CHAPTER III
MATERIALS AND METHODOLOGY

FIELD SAMPLING:

The Dhauliganga basin lying in greater range of the Himalaya enjoys summer, monsoon and winter seasons. The basin is covered with a thick layer of ice and snow during the winter season and becomes extremely difficult to approach. Moreover, the discharge in the winter season is quite insignificant in relation to other seasons, it is a well established fact that the sediment yield has a positive and quite significant relationship with discharge. Keeping all these factors in mind as well as accessibility water samples of Dhauliganga were collected on the basis of purposive sampling during summer season (May and June, 1986) and monsoon season (August, 1986). During summer season two litres of water was collected from the surface of water in polythene bottle for each sample. pH and conductivity of samples were measured in the field by consort portable pH-conductometer and the samples were sealed and sent to the geochemistry laboratory of School of Environmental Sciences, Jawaharlal Nehru University, New Delhi, where they were stored in a cold room (temp. 3°C). The sampling locations are shown in Fig.3.1. The river water samples were collected from both the banks of the main channel before
and after joining of tributaries and as well as tributaries samples were also collected. At the same time newly deposited river bed sediments were collected all over the basin in the main channel and tributaries. Approximately one kg of samples were collected and packed in polythene bags for each location (Fig. 3.1). The samples were sealed and brought to the laboratory and stored in the cold storage.

During monsoon season (August, 1986) only one litre of water was collected (because of high concentration of suspended sediment) for each sample from the similar locations (Fig. 3.1), pH and conductivity were measured in the field and the samples were sealed and sent to the laboratory and kept in cold room.

LABORATORY ANALYSIS:

Water Quality Analysis:

The pH, alkalinity and conductivity for each sample are measured immediately after its arrival in laboratory. Standard methods are applied to estimate the various dissolved species by using suitable methods and a brief description of methods adopted are furnished below:

pH and Conductivity:

The pH of water samples is measured by Elico pH meter model LI-10T; for precision of results and its variation from the field, measured pH is also taken into account. The instrument first is set for standard pH 7 buffer at temperature
23°C and then the sample's pH are taken. The cross-checking is also being done.

Specific conductivity of the samples in m MHO/cm is measured with a systronic Direct Reading conductivity meter 303. The instrument is celebrated and set for 0.01 KCl standard at 23°C.

**Bicarbonate:**

The bicarbonate concentration is determined by titrating the standard bicarbonate solution against 0.02 N HCl using methyl orange as indicator. Bicarbonate is again estimated by a different method. In this method no indicator is used, instead pH meter electrode is dipped into the solution and HCl is added through a burette. The volume of 0.02 N HCl to bring the pH of standards as well as water samples to end point of 4.5 pH are recorded. A standard graph is plotted against the bicarbonate standard concentration and the volume of HCl consumed. Bicarbonate concentration of water samples is calculated from the standard graph. An average of the two observations for bicarbonate is considered in the text and for various calculations. Ca (HCO₃)₂ salt is used for preparing standard bicarbonate solution.

**Silica:**

Standard solutions of 0.5, 1, 2, 4, 6, 8 and 10 ppm Si O₂ are prepared by dissolving Na₂ Si Fe and diluting the
solution in various proportions. 25 ml of each standard and water samples is taken out. In this 10 ml ammonium molybdate solution (the solution is prepared by dissolving 2 grams of ammonium molybdate in 10 ml of distilled water and adding 6 cc of conc HCl. This solution is then diluted to make the total volume 100 cc. by adding distilled water) and 15 ml of reducing regent is added (prepared by mixing 10 ml metal sulphite solution, 60 ml of 10 per cent oxalic acid and 120 c.c. of 25% sulphuric acid and diluted by distilled water to make up the volume to 300 ml. Metol sulphite solution is prepared by dissolving 5 grams of metol in 210 ml of distilled water. Again 3 grams of sodium sulphite is added and dissolved, then distilled water is added to make up the volume upto 250 cc.). The samples are stirred properly and kept for 3 hours to let the reaction to be completed. The optical density is measured with Cecil 594 Spectrophotometer at 650 nm for standards and water samples. Standard graph is plotted for standard silica concentration versus optical density (absorption). The silica in the water samples is estimated by comparing their optical density volumes with the standard graph.

