atomic absorption spectrophotometry, due to the high salt content of the extraction solution; to

minimize this problem, a chelation-extraction step is required before analysis (Teissier et al., 1979).Consideration of these problems led us to eliminate the dithionite-citrate couple from further study.

d.**Bound to Organic Matter** –To the residue from bound to Fe-Mn oxide were added 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 adjusted to pH 2 with HNO_3, and the mixture was heated to 85 ± 2 °C for 2 h with occasional agitation. A second 3-mL aliquot of 30% H_2O_2(pH 2 with HNO_3) was then added and the sample was heated again to 85 ± 2 °C for 3 h with intermittent agitation. After cooling, 5 ml of 3.2 M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was diluted to 20 ml and agitated continuously for 30 min. The addition of NH_4OAc is designed to prevent adsorption of extracted metals onto the oxidized sediment. Hydrogen peroxide in an acidic medium is generally used to oxidize organic matter in soil and sediment analysis, even though oxidation of all forms of organic matter may not be complete. More efficient methods for destroying organic matter do exist,but they usually suffer from a lack of specificity in the sense that they may also affect a partial attack of silicate lattices. In the present study, a method involving treatment with hot hydrogen peroxide in a nitric acid medium was adopted.

e.**Residual**–The residue from (d) was digested with a HF-$HClO_4$ mixture according to the procedure described above by centrifuging and washing.

After the completion of thecentrifugation now all samples are evaporated by hotplate keeping samples in Teflon vial with maintaining temperature 160^0C.After the complete evaporation of the of sample,1ml HNO_3 added with dry sample and mix properly with maintain previous temperature for the evaporation.The samples are mix with 5 ml of HNO_3three times and maintain volume make up of 15 ml for each sample. After this the samples were diluted to 10X using MQ grade water. Trace metals concentration of samples were analysed using ICP-MS installed at Central Instrumentation Lab, Central University of Punjab, Bathinda.

Chapter-3
Result and Discussion

3.1 Mineral phase analysis using XRD

Homogenized powered sediment samples were analyzed as per the details given in the methodology sections. Using X-pert high score software XRD spectrums were analyzed to semi-quantify and to identify different mineral phase present in the samples. Using this method precise quantification is not possible but it will provide semi-quantification of minerals present the sediments. The important and abundant mineral present in the sediments listed in the Table 2a,2b and 2c.The percentage of the individuals mineral presents are also listed in the above tables.A typical XRD spectrum with different mineral peak is shown in above figure 2.The spectrum of each sediment were compared with one another and also compared with bedload sediments to see the variations in the mineralogical composition. The XRD analysis data shows about the mineral present in the fresh basalt (Table 2a, Figure 3),weathering profile (Table 2b) and bed load sediments (Table 2c). The fresh basalts of Rajmahal area mainly composed sodic plagioclase,pyroxene rich in augite,olivine as it is tholeitic Basalt flows, quartz and some mafic rich hornblende. The quantity of the above mineral changes from fresh basalt to weathering profile and from weathering profile to bed load sediments. Ilmenite is a common accessory mineral in igneous rocks. Most ilmenite forms during the slow cooling of magma chambers and is concentrated through the process of magmatic segregation.Ilmenite has a high resistance to weathering but due to disintegration of primary rock grains of ilmenite disperse within the sediment.Due to high specific gravity of ilmenite grains it segregate during stream transport and accumulate as “heavy minerals” in bed load. Ilmenite generally decreases from top to bottom,as the bottom portion were very high resistance to weathering as compare to the upper portion of the weatheringprofile.

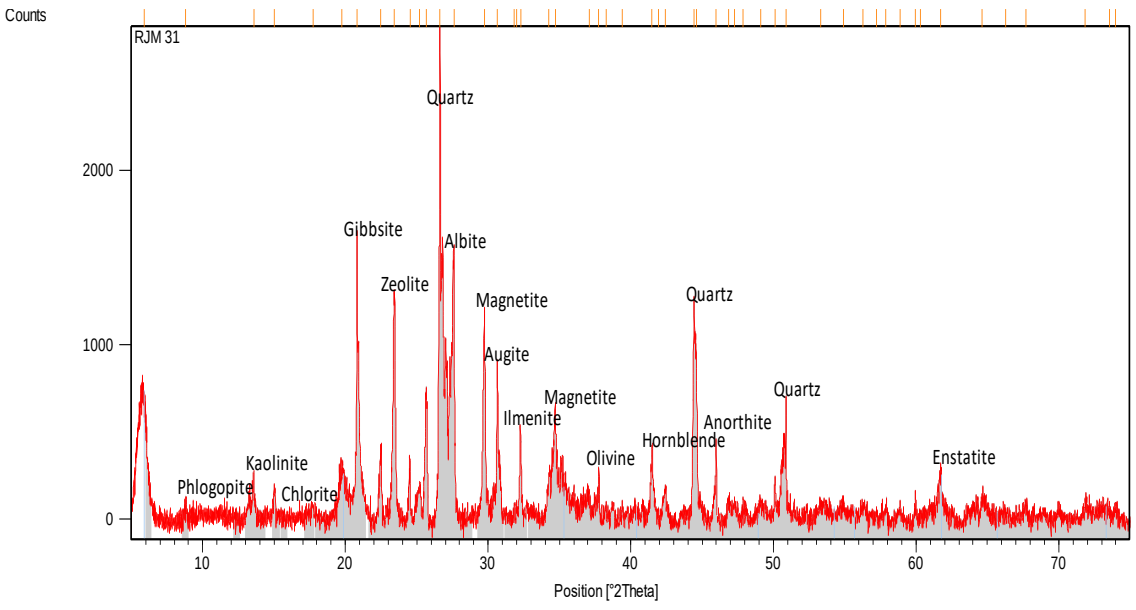


Figure 2. Spectrum showing different minerals peak

Table 2(a) XRD data of fresh Basalts-

Mineral Name	Semi Quantification [%]
Olivine	9
Albite calcian low	27
Augite	10
Quartz	7
Magnetite	5
Nepheline	6
Hornblende	6
Anorthite	32

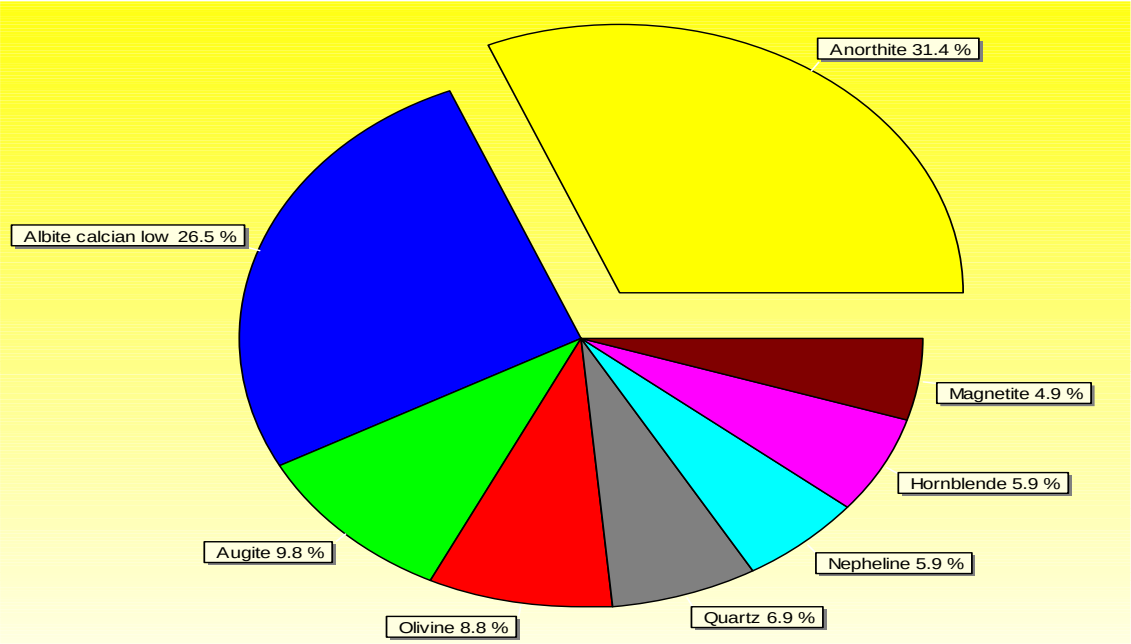


Figure 3. Pie chart showing fresh Basalts minerals

The albite composition in weathering profile generally increases from upper profile to the bottom of the bed (table 2.b, Figure 4) as the weathering rate mainly higher in the upper profile and the lower are far away from weathering reagents. Quartz is the most unwanted mineral in every rocks, its quantity generally increase from top to bottom of the bed. As the quartz the most resistant mineral to weathering, it just broken into smaller fragments so there is variation in quantity from top to bottom. Magnetite as the iron bearing mineral is the prominent mineral in profile and also its quantity increases from top to bottom. Like this the other mineral like pyroxene also increases from top to bottom. Chlorite, olivine and anorthite concentration are higher in the weathering prominent profile as compare to the lower one.

