NUTRIENT TRANSPORT IN GOMTI RIVER

DISSERTATION SUBMITTED TO THE JAWAHARLAL NEHRU UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF THE DEGREE OF

MASTER OF PHILOSOPHY

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CERTIFICATE

This is to certify that the dissertation entitled "*Nutrient Transport in Gomti River*" comprises the work done in the School of Environmental Sciences for the partial fulfillment of the degree of *Master of Philosophy*. This work is original and has not been submitted in part or full, for any other degree or diploma of any other university.

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CONTENTS

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CHAPTER	Page numbers
Certificate	
Acknowledgements	
List of Tables	
List of Figures	
I: INTRODUCTION	1-7
II: LITERATURE REVIEW	8-13
III: STUDY AREA DETAILS	14-21
IV: MATERIALS AND METHODS	22-30
V: RESULTS AND DISCUSSION	31-72
VI: CONCLUSION	73-75
REFRENCES	

.

APPENDIX

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LIST OF FIGURES

- Figure 1: Flowchart of river geochemistry
- Figure 2: Sampling sites in Gomti River Basin.
- Figure 3: Geological map of Gomti River Basin.
- Figure 4: Soil type map of Gomti River Basin.
- Figure 5: Vegetation types map of Gomti River Basin.
- Figure 6: Downstream Variation of Cations And Anions During Monsoon Season
- Figure 7: Downstream variation of Cations and Anions during Postmonsoon
- Fig 8: Piper diagram for Monsoon season
- Fig 9:- Piper diagram for post-monsoon
- Fig10: Gibbs diagram for Gomti water samples during Monsoon season.
- Fig 11: Gibbs diagram for Gomti water samples during Post-Monsoon season.
- Fig 12 : log PCO₂ vs log (Ca / Mg) during monsoon

Fig 13: log PCO₂ vs log (Ca / Mg) during Post-monsoon

Fig 14.a : Log (Na/H) vs Log H4SiO4 for monsoon season.

Fig: 14.b : Log (K/ H) vs Log H4SiO4 for monsoon season

Fig: 14.c : Log (Ca/H) vs Log H4SiO4 for monsoon season.

Fig 14.d : Log (Mg/H) vs Log H4SiO4 for monsoon season.

Fig 15.a: Log(Na/H) vs $Log H_4SiO_4$ for post-monsoon season

Fig15.b : Log (K/ H) vs Log H4SiO4 for Post-Monsoon

Fig 15.c: Log(Ca/H) vs Log H₄SiO₄ for post-monsoon season

Fig 15.d : Log(Mg/H) vs Log H₄SiO₄ for post-monsoon season

Table 1: Hydrological Data on Rivers in South Asia

Table2: Drinking water quality standards as recommended by

WHO, 1996.

Table 3: Drinking water Characteristics (IS:10500:1991)

(BIS, 1991)

- Table 4: Monsoon Water Analysis (All Values in mg/L Except pH and EC (mS/cm) and As in ppb)
- Table 5: Post Monsoon Water Analysis all Parameters are in mg/L except pH and EC (mS/cm)

Table 6: Correlation Matrix of Water Samples During monsoon Season

Table 7: Correlation Matrix of Water Samples during Post Monsoon

Table 8: Factor analysis of water sample for Monsoon season

Table 9: Factor analysis of water samples for Post- monsoon season

Table 10: chemical characteristics of soil samples during monsoon.

Table 11: Chemical Characteristics of Soil Samples during Post Monsoon

Table 12: correlation matrix of sediment samples during monsoon season all values in % except TP, Tsi, Al IN µg/g and Na, K IN mg/l

Table13: Correlation Matrix of Sediment Samples during Monsoon Season (all values in % except TP, Tsi, Al in µg/g and Na, K in mg/l)

CHAPTER – I

INTRODUCTION

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CHAPTER - I

INTRODUCTION

Rivers and their corridors are important components of the terrestrial ecosystem. Rivers represents an important mode of transport for terrestrial material to the ocean in both dissolved and suspended forms. The chemistry of the water depends upon the physico-chemical and biological interactions between the water, rock and soil in the drainage system. The anthropogenic input of materials and atmospheric inputs considerably alters the river water chemistry (http://envisjnu.net/subject/river/).