Chloride:

Chloride is estimated by titrating standard chloride solution of 5, 10, 25, 50, 75, 100 ppm against silver nitrate (Ag NO₃). Potassium chromate (K₂ Cr O₄) is used
as indicator. Standard graph is plotted against the concentration and the volume of silver nitrate solution consumed to reach the end point. The chloride concentration of water samples are determined by the comparison with standard graph. NaCl salt is used to prepare standard chloride solution.

**Phosphate:**

Phosphate standard solution of different concentrations ranging from 0.001 ppm to 5 ppm are prepared from potassium dihydrogen phosphate (KH₂PO₄). Four ml from each standard and water sample are pipetted out into 100 ml volumetric flask and 5 ml of molybdate solution and 2 ml of ascorbic acid solution is added and mixed well. The mixture is diluted to 100 ml and extinction is measured with Cecil spectrophotometer at 882 nm after ten minutes. Molybdate solution is prepared by dissolving 4.8 grams of ammonium molybdate (NH₄)₆Mo₇O₂₄·4H₂O and 0.1 gram of sodium anti-monytartrate (Na(Sbo)C₄H₄O₆·½H₂O) in 400 ml of 4N H₂SO₄ and making the total volume upto 500 ml with the same sulphuric acid. Ascorbic acid (about 0.1 m) is prepared by dissolving 2.0 grams of ascorbic acid in 100 ml water. This solution can be used for one week if kept in refrigerator.

**Sulphate:**

Sulphate ion is precipitated in a hydrochloric acid (HCl) medium with barium chloride (BaCl₂) so as to form
at 30 seconds intervals for 4 minutes. Because maximum turbidity usually occurs within 2 minutes and readings remain constant thereafter for 3 to 10 minutes, the reading of turbidity is considered to be the maximum at 4 min. interval.

Preparation of calibration curve:

Sulfate concentration is estimated in sample by comparing turbidity reading with a calibration curve prepared by carrying sulfate standards through the entire procedure. Photometer is set at zero sulfate concentration using distilled water. Reading is determined on a distilled water control sample treated for sulfate analysis, and by substraction, this result is used to correct readings on standard sulfate and samples. Standards are spaced at 5 mg/L increments in the 0 to 40 mg/L sulfate range. Above 40 mg/L the accuracy of the method decreases and the suspensions of BaSO₄ loses stability. The reliability of the calibration curve is checked by running a standard with every three or four samples. Correct colour and turbidity is corrected in the sample by running blanks from which the BaCl₂ is withheld.

Calculation: \[ \frac{mg SO_4/L}{ml \text{ sample}} \times 1000 \]

Nitrate:

The nitrate in the acidifield water is reacted with brucine to form a color which is determined specatrophotometrically at 410 nm.
Reagents:

Conc sulfuric acid 98% and diluted sulfuric acid 88%
Mix cautiously 1000 ml 98% N₂SO₄ into 250 ml of distilled water.

Stock Solution:

1 g brucine sulfate and 0.12 sulfanilic acid are dissolved in 70 ml of hot water and 3 ml conc HCl. Which is then cooled and diluted to 100 ml. This reagent is stable for 3 to 6 months if kept in a refrigerator.

Mixed reagent:

Just prior to use, 400 ml of a 30% NaCl solution is mixed with 100 ml of freshly prepared stock solution.

Stock Solution:

100 g No₃⁻/ Ml dissolved 0.163 g of potassium nitrate in distilled water and diluted to 1 litre sterile solutions should stay stable.

Dilute standard:

10 g No⁻³/ Ml pipet 10 ml of stock solution into a 100 ml volumetric flask and diluted to mark. Prepare fresh.