The XRD data of the bedload sediments are mainly rich in mineral likes kaolinite, pyroxene,stilbite,clinoenstatite,gibbsite and olivine. From the bedload the minerals are same but it is different than the weathering profile sediments.The clay minerals mainly formed by loss of silica

from weathering profile that are rich in alumina-silicates. Kaolinite formed by loss of cations like Ca, Na, K and silica and separation of Al and Fe from Feldspar and further loss of silica converts the kaolinite to gibbsite.

Feldspar – (loss of cations like Ca, Na, K) →kaolinite – (loss of Si) →gibbsite($Al(OH)_3$)

The bedload sediments are also contain the same minerals as the above except Ankerite and stilbite. The clay mineral generally increases from profile to bed load sediments and their formations illustrated by reaction given below-

Metals in minerals are exchanged by H^+ with cation release as metal cation(K^+,Ca^{2+},Na^+. etc) and potential neoformation of clay mineral (kaolinite,smectiteetc.) retained from ions (Al^{3+},O^{2-},Si^{4+}).*K-Feldspar* + H^+ = *Kaolinite* + K^+ + H_2SiO_4

Weathering of Na-feldspar (albite) to kaolinite*: albite + carbonic acid + water → sodium ion + bicarbonate ion + silicic acid + kaolinite*

$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow 2Na + 2HCO_3 + 4H_4SiO_4 + Al_2Si_2O_5(OH)_4$

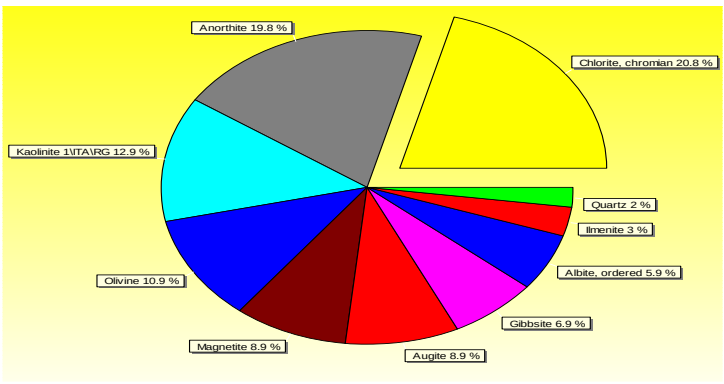
From the XRD spectrum of the fresh basalt,weathering profile and bedload sediments the distributions are mainly same mineral composition except clay mineral that are formed by chemical weathering. The XRD spectrum,table and description suggest that the mineral presents in fresh basalt,weathering profile and bedload sediments and their distribution in different phase by change in quantity and the appropriate chemical agents that required for modifying their composition from source rock to bed load sediments.

Table 2(b) XRD data of weathering profile

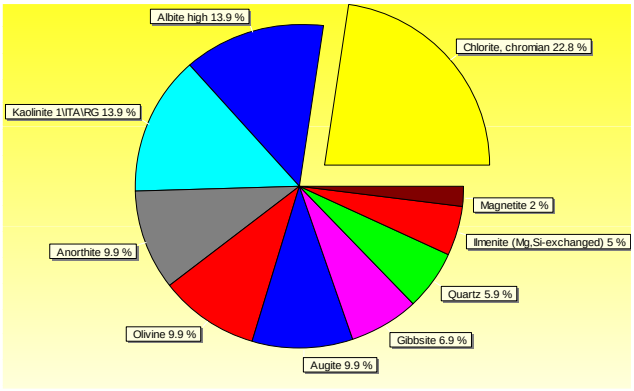
Sample name	**Ilmenite**	**Albite**	**Quartz**	**Magnetite**	**Augite**	**Kaolinite**	**Gibbsite**	**Chlorite**	**Olivine**	**Phlogopite**	**Anorthite**
RJM-4	3	4	2	9	9	13	7	21	11		20
RJM-13	5	14	6	2	10	14	7	23	10		10
RJM-22	3	14	5	2	14	11	6	19	11	3	12
RJM-31	1	8	14	14	12	8	4	13	8	18	
RJM-36	2	27	10	1	9		5	15	8	2	21

Table 2(c) XRD data of Bed load sediments

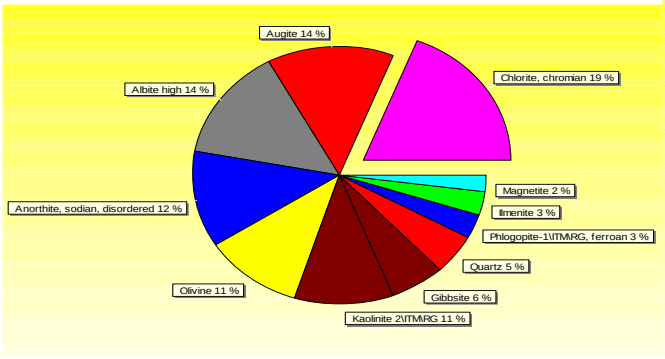
Sample name	**Quartz**	**Albite**	**Phlogopite**	**Ankerite**	**Stilbite**	**Clinoenstatite**	**Kaolinite**	**Gibbsite**	**Olivine**
LOC-5	45	6	9	2	2	13	7	7	9
LOC-14	43	6	7	2	1	10	19	4	9
LOC-18	52	5	13	1	1	5	16	4	5



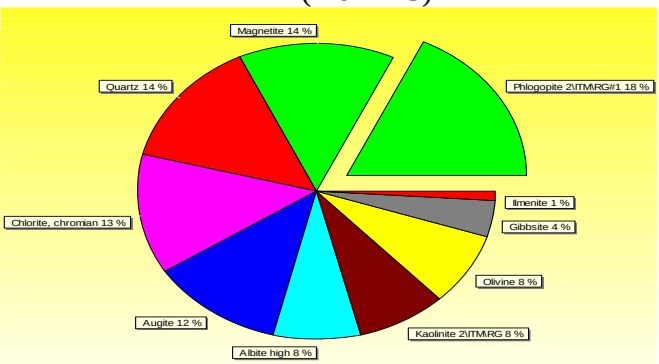
(RJM 4)



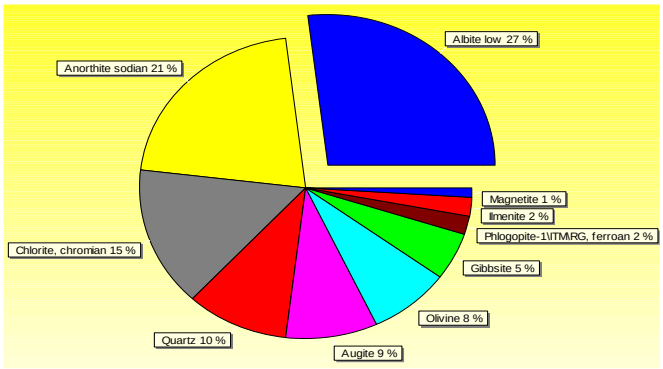
(RJM 13)



