CHAPTER - III

METHODOLOGY
CHAPTER - III
METHODOLOGY

3.1 Study of previous literature

Miller and Given, (1986,1987), have pointed out that inorganic elements may be present in low rank coals in a variety of forms including carboxylate salts, chelated coordination complexes, and discrete mineral phases. This is particularly true of trace elements, which may be present in their own minerals or by isomorphous substitution of clays, pyrite or carbonates or adsorbed on particles of sand or organic matter.

M Pires et al (1997) found that elements like B, Be, Br, Ge, V were associated to the organic fraction of coal while As, Cd, Cu, Co, Dy, Hg, Lu, Mo, Ni, Pb, Se, W & Zn occur mainly in sulphide minerals and Ba, Cr, Cs, Ga, Mn, Rb, Sb, Sn, Sr, Ta, U & Zr are distributed in nonsulphide fractions (such as aluminosilicates, carbonates, sulphates, etc.) In several phases Ni-sulfide, nonsulfide, organic and sulfate (especially in Spanish coal) Co-inorganic & sulfide, Cu-sulfide and other minerals are present but with high variability among the studies. The elements Pb & Co appear to be supplied by the woody portion of the proto-coal material, where as Ga, Nb, Ni, Cr and In can be attributed to the nonwoody portions of the proto-coal. Cu, Mo, Cr appear to come from both organic and inorganic sources where as V, Mn, Sr, La, & Ba have been attributed to an extraneous inorganic source (Ghosh et al, 1987).

Colin R et al (1999) studied mineral matter and trace elements in coal of the Gunnedah basin, Australia, and found that quartz, illite and other minerals of detrital origin dominate the coals in the upper part of the sequence, where as authigenic kaolinite is abundant in coals from the lower part of the Permian succession. These minerals are all reduced in abundance, however, pyrite is a dominant constituent in coals formed under marine influence at several stratigraphic levels. Calcite and dolomite occur as cleat and fracture infillings,
mostly in seams near the top and bottom of the sequence. The potassium bearing mineral in the detrital fraction are associated with significant concentrations of rubidium and the authigenic kaolinite with relatively high portions of titanium. Zirconium is also abundant with 

\[ \text{trace elements} \text{ } \]

high concentrations of arsenic and minor proportions of thallium. Small concentration of Cl present in the coal are inversely related to the pyrite content.

\[ \text{trace elements} \text{ } \]

Strontium and Barium are strongly associated with the cleat filling carbonate minerals. Ge & Ga appear to be related to each other as are Ce, La, Nd and Pr but none of these showing relationship to the organic matter as a particular mineral component.

\[ \text{trace elements} \text{ } \]

Al, Cr, Fe, Mn and Na were found to be inorganically bound in the coal while As, B & S are associated with the organic fraction of coal (Goodarzi et al, 1988).

\[ \text{trace elements} \text{ } \]

The statistical approach of the distribution of trace elements and their organic / inorganic affinity in lower Gondwana coals of India was given by Mukherjee et al (1988). About eighteen trace elements i.e. B, Ba, Co, Cu, Ga, Ge, La, Mn, Mo, Nb, Ni, Pb, Sn, Sr, V, Y, and Zr were found.

\[ \text{trace elements} \text{ } \]

An attempt was made to correlate the coals of different coalfields on the basis of multivariate analysis, in addition, the organic inorganic affinities between the trace elements were established by the coefficients of correlation and ash present.

\[ \text{trace elements} \text{ } \]

It was inferred that Ge, Cr, Y, and La occur in these coals as organometallic complex and chelates. The elements Ni, Co, Ga, V, and Cu, show both organic and inorganic association, where as Mn & Ba are exclusively incorporated in the inorganic fractions.
Mukherjee et al (1992) studied the trace elements of Tertiary coals of India. The trace elements found were Ge, Ni, Co, Cu, Pb, Mo, Zr, Mn, Gr, Ba, Ga, V, Sr, B, Nb, Sn, La and Y. There are differences in trace elements concentration between the Eocene coals of north-eastern and north-western India. A significant difference also existed between the Eocene and Oligocene coals of North Eastern India.