Procedure:

10 ml aliquot of sample filtrate in a 50 ml cylinder is taken. 2.5 ml of mixed reagent is added and is mixed thoroughly then 10 ml of 88% H₂SO₄ is added placed in a
boiling water bath for 20 minutes. Then it is cooled quickly. On a suitable spectrophotometer at 410 nm any time within 24 hours against the blank is read. Standard curve is prepared by diluting 2 to 10 ml aliquots of dilute standard solution to 10 ml according to the said procedure. A straight line is obtained by plotting the absorbance at 410 nm against the number of micrograms of nitrate ion.

**Sodium, Potassium, Calcium and Magnesium:**

Na, K, Ca, and Mg are analysed by carl zeiss AAS-I spectrophotometer in emission and absorption mode. The standard graph is made for estimation of sodium, potassium, calcium and magnesium. The values of water samples are compared with standard graph to get the concentration of Na, K, Ca and Mg. All standards were prepared with their chloride salt.

**Total Dissolved Solids:**

The estimation of total dissolved solids has been done by measuring the conductivity by the following formula:

\[ \text{TDS} = AK \]

Where, TDS = Total dissolved solids concentration (ppm)

\[ K = \text{Conductivity (} \mu\text{mhos} \) \]

\[ A = \text{Conversion factor} \]

**Suspended Sediment Separation:**

Suspended sediments were separated by 0.45 \( \mu \text{m} \) millipore filtration in the laboratory using vacuum pump.
RATES OF DENUDATION:

The calculation involves the conversion of the sediment and solute yields into volumes or depths per unit area, and therefore involves volumes of specific gravity i.e.

\[ \frac{\text{Denudation in } m^3/\text{km}^2/\text{year}}{\text{or } \text{mm/1000 years}} = \frac{\text{Total load (tonnes)}}{\text{Area (km}^2) \times \text{specific gravity}} \]

SEDIMENT ANALYSIS:

Removal of organic matter:- The removal of organic material from the bed and suspended sediments is carried by treatments with 35% hydrogen peroxide (H\(_2\)O\(_2\)). The H\(_2\)O\(_2\) mixed samples were kept on water bath at least for 6 hours to remove the moisture content. The organic matter free sediments, are used for minerological analysis and grain size distribution analysis.

Grain size analysis:- The bed sediment grain size analysis is done by standard seiving method. The samples are seived on a ILM Labour seive shaker mounted on a mechanical RO - Tap shaker for 15 minutes. The various fractions retained on the seive are weighted on a single pan electronic balance. Cumulative weight percentages are calculated and cumulative frequency distribution curves are plotted for each sample, from which the corresponding \(\phi\) values of 95, 84, 75, 50, 25, 16 and 5 percentile are calculated. The different statistical parameters are
calculated following the method of Folk and Ward (1957):

i) Mean size: \( M_z = \frac{\phi_{16} + \phi_{50} + \phi_{84}}{3} \)

ii) Inclusive graphic standard deviation (sorting):
\[
\sigma = \frac{\phi_{84} - \phi_{16}}{4} - \frac{\phi_{95} - \phi_{5}}{6.6}
\]

iii) Inclusive graphic skewness:
\[
SK = \frac{\phi_{16} + \phi_{85-95} + \phi_{5} + \phi_{95-2\phi_{50}}}{2(\phi_{84-\phi_{16}}) + 2(\phi_{95-\phi_{5})}}
\]

iv) Graphic Kurtosis: \( KG = \frac{\phi_{95} - \phi_{5}}{2.44 (\phi_{75} - \phi_{25})} \)

Mineralogy:

The bulk mineralogy of bed sediment and suspended sediment is studied by X-ray diffractograph technique. The slides are prepared by mounting sediment by drop on slide (Gibbs 1967) and are uniformly spread on the glass-slide to avoid differential settling of particles (Stockke and Carson 1973). The samples are glycolated and run on philips X-ray Diffractometer using Cu, Kα radiation source and Ni filter. The chart device 1 cm/minutes goniometer, 1°/minute and intensity 2x10² are maintained.