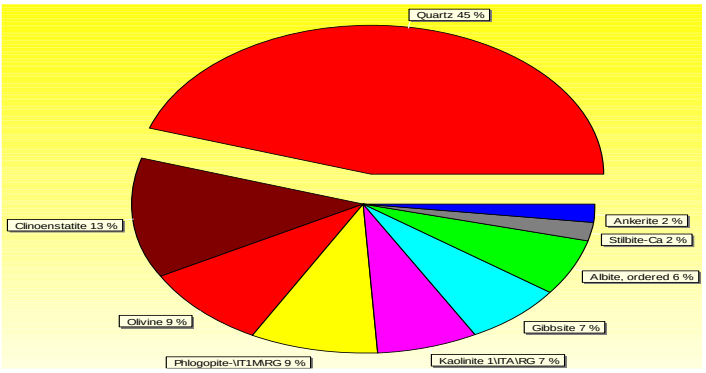
(RJM 22)



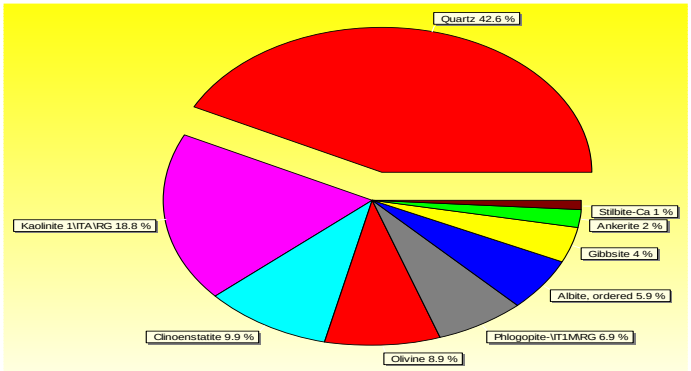
(RJM 31)



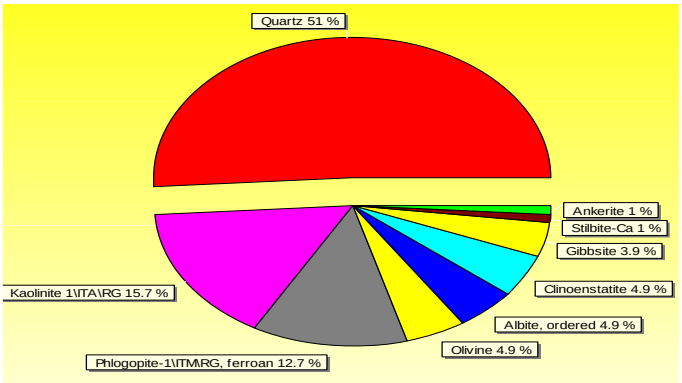
(RJM 36)



(LOC 5)



(LOC 14)



(LOC 18)

Figure 4. Pie chart showing mineral distribution in weathering profile and bed load sediments

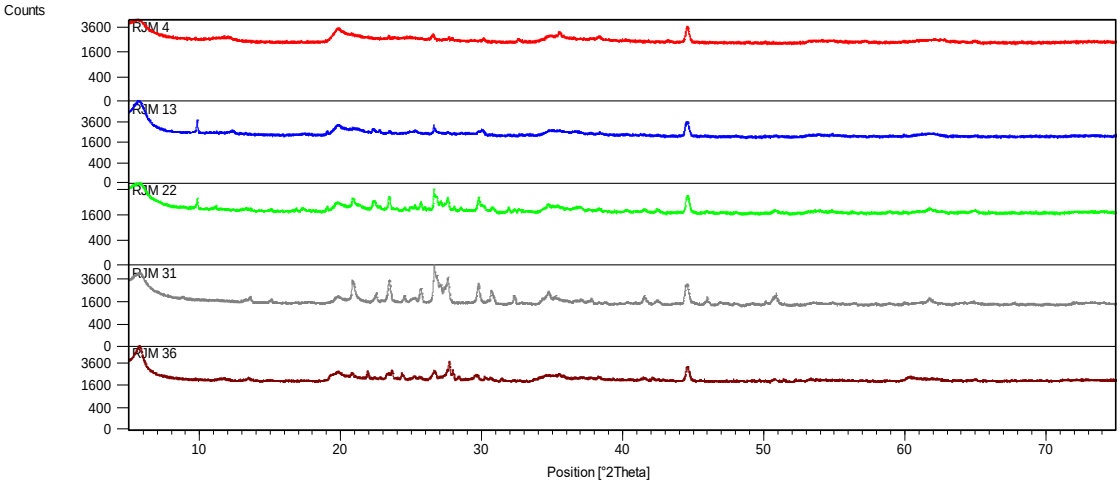


Figure 5. Comparison of XRD spectrum of weatheringprofile sediments

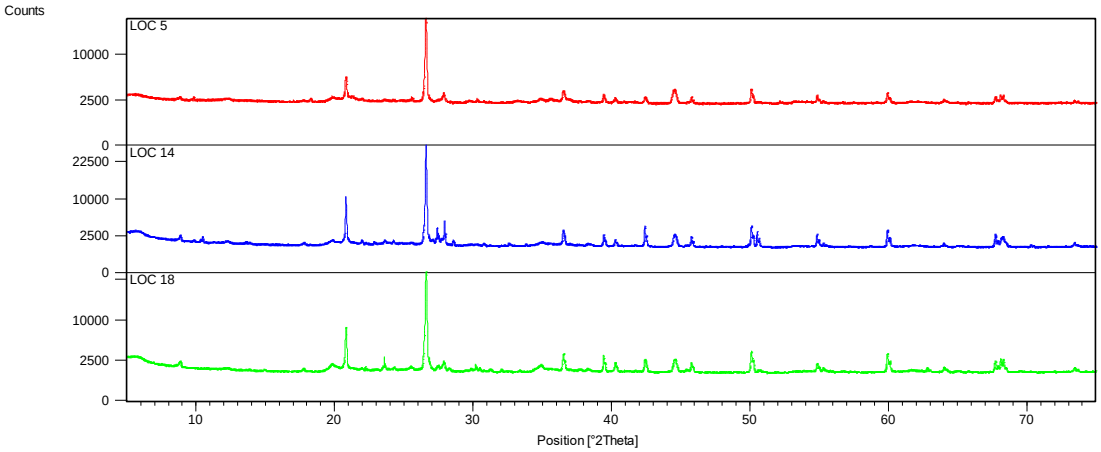


Figure 6.Spectrum comparing Bed load sediments

3.2. Chemical analysis of bulk sediments using XRF:

Major oxides of bulk sediments were analysed using XRF and results are given in the table 3.

Table 3.XRF analyses of bulk sediments-

Sample name	**RJM 4**	**RJM 13**	**RJM 22**	**RJM 31**	**RJM 36**	**LOC 14**	**LOC 18**
Al_2O_3 (%)	16.636	14.955	13.691	13.235	13.743	9.771	13.251
CaO (%)	1.633	2.396	2.086	1.028	3.07	1.256	1.108
Fe_2O_3 (%)	16.778	14.891	12.114	9.187	13.514	6.829	7.189
K_2O (%)	0.335	0.709	3.176	6.596	1.357	1.68	1.799
MgO (%)	1.055	2.693	1.268	0.926	4.863	0.946	1.317
Na_2O (%)	0.016	0.029	0.115	0.1	0.685	0.446	0.336
SiO_2 (%)	48.988	51.908	54.679	55.072	51.809	62.216	59.758
MnO (%)	0.28	0.1	0.15	0.08	0.18	0.1	0.14

Table 4: ICP –MS result (raw data: without dilution factor and normalization) of trace metal concentration of different phase in ppb.

