MATERIALS AND METHODS
MATERIAL AND METHODS

For the present hydrochemical study the systematic sampling was done during August, 2000; November, 2000; and May, 2001 from the Dhauliganga river. Samples were collected from the entire length of river from upper region to its confluence to river Kali. The sampling locations are given in Figure 4.1 and Table 4.1. The detail of sampling and analytical procedures for water and sediments are discussed as following:

SAMPLING METHODS

4.1 Water Samples

Prior to each fieldwork polythene bottles of one liter capacity were washed in the laboratory with dilute hydrochloric acid and then rinsed twice with double distilled water. At the sampling sites, bottles were rinsed with river water before collection of water sample. About one liter water samples were collected from each sites following the method Ostrem (1975). Sampling was done for three times (Aug. 2000, Nov. 2000 and May 2001) to broadly cover the seasonal variations in solute load. Samples collected during August, November and May represent Monsoon, Postmonsoon and Premonsoon seasons respectively. Samples were collected from swift flow of river and as far from the river bank as possible.

4.2 Bed Sediments

24 freshly deposited bed sediment samples were collected from Dhauligana River during August, November, 2000 and May, 2001. The bed sediments were collected by scooping with plastic spade from the upper 5 cm from a water depth of about 15-30 cm. The collected samples were then packed and sealed in prewashed polythene bags and transferred to laboratory, where they were dried at room temperature.
Table 4.1: Details of Sampling Sites, Sample Number and Downstream Distance

<table>
<thead>
<tr>
<th>Sampling site No.</th>
<th>Samplng site</th>
<th>Water Sample No.</th>
<th>Suspended Sediment Sample No.</th>
<th>Bed Sediment Sample No.</th>
<th>Distance from source to mouth (Km)</th>
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Fig 4.1 Sampling Locations in Dhauliganga River Basin
4.3 Suspended Sediments

For suspended sediments, five liter water samples were collected in plastic cans. The collection was done from a sufficient distance of river bank by placing the can mouth against the flow direction, at depth of 30-45 cm from the water surface. The plastic cans with water and suspended sediments were kept for a week to get settle the sediments. The upper 4 liter water was then decanted and remaining water with sediments were poured into one liter polythene bottles and transferred to laboratory. The suspended sediments were separated by 0.045 μ Millipore membrane filter using vacuum pump.

**ANALYTICAL METHODS**

4.4 Separation of suspended sediments

Suspended sediments were separated from the water samples in the laboratory by using 0.45μ Millipore membrane filters of 47 mm diameter. Vacuum pump was used for faster filtration. Weight of the suspended sediment was found out by weighing the filters before filtration and subtracting this weight from the weight of the filter with sediment after the filtration. Before taking the weight of the sediment on the filter paper, it was kept for one week in dessicator to remove moisture from the sediment. Volume of the samples was measured by glass measuring cylinder. Total suspended matter was calculated for one liter water samples from the volume of filtered water and the weight of the sediment.

4.5 pH

pH of water samples were measured by Consort microcomputer (P-307) ion meter. Before measuring the pH of water samples, the electrode was immersed for 10 hours in 0.1 N HCl, to make it stable. After rinsing the electrode with distilled water the instrument was calibrated with a buffer solutions of pH 4.0 and 9.2. After that the electrode was immersed in samples and pH of each sample was recorded. The samples were stirred well during measurement to provide homogeneity.
4.6 Electrical conductivity

Electrical conductivity (EC) was measured by using Pentax EC meter. It provides measurement of EC by a cell consisting of two platinum electrodes to which an alternative potential is applied. The corresponding is proportional to conductivity of the ionic solution in which the cell is applied. For EC measurement, the instrument was calibrated and set for 0.01 M KCl standard. The conductivity was measured in μS cm⁻¹ for water samples.

4.7 Bicarbonate

Bicarbonate was determined by following potentiometric titration method. Standards of HCO₃⁻ were prepared for required concentration from chemical salt NaHCO₃. 50 ml of each standard and samples were titrated against 0.006 N HCl. pH 4.5 is taken as the endpoint of the reaction. A graph was plotted for standard concentrations against the volume of HCl consumed. The concentrations of the samples were determined from the graph plotted for standards.