The result showed that some of the elements were significant for the identification and correlation of the coal seams. The element Cr can be used as a marker or index element for the Oligocene coals of the Makum and Dilli-Jeypura coalfields of North Eastern India, and Mn for the Eocene coals of Meghalaya of North Eastern India. The interpretation of organic / inorganic association of the trace elements indicates that elements such as Ni, Co, Ba, V, Sr, Cr, Y, Ge, & Nb are associated with the organic tractions. Pb and Cu show affinity with both the organic matter and sulphides. Mn shows affinity with the organic matter and mineral matter, while Ga is exclusively related to the mineral matter.

Further it has been revealed that the Eocene and Oligocene coals of North Eastern India originated under marine conditions. In contrast the Eocene coals of North Eastern India gave significant evidence of a high influx of fresh water during coal and show parity with the fluviolacustrine coals of lower Gondwana, as far as the concentration of the trace elements are concerned.

Pioneering work in the field was conducted by Mukherjee and Dutta (1950) on the constituents of the ashes of some Indian coals. Iyer and Sundaram (1955) carried out spectrographic examination at the University College of science, Calcutta on the samples of coal ash received from the Barely pit, Singarani coal-field, dust from dust catcher at the iron blast furnaces, slag from blast furnace making ferro-manganese, for studying their germanium contents and reported its percentage as 0.04, 0.0018 and 0.0029 respectively. Das 1958 of Calcutta University spectrographically found out the presence of germanium in coals of the Talchir coalfield, Orissa for the first time. Borreswar Rao and Venkateswar Rao (1965) of
Andhra University, Waltair studied a few random samples collected from Singarem, Jharia and Bokaro coal fields and observed that germanium and copper were probably introduced as solutions to a coal forming environment, where as other elements accumulated with biological material which was later coalified, Banerjee, Rao and Lahiri (1972) of CFRI, Dhanbad initiated a more or less systematic survey of Indian coals for their germanium content. The team studied spectrographically a large number of samples of coals drawn from certain Central Indian coalfields, Tertiary coalfields of Assam and Lignite fields of Palana, Kashmir and South Arcot, district of Tamilnadu. Their study revealed that germanium content has no definite relation with the formation of coal in respect of space and time, though weathering and erosion of rocks before and during the deposition of coal beds could be a factor in the enrichment of the elements in coal. The germanium content shows much variation from nil in coals of Pathakherawardha Valley and Kamptee coal fields through moderate values in the mature Jharia coals (around 100 ppm) to relatively high value (around 200 ppm) in Talchir and Godavari Valley coals. The Tertiary coals of Assam are reported to contain germanium as high as 350 to 650 ppm. Kashmir, South Arcot and Palan lignites yielded low values of 21, 24 and 27 ppm respectively. Mukherjee and Ghose (1976) studied spectrochemically the coals of lower Barakar and Upper Karharbari Formation of the North Karanpura coalfield, Bihar and observed that V, Pb, Co, Cu and Zr are more enriched in the coal samples of the upper measures. The concentrations of Sn, Ge, Mo and Li, however were found more or less uniform in both the formations. It was further observed by them that most of the trace elements in coals of the upper measures are associated with organic fractions, whereas the samples of lower measures are related mainly to the inorganic fractions. Chaudhun, Das, Gupta and Kathing (1979) of North Eastern Hill University studied eight coal samples from different mines, one each from fly ash and trolley ash form a thermal power station, all located in the state of Meghalaya. The study indicated that germanium content in fly ash (1.2 to 1.5%) is relatively higher than that in the corresponding coal samples (1.0 to 1.2%) used in the plant.
This increase in the elemental content according to the authors might be due to the escape of some of the Metals as “Ge” and consequently its accumulation in the fly ash. An enrichment of about 20% of germanium in fly ash indicated a very high ash content in coal. This study further revealed the possibility of extracting germanium from Indian coals. Mulick and Ahmed (1979), observed abnormally high contents (2000 to 3700 ppm) of Mo, Zr, and Pb in Jharia and Raniganj coalfields. The above-mentioned findings of germanium in coal/fly ash samples from Meghalaya and Molybdenum, Zirconium and lead from Raniganj and Jharia coalfields, according to the present authors, appear to be abnormally high and unusual.