Several studies have focused on the transport of material with in the rivers and streams in order to establish biogeochemical budget of weathering and to estimate the denudation rates of catchments areas. Most of the work in India was done on large rivers like Ganges, Brahmaputra, but very little is known about the transport of terrestrial material by small rivers, which are having homogenous lithology with smaller drainage basin area. So the biogeochemical studies of smaller rivers are more appealing and important to exactly estimate the material transport and to develop any meaningful model for effective and reliable budgeting of material transport to ocean.

Among the various types of inland freshwater bodies, the riverine system is a unique type of ecosystem that generally covers different types of climatic zones, landscapes and biogeographic regions. Rivers are complex lotic systems of floating water draining specific land surfaces known as watersheds or catchment area. The hydrodynamic characteristics of a river are dependent primarily on size of the river and the climatic and drainage condition with in the catchments area. The major advantages of lotic system are that there is no gravity and there are no waste disposal problems. However, Cleanliness of River is vital to the aquatic life and much of the cleanliness is dependent on land use activities in the river basin or catchments area.

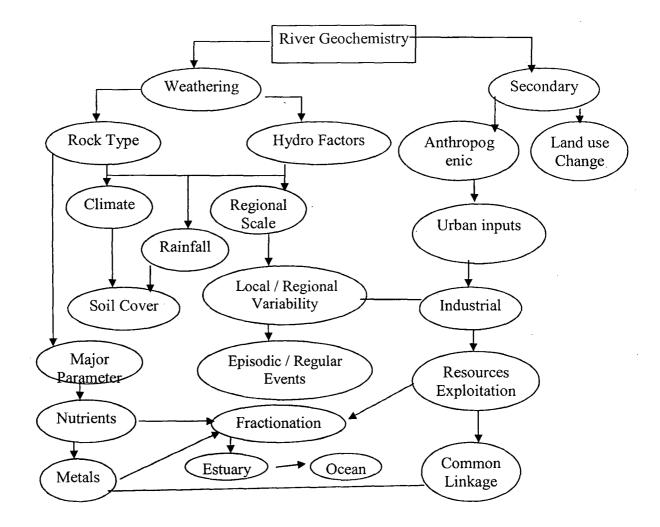


Figure 1: Flowchart of river geochemistry

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Table 1: Hydrological Data on Rivers in South Asia

(<u>http://envisjnu.net/subject/river/</u>)

	Run-Off	Area	Specific Yield
River Name	(km³ yr⁻¹)	(km²)	(mm yr⁻¹)
Manjira	4.1	21694	189
Sabarmati	4.1	21674	189
Chambal	4.8	23025	208
Indus (India, Pakistan)	73.3	321289	228
Gomti	7.4	30437	243
Cauvery	21.4	87900	243
Sutlej	14.6	57000	256
Krishna	67.8	258948	262
Tapti	18.4	65145	282
Mahi	11.8	34842	339
Padma (Bangladesh)	350.5	980000	358
Yamuna	131.7	366233	360
Subarnareka	10.8	29196	370
Godavari	119.0	312812	380
Narmada	41.3	98796	418
Pranhita	43.0	100000	430
Sone	31.8	71200	447
Ramganga	15.2	32400	469
Mahanadi	66.9	141589	472
Damodar	9.8	20000	490
Ravi	7.7	14442	533
Ganges	525.0	861404	√ 609657
Hoogly	493.0	750000	657 699
Brahmani	36.2 14.7	51822 20303	724
Beas Ghaghra	94.4	127000	743
Gandak	52.2	64300	812
Bharatpuzha	5.1	6186	824
Periyar	4.9	5398	908
Kosi	57.2	62000	923
Chalakudi	1.6	1704	939
Kadalundi	1.1	1122	980
Kalinadi	3.7	3750	987
Achenkovil	1.5	1484	1011
Jamuna (Bangladesh)	654.5	580000	1128
Pennar	67.8	55213	1228
Mandovi	1.6	1150	1391
Pamba	3.4	2235	1521
Manimala	1.6	847	1889
Megna (Bangladesh)	151.5	80000	1894
Zuari	1.1	550	2000
Kallada	3.4	1699	2001
Chaliyar	5.9	2923	2018
Muvatupuzha	3.6	1554	2317
Brahhmaputra (India)	537.2	194413	2763
Other small rivers	162.2	599501	271
India total	1850.0	3288000	563
World total	40856.0	10100000	405

Riverine systems play a major role in the nutrient dynamics i.e. their transportation from the land masses and atmosphere to the oceans and frequently serve as reservoirs for numerous compounds (Ramesh et al., 1995).