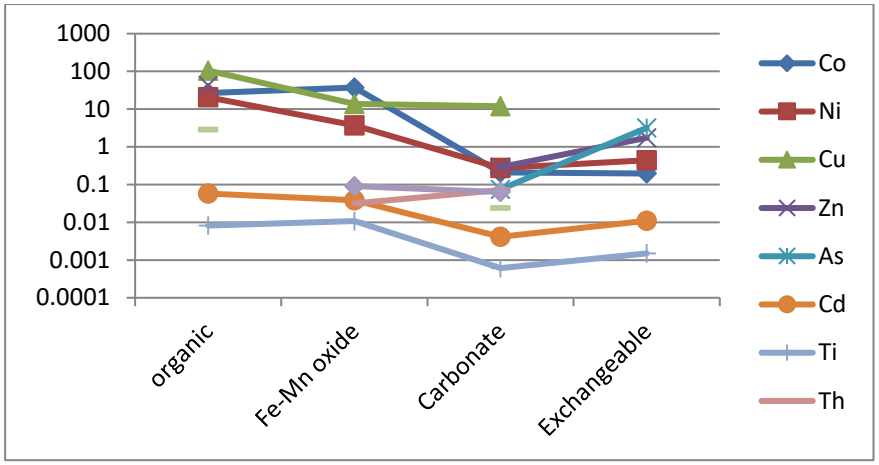
Sl. no.	Sample Name	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	TI	Pb	Th	U
Organic Phase													
1	RJM 4/1d	232.7	140.1	722.7	336.6	1.6	119.5	0.5	508.1	0.4	24.6	12.7	1.1
2	RJM 13/2d	50.2	54.5	100.5	232.9	5.0	69.5	0.5	123.6	0.8	34.2	26.9	2.3
3	RJM 22/3d	155.6	151.8	180.4	504.8	3.1	1001.5	2.3	3014.8	0.7	52.4	37.3	1.8
4	RJM 31/4d	167.8	105.0	205.8	265.8	4.3	229.3	0.6	401.2	0.6	54.6	42.6	3.6
5	RJM 36/5d	107.1	192.8	454.8	381.4	0.9	121.5	0.2	595.2	0.1	6.2	4.9	0.4
6	LOC 18/8d	132.5	114.1	277.7	339.7	1.0	899.5	0.6	1626.8	0.4	35.7	26.7	1.1
7	RJM 22/9d	37.2	52.7	81.7	129.8	6.1	58.3	0.2	106.9	0.5	26.3	25.2	1.7
8	LOC 14/10d	113.3	122.5	151.1	358.5	3.4	938.3	1.8	2679.1	0.7	53.8	42.3	2.1
9	Blank/11d	0.2	1.0	12.5	42.9	2.3	16.8	0.1	6.4	0.3	2.6	23.2	1.4
Fe-Mn Oxide Phase													
10	Blank/11c	0.4	3.7	13.1	42.8	0.7	16.4	0.0	9.7	0.2	1.6	1.1	0.2
11	LOC 14/10c	84.3	18.5	26.4	111.5	0.6	27.8	0.2	131.3	0.1	13.5	1.4	1.1
12	RJM 22/9c	167.3	47.6	46.7	97.5	0.8	256.5	2.5	288.6	0.2	3.0	1.8	0.7
13	LOC 18/8c	85.6	16.9	13.5	90.8	0.7	26.4	2.8	113.3	0.3	13.5	1.2	0.7
14	RJM 36/5c	148.0	65.2	74.2	109.4	0.2	29.0	0.6	217.0	0.3	2.2	0.9	0.4
15	RJM 31/4c	307.1	46.5	32.2	69.3	0.4	105.5	0.9	137.5	0.1	5.7	0.5	0.6
16	RJM 22/3c	311.3	30.7	115.4	40.1	0.4	36.4	0.3	319.2	0.1	6.1	1.4	0.8
17	RJM 13/2c	191.0	35.1	52.5	75.9	0.2	166.8	0.8	246.6	0.1	11.8	1.6	0.4
18	RJM 4/1c	254.1	73.6	64.7	148.7	0.7	353.6	4.2	405.2	0.2	4.2	2.1	1.1
Carbonate Phase													
19	Blank/11b	0.3	0.4	22.2	8.0	bd	8.9	bd	1.3	0.1	0.2	0.1	0.3
20	LOC 14/10b	0.6	3.5	37.5	13.9	0.2	12.5	bd	81.7	0.3	1.1	0.7	0.7
21	RJM 22/9b	0.7	2.1	37.1	9.2	0.3	67.1	0.1	141.3	0.1	0.4	0.5	0.2
22	LOC 18/8b	6.5	5.8	54.8	13.4	0.5	16.9	0.0	113.0	1.2	2.1	1.2	1.4
23	RJM 36/5b	0.3	4.2	63.1	6.4	0.1	26.7	0.0	112.0	0.5	0.3	0.7	0.2
24	RJM 31/4b	1.5	5.4	86.3	16.7	0.3	24.0	0.1	65.7	0.7	0.9	0.5	1.1
25	RJM 4/1b	1.7	2.5	120.1	10.9	0.7	43.0	0.1	379.9	0.3	0.4	0.8	0.7
26	RJM 13/2b	3.1	2.8	103.4	11.2	0.5	61.4	0.1	155.4	0.1	1.5	1.6	0.4
27	RJM 22/3b	0.5	2.9	119.2	10.5	0.3	110.2	0.1	200.4	0.1	0.4	0.4	0.4
Exchangeable Phase													
28	Blank/11a	0.9	2.1	94.5	9.8	4.0	8.0	bd	5.4	0.1	0.5	0.4	bd
29	LOC 14/10a	1.4	5.5	81.5	21.0	13.6	83.5	0.1	161.2	0.3	0.4	0.4	bd
30	RJM 22/9a	2.9	6.9	52.4	15.2	24.1	417.4	0.2	330.1	0.2	0.4	0.2	bd
31	LOC 18/8a	4.5	6.2	41.2	23.1	21.0	125.3	0.1	148.0	0.1	0.3	0.3	bd
32	RJM 36/5a	1.9	9.8	14.5	12.6	18.8	497.8	0.1	404.6	0.5	0.3	0.2	bd
33	RJM 31/4a	3.9	15.9	17.1	30.1	30.6	315.2	0.3	164.2	0.6	0.4	0.1	bd
34	RJM 4/1a	2.4	5.8	12.5	26.3	35.2	484.8	0.1	1095.4	0.1	0.2	0.1	bd
35	RJM 13/2a	5.9	14.6	11.0	24.0	37.4	666.9	0.3	737.5	0.1	0.6	0.1	bd
36	RJM 22/3a	2.8	8.5	6.2	20.2	41.0	589.6	0.4	488.4	0.1	0.3	0.1	bd

Table 5: Trace metal concentration in different phases of sediment in ppm.bd: below detection limit.