Dey (1980) studied the matrix of diamictites of the basal member of the Gondwana group of the eastern parts of the Extrapeninsular region (Sikkim) and Peninsular region and observed unusually high B, Mn, and Cu contents. According to him, they were deposited under marine environment.

The coal wing of the geological survey of India initiated programme on “study of trace elements in Indian coal, lignite and associated rocks” from 1978. Some initial studies on certain selected tertiary coalfields of North Eastern India and two Gondwana coalfields namely Raniganj and Darjeeling were carried out during 1977-78. This preliminary work indicated that the Tertiary coals, in general contain more trace elements quantitatively than the Gondwana coals (Raniganj and Darjeeling coalfields). Mukherjee et al. (1950) observed that the tertiary coals, Oligocene coals of Assam (i.e., Makum coalfield) have been found to contain higher percentage of trace elements in comparison to coals of Meghalaya (west Darrangiri and Langrin coalfields). Goldschmidt (1950) in his pioneering work indicated that germanium is 1600 times more concentrated in ashes of certain coals than in average rocks. Stadnichenko et al. (1953) in their studies on the germanium content in American coals have observed that the highest concentrations of germanium are found in coaly logs and pieces of woody coals occurring as isolated pieces in sediments.

Lessing as reported by Goldschmidt (1950) found that there are two kinds of ashes in coals, the inherent ash and the ash of the mineral substance present as
impurities. Germanium is found to be concentrated in the inherent ash. Goldschmidt (1950) further observed that high contents of germanium and other rare elements can only be expected in ash from coals having less percentage of ash while the converse may not be true.

Morgan and Davis (1937) succeeded in isolating considerable quantities of germanium and gallium from the ash of the Northumberland coal. Ivanon-Ennin, Kostrikin, Russanov and others from Russia (1976) studied germanium and gallium contents in certain ashes from coals and found maximum percentage of these elements comparable to those in the ash of the Northumberland coals. In New Zealand, Sim (1977) studied distribution of 29 trace elements to differentiate New Zealand coals from various overseas varieties.

Youth (1977), working on Taiwan coals, utilized trace elements for differentiating the coal bearing formation and recorded random distribution of Ge, Ba and Ni. Na/K ratio could be used to determine the rate of sediment accumulation. Slow accumulation of sediment results in the degradation of illite and an increase in Na/K ratio. Nicholls & Lonngs, 1960) Xavier Querol et al. (1985) studied the trace elements in sub-bituminous coal and their behavior during combustion in a large Power Station were characterised by their content and distribution in fuel (organic and/or inorganic affinities) and in combustion wastes (partition and volatility). Among the findings is the important role of anhydrite \( \text{CaSO}_4 \) in the sorption of trace elements such as As, B, Ge, Se, Pb, Mo, Zn, and Ti from fuel gas and in reduction of emissions of these potentially toxic elements, calcium oxide has a high sorption capacity for some of the elements studied.

The mobility of more than thirty trace elements from four Spanish coals was investigated using sequential extraction procedure. The result demonstrates that the elements associated with sulphides, sulphates and organic matter in coal show the highest extraction rates, while elements with aluminosilicate affinities have lower mobilities. Querol et al. (1996) M.B. Folgueras et al. (2003) studied the influence of sewage sludge addition on the volatility of 37 trace elements during coal.
Combustion experiments were performed in a laboratory electric furnace at 800, 900, 1000 and 1100 °C. The results have confirmed that the high Cl contents of the sludge can produce a pronounced effect on the volatilization of some trace elements (Ag, Cd, Cs, Cu, Li, Pb, Rb, and Ti) due to the probable formation of volatile chlorides, while the high CaO concentration increases the retention of some elements in ash such as As, Se and Te.