A reservoir basin represents a natural unit with in which one can examine weathering geochemistry, erosion on a continental scale and the movement of various biogenic elements (Gupta, L.P., 1994).

Unlike ocean chemistry which is globally rather homogenous, river water quality is highly variable by nature due to environmental condition such as basin lithology, vegetation and climate. There are three major natural sources of dissolved and soluble matter carried by rivers:

- The atmospheric inputs of materials
- The degradation of terrestrial organic matter
- The weathering of surface rocks. (Meybeck and Helmer, 1989)

These substances generally transit through soil and porous rocks and finally reach the rivers .On their way, they are affected by numerous processes such as recycling in terrestrial biota, recycling and storage in soils, exchange between dissolved and particulate matter, loss of volatile substances to the atmosphere, production and degradation of aquatic plants in river and lakes etc. As a result of these multiple sources and pathways, the concentration of elements and compounds found in rivers depend on physical factors (climate, relief), chemical factors (solubility of minerals) and biological factors (uptake by vegetation, degradation by bacteria).

The most important environmental factors controlling river chemistry are: Occurrence of highly soluble (halite, gypsum) or easily weathered (calcite, dolomite, pyrite, olivine) minerals; distance to the marine environment which controls the exponential decrease of ocean aerosols input to land (Na⁺, Cl⁻, $SO_4^{2^-}$, Mg²⁺); aridity (precipitation/runoff ratio) which determines the concentration of dissolved substances resulting from the two previous processes; terrestrial primary productivity which governs the release of nutrients (C, N, Si, K); ambient temperature which controls, together with

biological soil activity, the weathering reaction kinetics; Uplift rates (tectonism, relief) (Meybeck and Helmer, 1989) in brief we can say that the nutrient transportation in riverine ecosystem depends upon the geochemistry of the river, which is concerned with the processes that controls the distribution, movement and concentration/ dispersion of the elements with in the earth in space and time (Geological survey of Canada Calgary), organic geochemistry pertains to chemistry of the organic compounds, where as the inorganic geochemistry pertains to the chemistry of all inorganic compounds.

In natural waters there are many types of organic compounds, which will be classified by abundance into six major groups: humic substances, hydrophilic acid, carboxylic acids, amino acids, carbohydrate and hydrocarbon. The abundance of these compounds has been shown in the histogram of the dissolved organic carbon.50 percent of the DOC is aquatic fulvic and humic acids, the dominant group of the natural organic compounds in water. Humic acid account for 10 percent of the DOC and fulvic acid accounts for the 40 percent of DOC of most natural water.30 percent of the DOC is hydrophilic acids, the remaining 20 percent of the DOC are identifiable compounds.10 percent of carbohydrate, 7 percent carboxylic acids, 3 percent amino acids less than 1 percent constitute the identifiable compound.

Humic Acid

Soil humic substances are the colored, polyelectrolytic acids that are operationally defined by their isolation from soil with 0.1 N NaOH. Aquatic humic substances are defined differently than soil humic substances. Aquatic humic substances are operationally defined as colored, polyelectrolytic acids isolated from water by sorption on to XAD resins, weak base ion exchange resins, or a comparable procedure. they are non volatile and range in molecular weight from 500 to 5000 they originate in soil and plant systems, where they are leached by interstitial water of soil into rivers and stream. Generally, aquatic humic substances have an elemental composition that is 50% carbon, 4 to 5 % hydrogen, 35 to 40% oxygen, and 1 % nitrogen. The

major functional groups includes: carboxylic acids, phenolic and alcoholic hydroxyl groups, and keto functional groups.