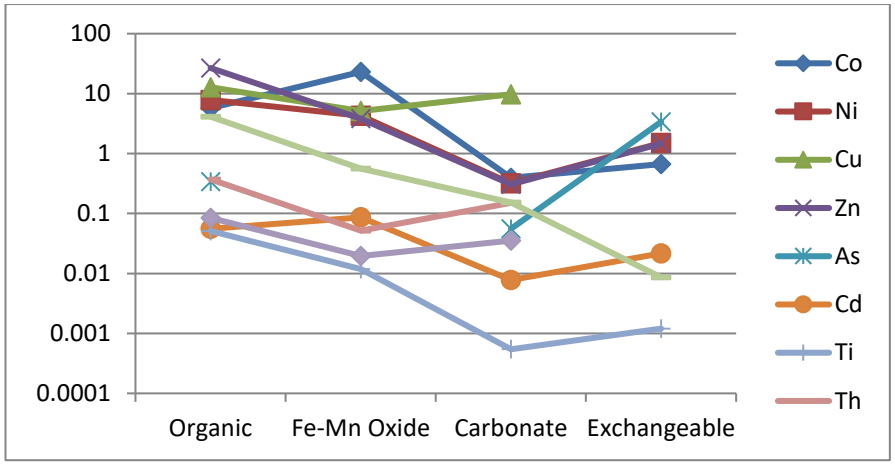
Sl.No.	**Sample Name**	Co	Ni	Cu	Zn	As	Cd	Ti	Th	Pb	U
Organic Matter											
1	RJM4/1d	26.59	20.59	105.17	42.27	bd	0.06	0.01	bd	2.88	bd
2	RJM 13/2d	5.75	7.84	12.76	26.77	0.34	0.06	0.05	0.37	4.13	0.08
3	RJM 22/3d	17.97	21.96	24.18	65.00	0.06	0.29	0.04	1.48	6.48	0.03
4	RJM 31/4d	19.07	15.51	28.88	32.44	0.26	0.07	0.03	2.06	6.89	0.23
5	RJM 36/5d	12.09	28.85	66.98	50.18	bd	0.02	bd	bd	0.47	bd
6	LOC18/8d	14.89	17.15	40.61	44.60	bd	0.08	bd	0.36	4.44	bd
7	RJM 22/9d	4.14	7.90	10.70	13.13	0.56	0.01	0.02	0.20	3.19	0.04
8	LOC 14/19d	12.59	18.73	21.73	48.85	0.16	0.26	0.04	2.05	6.94	0.08
Fe-MnOxide Phase											
9	RJM4/1c	37.37	3.70	13.68	bd	bd	0.04	0.01	0.03	bd	0.05
10	RJM13/2c	23.04	4.27	5.12	3.84	bd	0.09	0.01	0.05	0.56	0.02
11	RJM22/3c	30.85	9.47	6.68	13.08	bd	0.48	0.02	0.10	1.28	0.09
12	RJM31/4c	36.66	5.93	2.50	3.18	bd	0.10	0.01	bd	0.32	0.04
13	RJM36/5c	17.55	8.60	8.32	8.67	bd	0.07	0.00	bd	0.52	0.02
14	LOC18/8c	10.08	1.84	bd	6.31	bd	0.35	bd	0.01	0.07	0.05
15	RJM22/9c	19.62	6.24	4.68	7.36	0.01	0.31	0.01	0.07	1.53	0.05
16	LOC14/10c	9.80	2.12	1.86	9.47	bd	0.02	bd	0.02	0.18	0.09
Carbonate Phase											
17	RJM4/1b	0.21	0.27	11.94	0.29	0.07	bd	bd	0.07	0.02	0.06
18	RJM13/2b	0.40	0.32	9.76	0.31	0.06	0.01	bd	0.15	0.15	0.04
19	RJM22/3b	0.06	0.33	11.57	0.22	0.03	0.01	bd	0.02	0.03	0.03
20	RJM31/4b	0.18	0.65	7.87	1.00	0.03	0.01	bd	0.04	0.09	0.10
21	RJM36/5b	0.03	0.50	5.04	bd	0.01	bd	bd	0.06	0.01	0.02
22	LOC18/8b	0.80	0.72	4.06	0.63	0.06	bd	bd	0.11	0.24	0.13
23	RJM22/9b	0.08	0.23	1.85	0.13	0.03	0.01	bd	0.04	0.02	0.02
24	LOC14/10b	0.07	0.42	1.95	0.73	0.02	bd	bd	0.06	0.12	0.06
Exchangeable Phase											
25	RJM4/1a	0.20	0.44	bd	1.74	3.19	0.01	bd	bd	bd	bd
26	RJM13/2a	0.67	1.50	bd	1.47	3.38	0.02	bd	bd	0.01	bd
27	RJM22/3a	0.25	0.76	bd	1.04	3.70	0.03	bd	bd	bd	bd
28	RJM31/4a	0.40	1.68	bd	2.20	2.76	0.03	bd	bd	bd	bd
29	RJM36/5a	0.13	0.95	bd	0.27	1.54	0.01	bd	bd	bd	bd
30	LOC18/8a	0.47	0.51	bd	1.46	1.79	0.01	bd	bd	bd	bd
31	RJM22/9a	0.26	0.60	bd	0.59	2.16	0.02	bd	bd	bd	bd
32	LOC14/10a	0.06	0.44	bd	1.27	1.04	bd	bd	0.01	bd	bd

Table 6: Concentration common elements present in different phases of sediment in ppm.

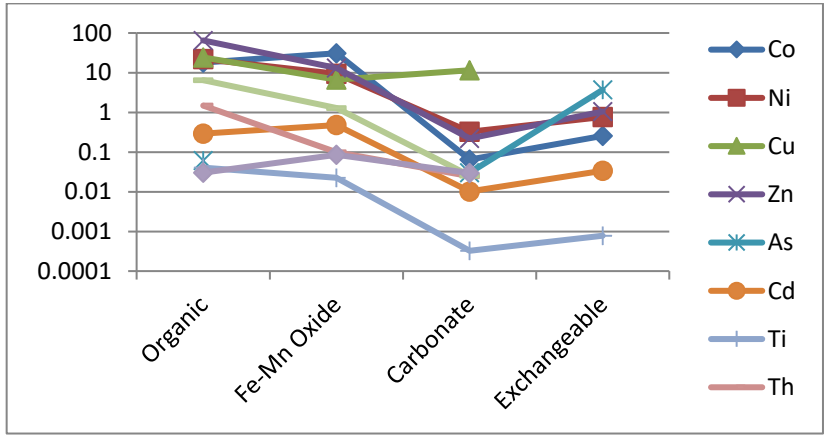
Sl.No.	**Sample Name**	Ba	Sr	Al	P	K	Mn	Fe	Ca
Organic Matter									
1	RJM4/1d	71.10	15.01	-	-	-	-	-	-
2	RJM 13/2d	16.30	7.54	-	-	-	-	-	-
3	RJM 22/3d	414.63	142.41	-	-	-	-	-	-
4	RJM 31/4d	56.78	31.55	-	-	-	-	-	-
5	RJM 36/5d	86.01	15.65	-	-	-	-	-	-
6	LOC18/8d	240.44	134.14	-	-	-	-	-	-
7	RJM 22/9d	15.13	6.32	-	-	-	-	-	-
8	LOC 14/19d	409.16	142.94	-	-	-	-	-	-
Fe-MnOxide Phase		**Ba**	**Sr**	**Al**	**P**	**K**	**Mn**	**Fe**	**Ca**
9	RJM4/1c	38.70	2.58	-	-	4.73	-	-	-
10	RJM13/2c	29.20	20.10	-	-	22.00	-	-	-
11	RJM22/3c	48.20	44.81	-	-	23.14	-	-	-
12	RJM31/4c	16.15	12.09	-	-	-	-	-	-
13	RJM36/5c	26.61	1.64	-	-	-	-	-	-
14	LOC18/8c	13.46	1.32	-	-	24.81	-	-	-
15	RJM22/9c	36.84	33.76	-	-	-	-	-	-
16	LOC14/10c	16.28	1.59	-	-	11.69	-	-	-
Carbonate Phase		**Ba**	**Sr**	**Al**	**P**	**K**	**Mn**	**Fe**	**Ca**
17	RJM4/1b	42.52	4.23	323.71	0.67	3.64	36.63	79.97	144.38
18	RJM13/2b	17.10	6.49	188.12	1.44	-	7.52	65.82	126.54
19	RJM22/3b	21.84	12.46	68.70	0.06	-	6.63	7.15	131.57
20	RJM31/4b	7.31	1.87	64.90	2.03	-	5.12	23.55	81.17
21	RJM36/5b	12.72	2.24	119.90	7.40	-	5.21	103.50	101.43
22	LOC18/8b	12.99	1.00	69.46	10.14	-	107.75	210.02	62.30
23	RJM22/9b	16.48	7.54	79.00	-	-	6.67	21.28	22.02
24	LOC14/10b	9.59	0.46	161.66	3.30	-	22.80	86.85	24.46
Exchangeable Phase		**Ba**	**Sr**	**Al**	**P**	**K**	**Mn**	**Fe**	**Ca**
25	RJM4/1a	110.84	55.74	8.57	2.57	48.34	22.57	63.51	-
26	RJM13/2a	73.65	76.47	8.50	3.18	78.21	12.92	56.49	-
27	RJM22/3a	48.07	66.97	-	1.70	97.87	8.96	42.86	-
28	RJM31/4a	16.29	36.19	-	2.22	83.37	7.55	23.19	-
29	RJM36/5a	41.45	58.17	11.05	0.81	-	5.72	52.37	-
30	LOC18/8a	14.96	14.02	3.20	2.65	142.96	92.17	17.37	-
31	RJM22/9a	34.46	49.40	-	-	63.41	7.20	24.12	-
32	LOC14/10a	16.72	9.18	2.98	1.44	50.62	24.59	13.08	-