4.8 Chloride

Chloride ion concentration was measured by the mercury (II) thiocyanate method (Florence and Ferrar 1970). The method involves the reaction of chloride with mercury (II) thiocyanate to form chloromercurate (II) complex ion, with the liberation of thiocyanate ions which then react with iron (III) to give the light red color. 20 ml of each standard and samples were pipetted out into a 25 ml volumetric flask. 2 ml of iron (III) nitrate regent (prepared by dissolving 15.1 gm of Fe(NO₃)₃·9H₂O in 45 ml of 72% perchloric acid and diluted to 100 ml with distilled water) and 2 ml of mercury thiocynate (saturated solution in ethanol) was added and total volume made to 25 ml with distilled water. After mixing well, solution was poured into the absorbance cell of the spectrophotometer and reading was taken against a regent blank at 460 nm after 5 minute and the chloride concentration was estimated by comparing reading with calibration curve prepared by carrying chloride standard through the entire procedure.
4.9 Sulfate

Sulphate concentration was measured by turbidimetric method (APHA 1985). The method is based on the principle that $\text{SO}_4^-$ is precipitated in an acetic medium with barium chloride ($\text{BaCl}_2$), so as to form barium sulphate crystal of uniform size. Light absorbance of barium sulphate suspension is measured by UV/VIS spectrophotometer at 420 nm and the concentration is determined by comparing the reading with standard curve. 100 ml of standard and samples were measured in a volumetric flask and 20 ml of buffer solution (prepared by dissolving 30 gm of $\text{MgCl}_2\cdot6\text{H}_2\text{O}$, 5 gm of sodium acetate, 1 gm potassium nitrate and 0.111 gm of sodium sulphate and 20 ml of acetic acid in 500 ml of distilled water and then the total volume was made-up to 1000 ml) was added and mixed with the help of magnetic stirrer. While stirring a spoonful of BaCl$_2$ crystal was added. This was stirred for 60 seconds with constant speed. After the stirring period, solution was poured into the absorbance cell of the photometer and absorbance reading was taken at 420 nm after 5 minutes. Sulphate concentration was determined by comparing reading with calibration curve prepared by carrying sulphate standard through the entire procedure.

4.10 Dissolved silica ($\text{H}_4\text{SiO}_4$)

The dissolved silica was determined by molybdosilicate method (APHA 1985). 20 ml of each standard and samples were pipetted out in to a 100 ml volumetric flask and 10 ml of ammonium molybdate solution (prepared by dissolving 2 gm of ammonium molybdate in 10 ml distilled water and 6 ml of conc. HCl and volume was made to 100 ml) and 15 ml of reducing agent (prepared by mixing 100 ml of metol sulphite solution, 60 ml 10% oxalic acid and 120 ml of 25% $\text{H}_2\text{SO}_4$ and the volume was made upto 300 ml) were added. The samples were stirred well and kept for three hours to complete the reaction. The optical density was measured for standard and water samples at 812 nm by using UV/VIS Spectrophotometer.
4.11 Phosphate

Phosphate was determined by the ascorbic acid method (APHA 1985). Phosphate standard solutions of different concentration were prepared from the potassium dihydrogen phosphate (KH$_2$PO$_4$). 40 ml of each standard and water samples were pipetted out into a 50 ml volumetric flask and 5 ml of molybdate antimony solution and 2 ml of ascorbic acid solution was added and mixed well. The mixture was diluted to 50 ml and absorbance was measured at 640 nm using UV/VIS spectrophotometer. Molybdate solution was prepared by dissolving 4.8 gm of ammonium molybdate and 0.1 gm of sodium antimony tartrate in 400 ml of 4N sulphuric acid and making the total volume to 500 ml with the same acid. Ascorbic acid was prepared by dissolving 2 gm of ascorbic acid in 100 ml water.

4.12 Nitrate

Concentration of nitrate in water samples was determined by brucine-sulphanilic acid method. The method is based on the reaction of the nitrate ion with brucine sulphate $13\text{N} \text{H}_2\text{SO}_4$ solution at a temperature of 100°C. The colour of resulting complex is measured at 410 nm. 10 ml of standard and samples were pipetted out into a 50 ml tube. 10 ml of $13\text{N} \text{H}_2\text{SO}_4$ solution was added to each tube with swirling and allowed tubes to come to thermal equilibrium in the cold bath. 0.5 ml brucine-sulphanilic regent (prepared by dissolving 1 gm brucine sulphate and 0.1 gm sulphanilic acid in 70 ml hot distilled water. 3 ml of HCl was added to this solution and volume made to 100 ml with distl. water) was added to each tube and mixed thoroughly. The tube rack was then kept in water bath at 100°C for 25 minutes. After that tubes were removed from the water bath and allowed to reach room temperature and the absorbance was measured at 410 nm against regent blank.

4.13 Ca$^{2+}$, Mg$^{2+}$, Na$^+$ and K$^+$

The content of major cations calcium, magnesium, sodium and potassium was determined on GBC 906 atomic absorption spectrophotometer (ASS). Calcium
and magnesium concentration were determined in absorbance mode and sodium and potassium in emission mode.

ANALYSIS OF SEDIMENTS

4.14 Sample Preparation:

Prior to sediment analysis, bed and suspended sediments were treated with 35% hydrogen peroxide solution to make them free of organic matter. The organic matter free sediments were used for chemical, textural and mineralogical studies.