The concentration of humic substances for various waters varies, in ground water and marine water the concentration of humic substances are lowest., it is 0.05 to 0.25 mg C/l. streams rivers and lakes vary in concentration of humic substances from 0.5 to 4.0 mg/l. Tea colored waters such as marshes bogs and swamps vary from 10 to 30 mg/l DOC as humic substances.

Humic substances that precipitate in acid are humic acid, and those in solution are fulvic acid. Generally the fulvic acids are more soluble in water because it contains more carboxylic and hydroxyl functional groups and is lower in molecular weight, from 800 to 2000. Humic acid is larger than 2000 and is often colloidal in size (Thurman, E.M., 1985).

Biogenic Silica

Silicon has a crucial role in many biogeochemical processes for example as a nutrient for marine and terrestrial biota, in buffering soil acidification and in regulation of atmospheric carbon dioxide. Traditionally, silica fluxes to soil solutions and stream waters are thought to be controlled by the weathering and subsequent dissolution of silicate minerals. Rate of mineral dissolution can be enhanced by biological processes, but plant also take up considerable quantities of silica from soil solution, which is recycled into the soil from falling litter in a separate soil plant silica cycle that can be significant in comparison with weathering input and hydrologic output (Derry, L.A. 2005).

In order to study the transportation of organic and inorganic nutrients in the Gomti basin the present study has been carried out with following objectives.

Objectives of the study

- Quantification of organic nutrients which includes dissolved organic carbon, humic acid in water and total carbon, inorganic carbon, organic carbon, humic acid and biogenic silica in bed sediments.
- To obtain the information about the quantity of inorganic nutrients in Gomti river by analyzing total nitrogen, total phosphorus, silica, alumina in suspended and bed sediments and dissolved silica, phosphate, nitrate, sulphate, fluoride, chloride, bromide, in water samples.
- To observe the impact of seasonal variation on the concentration of heavy metals, trace metals and nutrients in the Gomti basin.
- Use of statistical analysis and geochemical diagrams to understand the various factors controlling the water and sediment chemistry of Gomti basin.

CHAPTER – II

LITERATURE REVIEW

CHAPTER - II

LITERATURE REVIEW

The contribution of nutrients is very closely related to the specific hydrology of each supplying river basin. Nutrients are transported from one eco system to another ecosystem through biogeochemical cycles.

Torrcilla et al., (2005) studied nutrient mobility with in Ebro river and found that agricultural non point sources (NOP) account for 64% of NO₃ loads generated in the Ebro river while urban and industrial point sources (PS) are responsible for 88% PO₄-P and 71% COD loads and biological reactions were found to be a key factor in nutrient content and dynamics.

Singh M et al., (2005) presented a geochemical study of the Ganga alluvial plain weathering products transported by the Gomti river. The GAP weathering products were geochemically distinguished as arkose to lithernite in rock classification, chemically mobility, normalized with respect to TiO_2 in upper continental crust, indicates that Si, Na, Zr, Ba and Sr, mainly derived from feldspar, muscovite and biotite are lost during weathering. Iron and Zinc remained immobile during weathering and were strongly adsorbed by phyllosilicates and concentrated in fine grained sediment fractions. They reported that GAP has experienced chemical weathering of incipient to moderate intensity.

Jennerjahn et al., (2004) studied the effect of human activities on the biogeochemistry of a tropical river Brantas and coastal waters of Madura strait, Java, Indonesia. They observed high amount and reactivity of amino acid bound nitrogen in TSM and sediments of the river and dissolved organic nitrogen (DON) in river and coastal waters suggest that organic nitrogen plays a more important role for coastal food webs and nitrogen cycle in tropical regions, particularly under conditions of high agricultural runoff and urban waste disposal.

Singh M et al., (2003) stated that geogenic distribution of heavy metals in the Ganges river basin is the representation of fluvial processes operating on the Asian continents under monsoon controlled humid subtropical climate. The concentration of heavy metals in the Ganges river basin may act as sediment quality guidelines for governmental and environmental organizations for references values in assessing anthropogenic vs geogenic inputs in environmental studies. They further reported that as a major sediment transporting system in the world, the Ganges River contributes significantly to sediment bound heavy metal load to the Bay of Bengal.