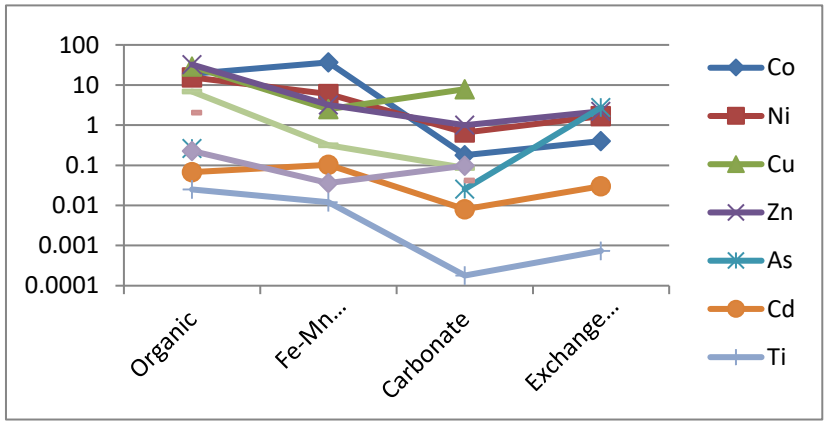
(RJM4)



(RJM 13)

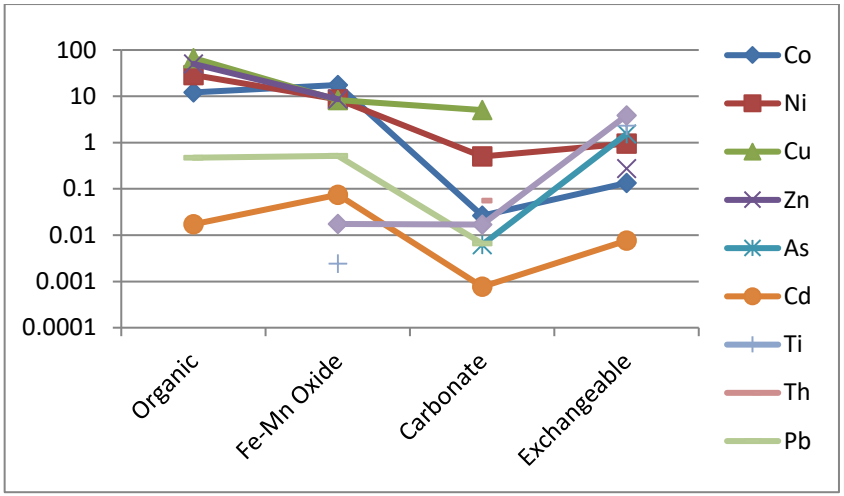


(RJM22)

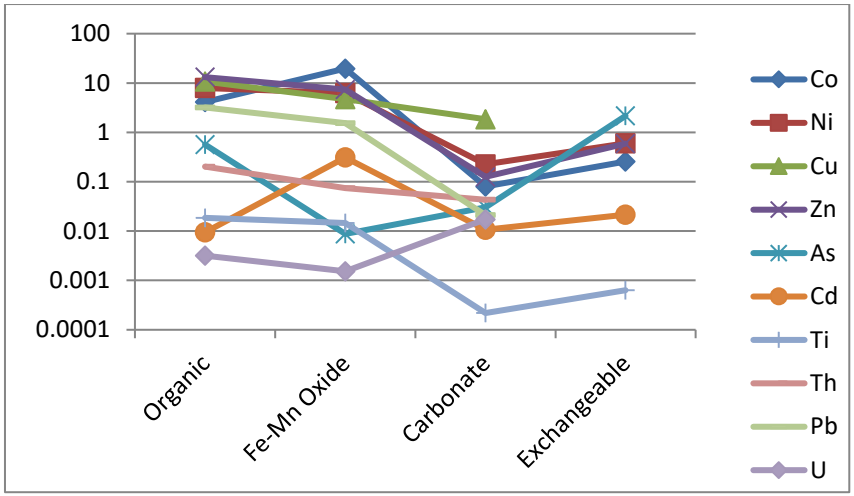


(RJM 31)

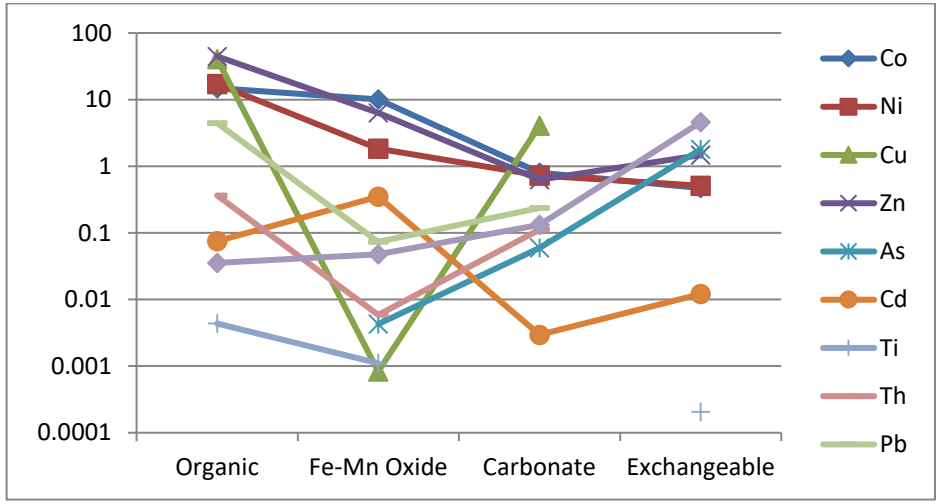
Figure 7 (A) Low concentration elements present in different phases of profile sediments.



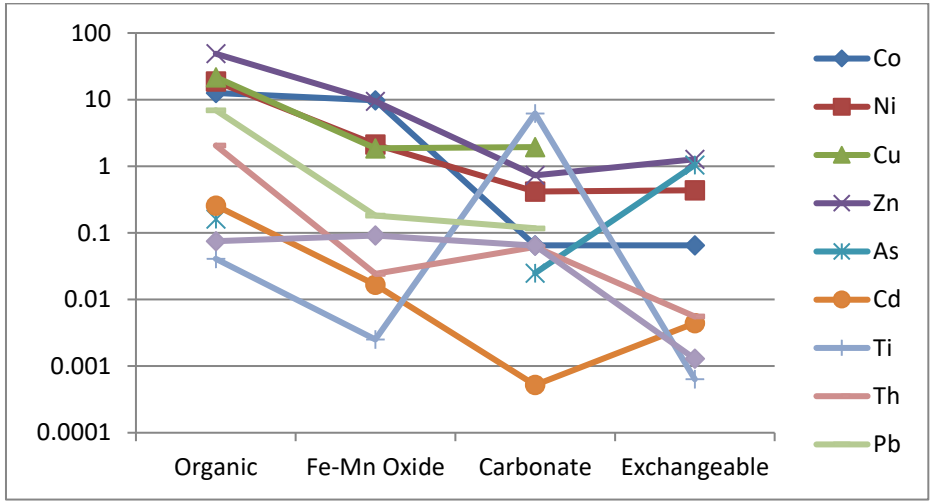
(RJM36)



(RJM 22)



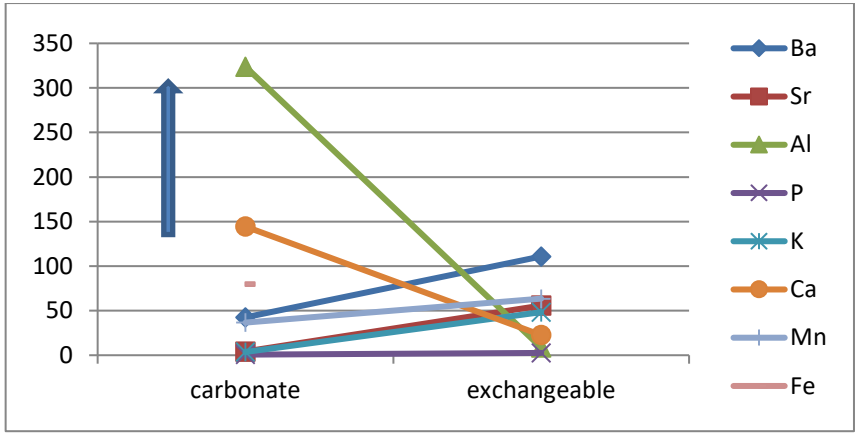
(LOC18)