Sediment Analysis

The sediments were analysed for Si and Al by preparation of Solution A, following the method of Shapiro and Burnock (1962). Rests of the elements were determined in solution B by ASS. The USGS rock standards (MAG, SGR, SCO and SDC) and Canadian soil standards (SO-I, SO-II, SO-III and SO-IV) were analysed along with the sediment samples to check the accuracy and precision of the measurements. A detailed description of methods adopted is described below:

SOLUTION A: 0.025 gm of fine sediment powder was taken in a 50 ml nickel crucible and 3-4 pallets of NaOH was added to the crucible. The crucible was gently heated on a burner 5 minutes and then it was heated to dull redness for 25 minutes. Then the crucible was allowed to cool down at room temperature and 30 ml water was added and kept for overnight. Then the solution was transferred to a 250 ml beaker. 5 ml of 1:1 HCL and 25 ml of water were added. The solution was boiled till it was clear and the volume was made to with 250 ml distilled water.

4.15 Determination of Silica:

8 ml of solution A reagent blank, standard solution and sample solutions were transferred to 250 ml volumetric flasks, 50 ml of distilled water was added to all the flasks, 2 ml of ammonium molybdate solution (prepared by dissolving
Materials and Methods

7.5 gm of ammonium molybdate in 75 ml of distilled water and adding 25 ml 1:4 H2SO4 acid ) was added and kept for ten minutes. 4 ml of 10% Tartaric acid solution was added with swirling the flask. 1 ml of reducing reagent (prepared by didissolving 0.7 gm of sodium sulphite in 10 ml of water and then 0.15 gm of 1-amino 2-napthol 4-sulphonic acid was added and stirred well. 9 gm of sodium bisulphite in 90 ml of water and this was added to first solution ) was added the volume was made up to 250 ml by adding the distilled water. The samples were stirred properly and kept for 30 minutes. The absorbance was measured for standared as well as samples at 650 nm in UV/VIS Spectrophotometer.

4.16 Determination of Alumina:

15 ml of solution A, reagent blank, standard solution were transferred to 100 ml volumetric flask. 2 ml of calcium chloride solution(prepared by dissolving 7 gm of CaCO3 and adding 100 ml of water and 15 ml of conc. HCl and dilute to 500 ml) was added. 1 ml of 10% hydroxylamine hydrochloride was added with swirling the flask. 1 ml of potassium ferricyanide(0.75%) was added to each flask and mixed. 2 ml thioglycolic acid solution (4%) was added and kept for five minutes 10 ml of algerine red-S-solution(0.05%) was added to each flask and the volume was made dup to 1000 ml by adding distilled water. The samples were stirred properly and kept for 50 minutes. The concentration was measured for standard and samples at 470 nm by using UV/VIS Spectrophotometer.

4.17 MAJOR AND TRACE ELEMENTS

The major elements (other than Si and Al)i.e. Ca, Mg, Na, K, Fe, Mn, Ti and trace elements like Cu, Zn, Ni, Cr, Sr were determined in bed and suspended sediments by Atomic Absorbance Spectrophotometer (AAS) following the Loring and Rantala method (1992).

For major elements 100 mg and for trace elements 1000 mg of finely ground samples was transferred to a Teflon bomb.1 ml of acquaregia (HNO3: HCl, 1:3) and 6 ml of HF was added slowly to Teflon bomb. The bomb was heateedd for 90
minutes at 130 °C and then cooled down to room temperature. 5.6 gm of boric acid crystal was dissolved in 20 ml of distilled water in 100 ml Teflon volumetric flask and the digested solution was added to this volumetric flask and volume was made up to 100 ml. The solution was allowed to settle (one week) for formation of borosilicate. The gelatinous precipitation of borosilicate was then separated by centrifugation. The solution was analysed for the major and trace elements by AAS following instrumental manual. USGS rock standards; MAG, SCO, SGR, SDC and Canadian soil standards SO-I, SO-II, SO-III, and SO-IV were used for calibration.

4.18 Grain size analysis

Grain size analysis was carried out for the bed sediments. The sediment samples were sieved for 20 minutes on electronically controlled electromagnetic sieve shaker FRITSCH ANALYSETTE-3. The various fractions collected on the sieves on a single pan balance. Textural analysis is carried out by (Folk and Ward, 1957) method.

4.19 Mineralogy

The mineralogy of suspended and bed sediments was studied by using X-ray diffractogram technique. The slides were prepared by drop on slide technique (Gibbs 1971). The samples were glycolated and run on Philips X-ray diffractometer PW 1140 using Cu, Kα radiation source and Ni filter. The chart drive speed 1 cm min⁻¹, goniometer 10. min and intensity 2x10² were maintained. Carrol (1970) and Lindholm (1987) data on identification of minerals by using x-ray diffraction technique are used for finding out the major minerals in the sediments.