Bajpayee and Verma, (1998) studied on distribution of carbon and phosphorus in river-back water system of Kerala and reported that Riverine runoff provides a powerful geochemical flow playing important role in the planetary mass exchange between world's land and the ocean and is strongly affected by human activities. Rivers receive water through precipitation and transport terrigenous material derived from land as a result of physical and chemical weathering of the surface rocks. About 89% of the total material transport takes place through the stream.

Natural biological and geochemical activities in soil and bedrock, as well as anthropogenic activities, are responsible for the composition of stream and river water which eventually reaches estuaries and the ocean. The sources, pathway and quantities of the transported matter will differ from basin to basin because of the different types of terrestrial ecosystems that exist and the various hydrological and climatic processes that occur in them. These transported matters carried by rivers on reaching estuaries undergo changes in species and quantity due to action of organism.

Ramesh et al., (1995) studied on the transportation of Carbon and Phosphorus by major Indian rivers and reported that the high concentration of P-PO₄ may be due to human interference. They investigated that the flux of P-PO₄ and particulate inorganic phosphorus (PIP) from the Indian rivers to the ocean is 19.5×10^{10} g yr⁻¹ and 1.5×10^{12} g yr⁻¹ respectively.

Artola et al., (1994) investigated the impact of development on the hydrology and nutrient in river basins draining into reservoirs and found that

changes in land usage such as urbanizations and recreational development can influence the contribution of nutrients to a basic river basin and therefore, the N/P ratio. They showed that greater part of N is contributed through basic land drainage, while P is obtained following surface runoff. Mistry of natural water is simply the application of organic chemistry to study earth processes involving the hydrologic cycle. Organic geochemistry of natural water is studied at two levels, one is macroscopic level and other is molecular level. There are at least five processes that affect the dissolved organic compounds in natural water. They are sorption/partition, precipitation, volatilization, oxidation/reduction (both chemical and biochemical), and complexation.

Richey et al., (1991) reported that carbon and nutrient fluxes in large floodplain rivers are presumably reflections of their watersheds and flood plains, and some extension of the properties of the smaller rivers that form them.

Organic Geochemistry

According to Thurman, (1985) organic geochemistry of natural water is simply the application of organic chemistry to study earth processes involving the hydrologic cycle. Organic geochemistry of natural water is studied at two level, one is macroscopic level and Other is molecular level. There are at least five processes that affect the dissolved organic compounds in natural water. They are sorption / partition, precipitation, volatilization, oxidation / reduction (both chemical and biochemical), and complextion.

Dissolved Organic Matter (DOM) And Particulate Organic Matter (POM)

Tranvik L.J. and Jansson. M., (2002) studied the effect of climate change on the terrestrial export of organic carbon and reported that DOM in the oceans represents one of the biosphere's principal stores of organic carbon. A large proportion of this matter is drained from the continents. They also suggested that rising temperatures may affect the transport of dissolved organic carbon (DOC) from peatlands to the oceans.

Kalbitz et al., (2000) reviewed the controls on the dynamics of dissolved organic matter in soils and stated that Dissolved organic matter (DOM) in soil plays an important role in the biogeochemistry of carbon, nitrogen, and phosphorus, in pedogenesis, and in the transport of pollutants in soils. They also reported that litter and humus are the most important DOM sources in soils. High microbial activity, high fungal abundance, and any conditions that enhance mineralization all promote high DOM concentration. DOM may be adsorbed strongly to mineral surfaces, resulting in low DOM concentrations in the soil solution. There are strong indications that microbial degradation of DOM also controls the fate of DOM in the soil.

Tombacz, (1999) studied the colloidal properties of Humic acids and stated that Humic Acids (HAs) can be dissolved or precipitated in aqueous media, can accumulate at interfaces, can form self-assemblages, can solubilize organic compounds, and can exists in different colloidal states depending on the solution conditions.