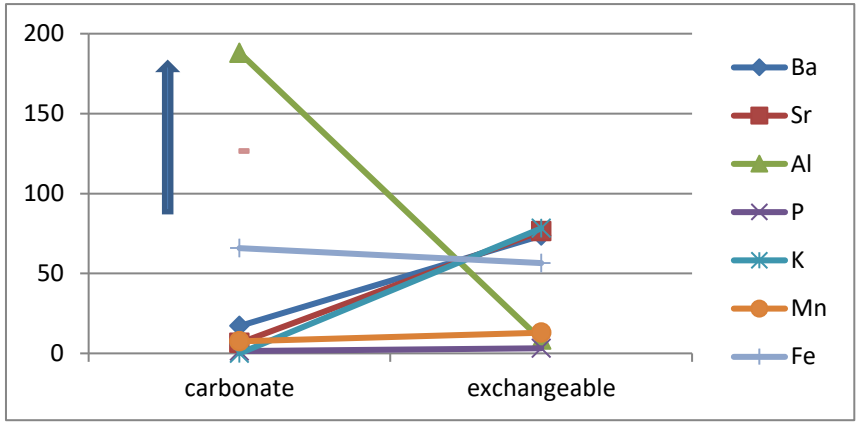
(LOC 14)

Figure 7(B) Low concentration elements present in different phases of bed loads and profile sediments.

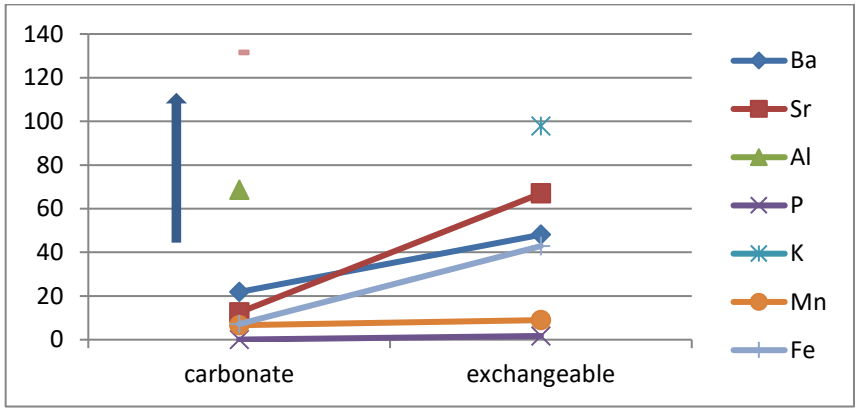
(B)High concentration elements showing different phases-



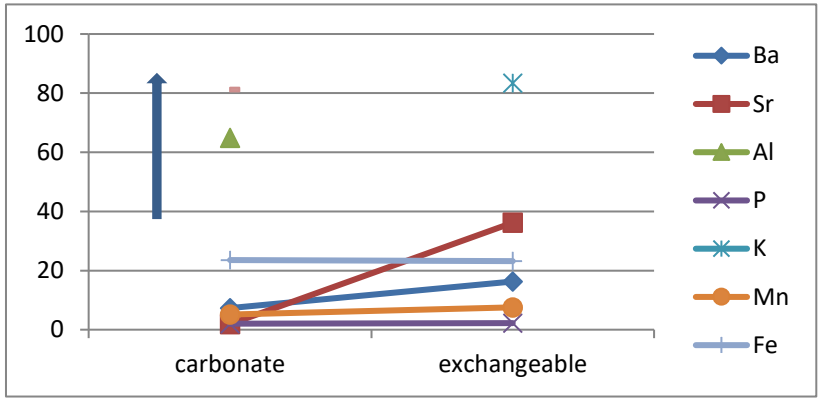
(RJM 4)



(RJM 13)

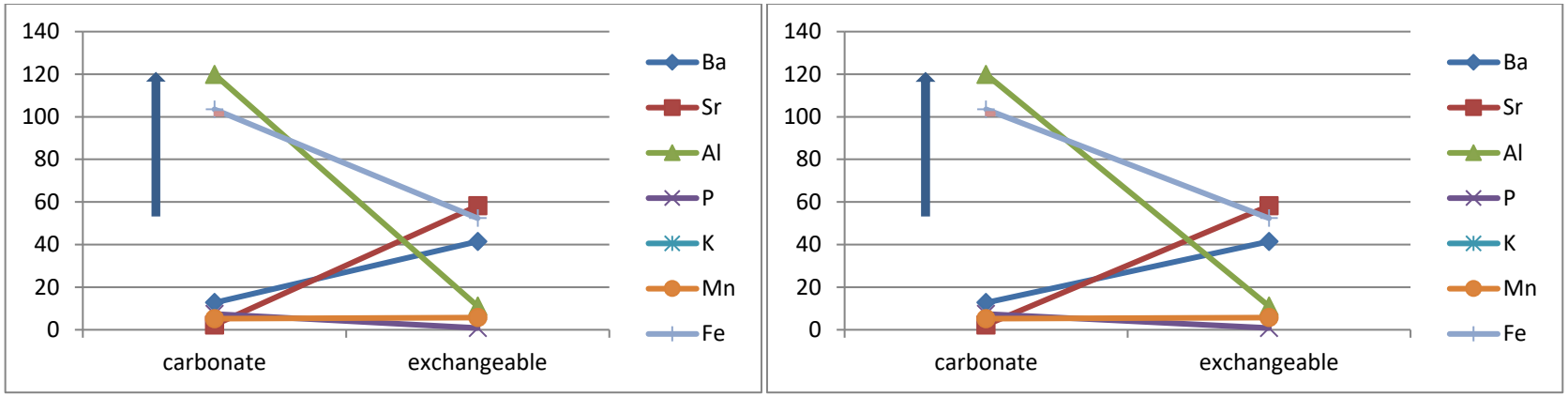


(RJM 22)



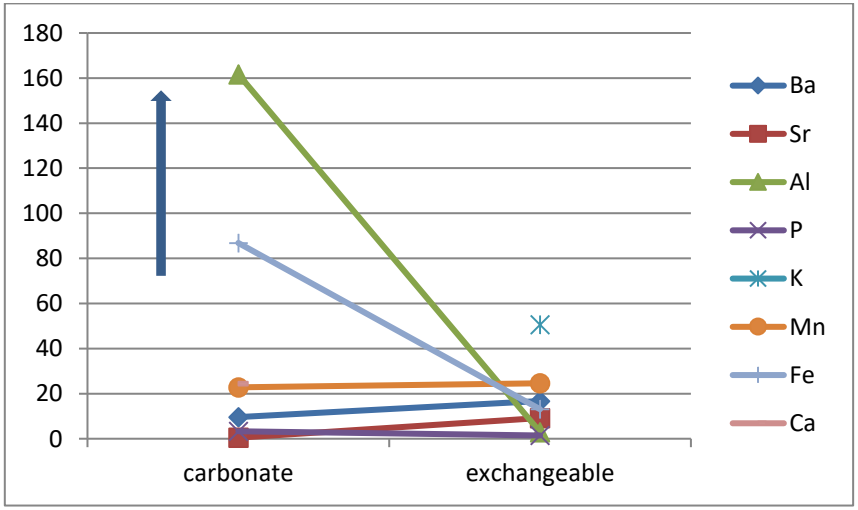
(RJM 31)

Figure 7(C) High concentration elements present in different phases of profile sediments.