Identification of Minerals: The minerals are identified on the basis of their most prominent X-ray diffraction peaks. The minerals present less than half per cent are mentioned in trace. The clay minerals 'Groups' observed in the study are (i) montamorillonite, (ii) Illite, (iii) Kaolinite, (iv) Chlorite. In addition to the clay minerals, several non-clay minerals are identified: (1) Quartz,

Montmorillonite: It is identified by its 001 X-ray diffraction peak at 17 Å in the Mg-saturated and glycolated sample. Sometimes, the broad nature of this is due to variations in expansion after glycolation and variations in crystallinity. Montmorillonite has its peak at 12.4 Å in the K-saturated sample.

Chlorite: Diffraction peaks for chlorite occur at 14.5 Å, 7.2 Å, 4.75 Å and 3.54 Å. The 14.5 Å peak is the 001 peak of vermiculite for the Mg-saturated and glycolated sample. The 7.2 Å peak is the 002 spacing and is shared with the 001 spacing for kaolinite. The 3.54 Å peak is easily confused with the 3.58 Å peak for the 002 spacing of kaolinite. Biscaye (1965) found that ratios derived from the 3.58 Å and 3.54 Å peaks are nearly the same as the ratios for the 7.16 and 7.08 Å peaks. Poor crystallinity for either chlorite or kaolinite can reduce the resolution.

Kaolinite: Well crystallized kaolinite has 001 and 002 d-spacing of 7.16 Å and 3.58 Å respectively. These peaks can be confused with the 002 and 004 of chlorite especially for chlorites rich in iron which give weak 001 and 003 peaks. K+ and Mg+2 saturation has no effect upon kaolinite.
Illite:- The main basal peak of the illite is at 10 Å with other peaks at 5 Å and 3.3 Å. The peaks remain unaffected upon glycolation and heat treatment.

Quartz:- The 3.34 Å (101) peak of quartz is four or five times more intense than the (100) peak at 4.26 Å, it nearly coincides with the strong (003) reflection of illite at 3.33 Å. Therefore, the area under the 4.26 Å peak is used as relative measure of quartz.

Amphibole:- The 3.30 peak at 2.82 Å is considered for amphibole.

Plagioclase:- The 3.20 Å peak is considered for the identification of plagioclase feldspar.

K-Feldspar:- It shows a characteristic peak at 3.25 Å.

Calcite:- It is primarily characterized by peaks at 3.04 Å.

Dolomite:- The peak at 2.89 Å is identified as dolomite.

Semi-Quartification of minerals:- There is no accurate procedure for quantitative analysis of sediment for various mineral compositions. In fact, there is not even agreement upon a method for semi-quantitative estimation of clay mineral composition. Controversy exists over whether to use peak areas or peak heights as approximations to clay percentages (Biscaye, 1965). In the present study peak height method which is easier and equally efficient has been applied.
GEOMORPHOMETRIC ANALYSIS:

In the present study, modern geomorphic techniques have been applied to measure the different aspects of flu-vially eroded landscape. Different aspects related to the nature of configuration i.e. relative relief, dissection index, average slope, stream frequency, drainage density have been evaluated to understand the nature of terrain. For the preparation of the maps of the aforesaid variables of basin morphometry, entire basin is divided into 1992 grids of 1 square kilometre. The values of the each grid for each variable is calculated and the areas of the different intensities have been demarcated by isoplething.

STATISTICAL ANALYSIS:

In order to study the spatial distribution of different variables, statistical measures have been used viz. mean, mode, median, range, inter-quartile range, quartile deviation, standard deviation, co-efficient of variation and variation etc. The nature of spatial distribution of important geomorphic parameters have been analysed on the basis of skewness and kurtosis.

To assess the impact of different geomorphic parameters on the distribution and development of average slope and drainage density correlation matrix and step-wise regression analysis have been done.