Gupta et al., (1996) studied particulate inorganic and organic carbon(PIC, POC), Particulate Nitrogen(PN) and Particulate Amino Acids (PAA, including to hexosamines (HA) on Godavari river. They found that during dry season POM in the upper reaches is relatively fresh and autochthonous, in the lower reaches it is degraded and inorganic suspended matter content is higher here. In the wet season (wet monsoon) heavy rains cause a basin-wide flushing of humus from entire catchment area consequently POM in the river is mainly degraded and allochthonous. Annual transport of the Godavari River amounts to 2.81*10⁶ ton POC, 0.29*10⁶ ton PN and 0.10*10⁶ ton Particulate Amino Acid Nitrogen. These amounts rank the Godavari river to one of the most important organic carbon transporting rivers in the world.

Ramesh et al., (1995) reported that the transfer of dissolved organic carbon (DOC) and particulate organic carbon (POC) from the Himalayan rivers is estimated to be about 7.6 and 9 million tons per year.

Humic Acid

Wang G.S. and Hsieh S.T., (2001) monitored natural organic matter in water with scanning spectrophotometer by using three commercially available humic acid and found no apparent differences between the spectra of the three humic acid and also found that the presence of nitrate nitrogen ($NO_3^{--}N$) greatly affects the spectra of the NOM and suggested that in order to monitor the NOM with minimum interference, area under the spectra between 250 and 350 nm should be used as a surrogate for concentration of NOM in water.

Pandey et al., (2000) determine the stability constants of Metal-Humic acid complexes and its role in environmental detoxification. They suggested that humic acid with hydroxyl-, and carboxyl-reactive groups can form coordination compounds with metals. The complexation of metal ions by humic acid is extremely important in affecting the retention and mobility of metal contaminants in soils and waters. The stability constants for different humic acid-metal complexes may help to predict the behavior of these compounds in the environment and also the strength of complexes formed. They also reported that organic legand like humic acid may render almost all metals immobile, thereby helping in detoxifying process.

Pandey et al., (1999) studied that free radicals play an important role in the binding of organochlorine pesticides and heavy metals with humic acid by forming a soluble complexes. They found the generation of free radicals in case of interaction of humic acid with ∞–HCH (Hexachlorocyclohexane), Cr, Cu and a hyperfine splitting pattern was noticed only in case of Mn.But such phenomena does not occur with Ca, Cd, Pb, As, Ni, Co, Zn and Fe.

Lovley et al., (1996) reported that some microorganisms found in soils and sediments are able to use humic substances as an electron acceptors for microbial respiration and this electron transport yields energy to support growth.

Biogenic Silica

Silica (SiO₂) is an important nutrient in the marine environment. Diatoms, Radiolaria, Siliceous sponges, and Silicoflagellates utilize this nutrient for growth and the formation of skeletal material. Siliceous biota removes nearly all dissolved silica from open ocean surface waters. After the death of the biota the siliceous skeletal materials dissolves as it settles through the water column enriching the deep waters with dissolved silica. Second main source Silica to the ocean is Submarine volcanism and associated hydrothermal emanations. Wolery and sleep in 1976 estimated that 0.3 to 0.9 ×10¹⁴ g SiO₂/yr are supplied to the oceans by hydrothermal emanations and third main source is glacial weathering.

Demaster D.J., (1981) reported that in addition to biological significance of silica, the flux of particulate silica from surface waters (and subsequent dissolution) plays an important role in the cycling of other elements in the marine environment such as Radium, Barium and Germanium.

Derry et al., (2005) studied the biological control of terrestrial silica cycling and export fluxes to watersheds of Hawaiian Islands. Their data imply that most of the silica released to Hawaiian stream water has passed through the biogenic silica pool, whereas direct mineral-water relations account for a smaller fraction of the stream silica flux. They also reported that other systems exhibiting strong Si depletion of the mineral soils and/or high Si uptake rates by biomass will also have strong biological control on silica cycling and export.

CHAPTER – III

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STUDY AREA

CHAPTER - III

STUDY AREA

The river Gomti, with its major tributary the Sai, is one of the major tributaries of the Ganges. Gomti originates from a natural reservoir in the swampy and densely forested area near Madho-Tanda (elevation of about 200m; North latitude28⁰34' and East longitude 80⁰07') about 3 km east of Pilibhit town in Uttar Pradesh and about 50 km south of Himalayas foot hills (Report of National River Conservation Directorate, May 2004).