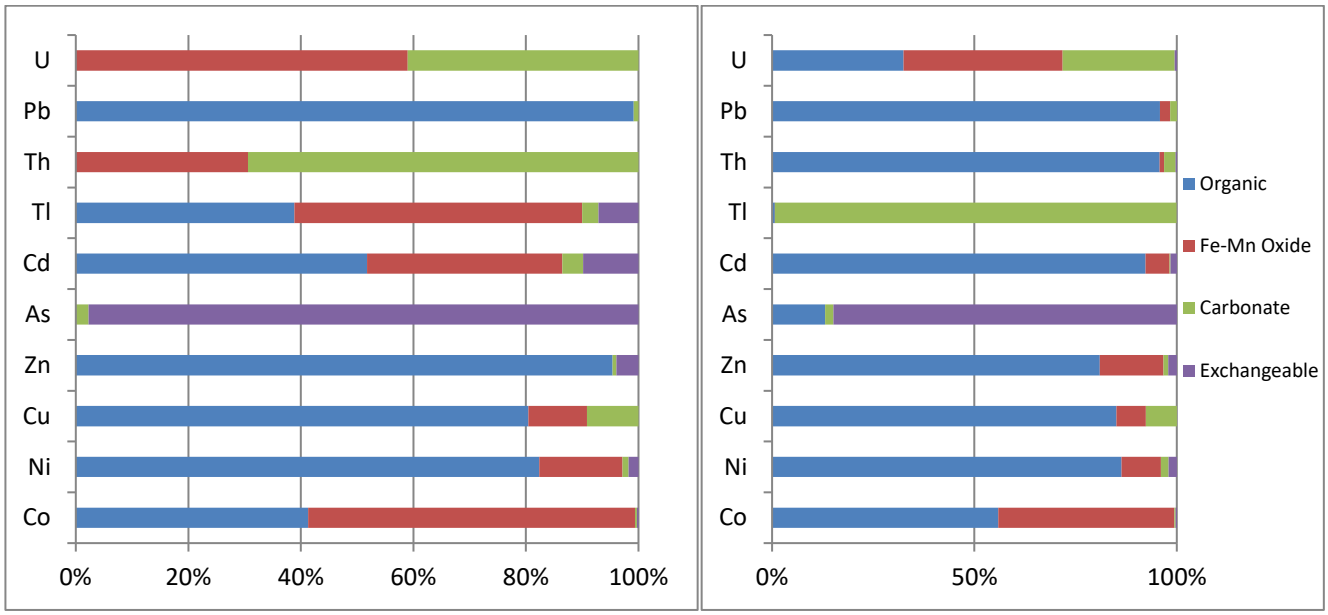
(RJM36)

(LOC 18)



(LOC 14)

Figure 7(D) High concentration elements present in different phases of bed loads and profile sediments.



(Weathering Profile) (Bed Load Sediments)

Figure8.Comparison of elemental distribution in weathering profile and bed load sediments

The ICP –MS analysis shows the trace elements distribution in different phase according to their concentration. First table (4) is for raw data after standardization by the estimated standard value. The second table (5 & 6) is for final analysis of data in ppm calculated from raw data. Selectivity of the extraction reagents towards specific geochemical phases is an important performance criterion for a sequential extraction procedure designed to determine the speciation of trace metals. The degree to which the desired sediments phases are solubilised and the degree to which it resists attack are considered by the sediments components that are solubilised during each successive extraction and thus are found in various leachates along with trace metals and the change in overall composition after treatments with each successive reagents.

Figure 7 (a, b, c & d) for each samples plotted separately depending up on the low and high elemental concentration. XRF table shows the bulk elemental percentage of the samples. This bulk results is compared with the sequential extraction results to know the distribution of elemental distribution with both bulk analysis and sequential extraction analysis. In weathering profile sediments the elemental concentration is generally high mainly in organic phases and generally decreases from organic phases to exchangeable phases. The concentration of Co,Cu,Cd,Zn,As and Tl are maximum in organic phases, minimum in carbonate phases and the trends slightly increases in exchangeable phases. The overall distribution in different phases are described below-

1. Exchangeable phase– Except As other element shows lower concentration in exchangeable phase. The lower concentration of Si, Al found in all samples indicates that $MgCl_2$ treatments not affect silicates, sulfides, or organic matter. Thermodynamic calculations indicate that Fe and Mn oxides should not be significantly solubilized at pH 7.0, and concentrations of Fe in leachate 1 are indeed very low. Concentrations found for exchangeable cadmium, cobalt, nickel, lead, and zinc are lower than their respective detection limits; low concentrations of copper (0.15 and 0.2 ppm) and iron (0.4 ppm) are observed, as are relatively high concentrations of manganese (99 and 38 ppm). The relatively high concentrations of exchangeable manganese suggest that the metal exists in a reduced form; it is

recognized (42) that in most natural waters Mn(II) oxidation is a much slower process than Fe (II) oxidation.

2.**Carbonate phases –** The trace metal concentration associated with carbonate phase generally contains low concentration. The carbonate phase mainly contains mainly Ca, Mg types of minerals, which are replaced by minerals having same charge and same ionic radii. Concentrations found for cadmium and cobalt in fraction 2 are lower than their respective detection limits; the levels of nickel and iron, though detectable, remain low (<4%) compared to the total metal concentrations. For copper, zinc, and manganese, however, the observed concentrations represent an appreciable proportion of the total metal: 16-18% Cu; 13-16% Zn; 13-28% Mn. U is the most prominent mineral and Tl and 27% of U in weathering profile.

3. Fe-Mn Oxide phase – Fe-Mn Oxide phases are mainly shows higher concentrations due to oxy-hydroxides phases associated with this. Oxy-hydroxides are mainly responsible for the concentration of elements in a particular phase. With the exception of cadmium, the trace metal levels in fraction 3 are relatively high and represent a large fraction of the total metal concentrations: ~40% Co; >20% for Cu, Ni, and Pb; 13-14% Fe; 15-24% Mn. Assuming that $Fe(OH)_3$ and MnO_2 are representative empirical formulas for the Fe and Mn oxides, respectively, and that the observed trace metals originate only from Fe- oxides, one can calculate the trace metal concentrations in the Fe- oxide phases; the results illustrate the strong scavenging efficiency of Fe- oxides for trace metals .

4**. Organic matter phase –** The trace elements concentration of the organic matter phase is very high because of the organo-metal complexes associated with organic matter. Levels of cadmium and cobalt found in fraction 4 are once again lower than their detection limits. The remaining metals are present in detectable quantities, but only 50-70 % of Pb, Ni,Cu, Zn,Tl and Th and 0-20% of Co,Cd and U in weathering profile and 50% Ni,Co,Zn,Cd,Th,Pb, Co and 32% of U in bed load sediments.

The above discussion mainly about the distribution of trace elements in different phase and now comparing between weathering profile and bed load sediments infigure 8 theelemental association with respect to their phases are interpreted. Cu,Ni,Tl,Cd are presents in all phases in weathering profile as well as bed load sediments. U and Th are presents in 2^{nd} and 3^{rd} phase in weathering profile, in bed load except this it also resents in organic matter phases. Pb is stable in carbonate and organic matter phase in both the sediments. Zn is associated with exchangeable and organic matter phase, while Co is with Fe-Mn oxide phases and organic phases in both the samples. As is the main prominent mineral in exchangeable phase in both the samples. The elements were prominent in certain phases on the basis of their geochemical behaviour.

Chapter-4

Conclusion

Based on the XRD, XRF and ICP-MS analysis of weathering profile and bed load sediments the following conclusions were drawn.

- Semi-quantification and mineral phase identification from XRD analysis shows mineral distribution and indicate the clay mineral percentage is high in the weathering profile sediments. Quartz concentration is higher in the bed load sediments. It is concluded that the neoformation in the weathering profile leads to the higher percentage of clay during chemical weathering. Subsequent transport of sediments from source region to the lower reach by stream/river leads reduction of clay minerals in the bed loads. Mineralogical sorting gives rise to higher quartz concertation in bed loads.

- Sequential leaching of weathering profile sediments indicate that the partitioning of trace elements like Pb,Ni,Cu,Zn,Tl andThin organic phase is high and it contains 50-70% of the total. Whereas, element like Co, Cd, U is in lower concentration which is varies between 0 – 20 %. Co and Cd are stable in Fe-Mnoxide phases and shows notable higher concentration. Concentration of U in carbonate phase is higher and Asis higher in exchangeable phases.

- Except As, U Tl all other element shows higher (> 50%) partitioning in the organic phase of the Bed load sediments. Fe-Mn oxide phases consist of nearly 50 % of Co. As is mainly prominent in exchangeable phases similar to weathering profile sediments. Tl is confined to carbonate phase of bed loads. Distribution of U in nearly equal in carbonate, organic and Fe-Mn oxide phases.

- As different metals for organo-metalic complexes it is reach in organic phases of the sediment.

Future work-

- The residual sediment phase needs to be analysed for comparing with bulk chemistry. This analysis will be carried out after digesting residual sediments with HF-HNO_3-HCl mixture.

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