Twelve hand-picked vitrinite concentrates and companion whole-coal samples were analyzed for trace and minor elements by Instrumental Neutron Activation Analysis (INAA) and Direct-Current-Arc-Spectrographic techniques (DCAS). The vitrinite concentrates contained 94 to nearly 100 vol% Vitrinite compared to 71-95 vol% in the companion whole coals. The ash contents of the vitrinite concentration were 2 to more than 19 times than the ash contents of the companion whole coals (C A Palmer and P C Lyons 1990).

A sequential extraction procedure using acid digestion in a CEM MDS-81D microwave system is reported for the investigation of trace and minor elements in coals in mineral phases and organic matrix. The association of major, minor and trace elements with mineral and organic phases is suggested for a suit of certified reference coal samples. In stage 1, a significant percentage of the total Ba, Co, Cr, Cu, Mn, Ni, Pb, and Sr was extracted. In stage 2, a proportion of the Cu, Mn, Ni, Pb & Zn was dissolved implying the occurrence of these elements in pyrite. An association with organic matrix is suggested for Cr and also for Ba and Sr in lower rank coal (Kay L Laban, Brian P Atkin 1999).

A I Karayigit et al. (2000) investigated the distribution of trace elements in the lower Eocene coal seams mined in the Yenceltek, Kucukkohne and Ayridam from the Sorgun basin in relation to ash content and maceral composition. Most of the major and trace elements studied are enriched in high-ash samples, while Ba, Br, Mn, and W showed relative enrichments in low ash samples.
Singh et al. (1983) attempted the study of trace elements determinations of fifteen coal samples in order to know their distribution, behaviour and association with the organic and inorganic fractions in the coal. The elements determined by spectrographic analysis were W, V, Cr, Sc, Y, Cu, Co, Pb, Be, Ni, and Ba. The result indicates that the concentration of trace elements in these coals varies greatly from bottom to top sections. The elements V and Co were extremely poor in top and middle sections, whereas in the bottom section they were fairly distributed. 'Be' was extremely poor in the bottom section and fairly distributed in the middle and top sections. W, Sc, Y showed poor concentration in the bottom section as compared to the middle and top sections. Ni was fairly distributed in the bottom section where as its concentration is poor in the middle and top sections. Cr and Cu were fairly distributed in the bottom, middle and top sections. Ba has unusually high concentration in all the sections.

D C Gupta (1999) studied the environmental aspect of selected trace elements associated with coal and natural water of Pench valley coalfield and their impact on human health. For this study, composite samples of coals from Eklehra, Rawanwara Khas and Shivpur open cast collieries were prepared for spectrographic analysis of Co, Cu, Cr, Mn, Ni, and Pb. The concentration of these elements ranged from 17-36.5 ppm, 66-105 ppm, 55-58.5 ppm, 745-935 ppm, 59-78 ppm, and 18.5-22 ppm respectively. The study of trace elements in natural water suggested that the concentration of the above elements were above the safety limit in a majority of samples and were hazardous to human health.

Na/K ratio may indicate rate of deposition, the higher the ratio the slower the rate of deposition and vice versa, Goodrazi and Cameron (1987), Goodrazi and Gentazis (1987).