Gomti is 940 Km long and has a catchments area of 30437 Km², which lies between latitudes 25⁰26.9'N and 28⁰9.1'N and longitudes 80⁰E - 83⁰9.6'N (Gupta and Subramanian, 1994). Throughout its stretch, there are few small tributaries (Kathna, Sarayan, Reth, Luni, Kalyani, and Sai rivers) originating with in short distances. Sai, major tributary of Gomti, meets with Gomti just before its confluence with river Ganga near Rajwari about 25 Km north of Varanasi district. Sarayan and Luni rivers are two main tributaries meeting the Gomti river before (45 Km upstream) and after (about 40 Km downstream) Lucknow city. Gomti is spread over twelve districts. The river with its tributaries flowing through the districts of Pilibhit, Shahjahanpur, Sitapur, Hardoi, Lucknow, Barabanki, Faizabad, Sultanpur, Jaunpur, Raibareli, Pratapgarh. Out of these twelve district Lucknow, Sultanpur and Jaunpur are the three major urban settlement on the bank (Report of National River Conservation Directorate, May 2004).

CLIMATE AND RAIN FALL

About 90 percent of rainfall in Uttar Pradesh is caused by the monsoon coming from bay of Bengal from June to September. When the monsoon moves westwards, its intensity decreases and affects its gravity. On account of this phenomenon the eastern part of the state receives more rainfall than the western part. The entire Uttarpradesh's Himalaya region except the snow bound areas, receives heavy rainfall more than 1200mm.

The Gomti drainage basin trends in a NW-SE with almost similar climatological features throughout the basin. The annual rainfall in the basin varies from 87 to 125 cm.

The Gomti river basin comes under the sub-tropical climate region. Variation in temperature is extreme: a maximum of, 48^oC in summer and a minimum of 2^oC in winter (Census of India, 1991).

GEOLOGICAL DETAILS

The Gomti basin lies in the great alluvial plain, which is of recent origin (Pleisticene-Holocene) .The depth of alluvium varies between 4000 and 6000 m. The abundance of calcareous matter in this region is as high as 30 percent (Wadia, 1981). Quartz is apparently the dominant mineral, accounting for about 74 percent of the mineralogy of the bed sediment of Gomti river, followed by feldspar(18.4 percent,12.2percent of which is plagioclase), and mica (7.5 percent).Other minerals altogether make up less than 1 percent of the mineralogy (Gupta and Subramanian, 1994).

SOIL TYPE

The soils of the state have been grouped into eleven major classes and twenty seven suborder associations which are shown on the map along with their characteristics. The following soil types are found in different parts of Gomti basin:

The Aqalfs-Aquepts-Udalfs(2), relatively have high base status with brown color and found in the inter-fluvial flood plain of Ganga-Sai rivers(in eastern Unnao, Southern RaiBareily, Pratapgarh and Jaunpur).