Goodrazi (1987 b) studied that 'Cr' is the element, which is more concentrated in coal deposited in fresh water environment than in coal deposited in a brackish water environment.
3.2. Fieldwork

3.2.1. Collection of coal samples

Representative samples of coal were collected both from open cast and underground mines, for the analysis of trace elements. Samples were collected from roof and floor strata of coal seams, measuring two meter on either side of the coal seams. A total of 100 coal samples were collected covering all the five coal seams of Barakar Formation and one coal seam of Karharbari Formation. The seam present under Karharbari Formation is concerned to the Talchir, Nandira, Deulbera, Underground and Balanda Open Cast Project. Other mines like Lingaraj, Jagannath, Ananta, Bharatpur, Kalinga are included under Barakar Formation containing seam II to IX. Representative samples of each mine were collected seamwise i.e. Seam I to Seam VI for trace element analysis. Samples were also collected from partings occurring just above and below a particular seam for study of same set of trace element analysis. Each sample, therefore, represents a definite stratigraphic position. Care was taken to avoid any superficial contamination while collecting the samples. Some quantity of each coal sample was then powdered using suitable mortar and reduced to 500mg by conning and quartering. Powdered samples were securely packed in polythene bags and then in cloth bags to avoid any contamination. The different mines from where the samples were collected for analysis have been shown in Fig 1 (b).

3.2.2. Collection of water samples

To study the contamination of trace elements in groundwater, water samples were collected from tube wells, dug wells located in active mining areas where chances of contamination are maximum. Altogether fifty water samples were collected from different localities covering almost all the working coal seams of Karharbari and Barakar Formation of Talchir coalfields. In order to study the
INDEX MAP SHOWING LOCATION OF STUDY AREA IN TALCHIR COALFIELD.
mobility and variations of concentrations of trace elements samples were collected from the same locations both during pre & post monsoon periods

**Method of sampling**

From each locality one sample was collected in sampling bottle. The bottles were previously cleaned by neutral detergent and concentrated nitric acid. These were then thoroughly cleaned with tap water and de-mineralized water. The quantity of each sample taken was one litre.

**3.3. Laboratory work**

Laboratory work includes analysis of coal and water samples for trace elements. For coal sample analysis, the following procedures were followed (Nadkarni, R.N. 1980):

1. Determination of ash content in the coal samples under controlled temperature so as to restrict loss of any trace elements from the coal ash.

2. Required treatment of the said ash sample for spectrographic analysis. The procedure adopted in preparing the samples for trace element study was as follows,

   The coal sample was powdered by steel and then with agate mortar. One gram of finely powdered coal was taken in a silica crucible. It was gradually heated to 275°C for one hour, then at 550°C for another hour and then at 750°C for next two hours with suitable electric furnace having arrangement of controlled air flow for oxidation. The prepared ash sample was taken for acid digestion.

   The procedure adopted for digestion of ash sample was
   - 0.5 gram of sample was taken in a 100 ml Teflon beaker...
3 ml of Aqua Regia, 1 ml of HClO₄ and 3 ml of HF was added to it and then it was covered with a Teflon lead.

It was then placed on a sand bath held at 200°C for one hour.

The lid was removed and the condensates were washed into the beaker.

The contents were evaporated to light HClO₄ fumes by hot plate for a few minutes.

3 ml of HF was added and then it was evaporated to dense HClO₄ fumes.

3 ml of HCl and some distilled water was added and then it was heated till complete solution.

It was transferred to a graduated flask and was converted to 100 ml by adding distilled water.

Then the solution was taken for trace element analysis by AAS.

For water analysis around 100 ml of collected water was simply filtered to 42 Whatman filter paper and the taken for analysis.

3.4 Analysis by Atomic Absorption Spectrophotometer

In Atomic Absorption Spectroscopy (AAS) the sample in solution is atomized by a flame or other energy source, where it produced atomic vapour of the same element being analyzed. Monochromatic light which has the same wavelength as that of the required element is then passed through the sample vapour. The atoms present in the ground state of the vapour absorb radiation from the monochromatic light source in proportion to their concentration present in the sample and shows autorecording of data by computer. The AAS used in the laboratory was Shimadzu 6401 F model of Shimadzu Japan. There were eight torrets in the instrument which helped measurement of eight trace elements at one stroke.