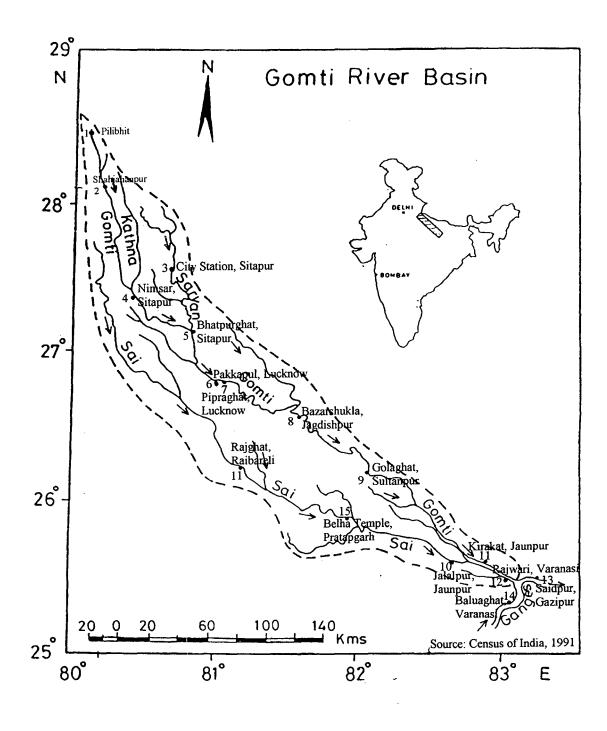
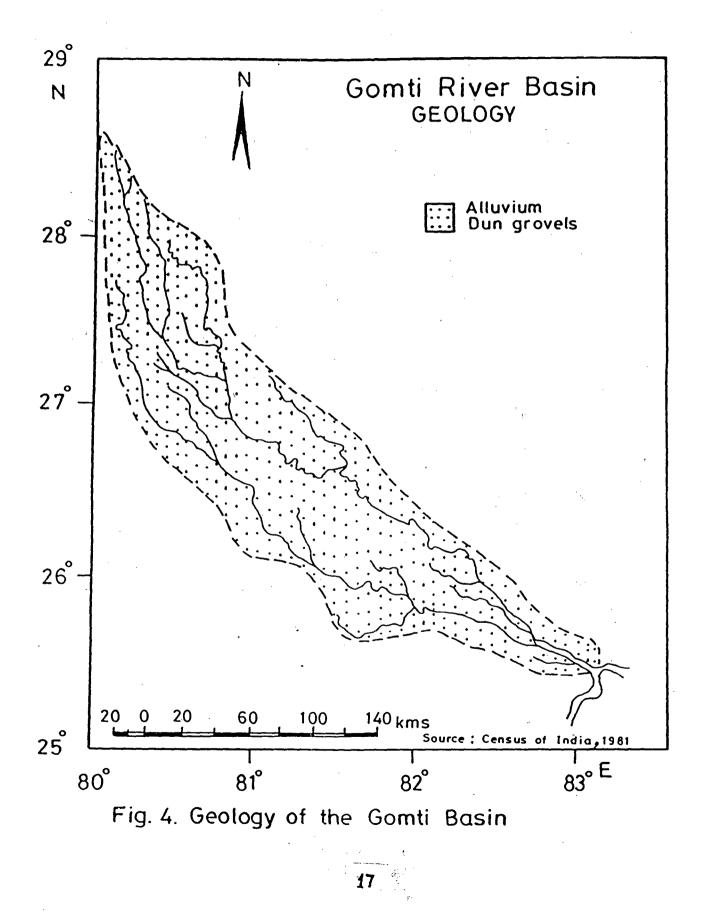
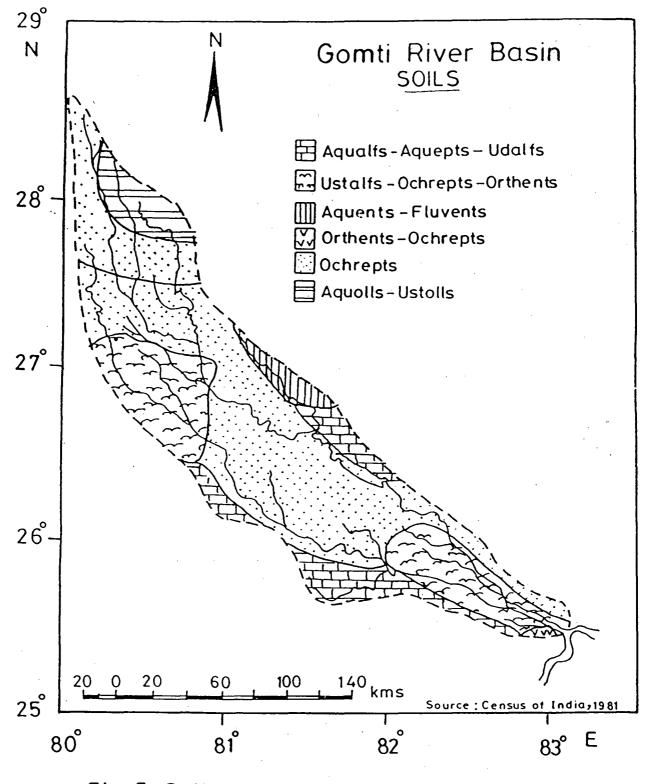
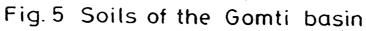
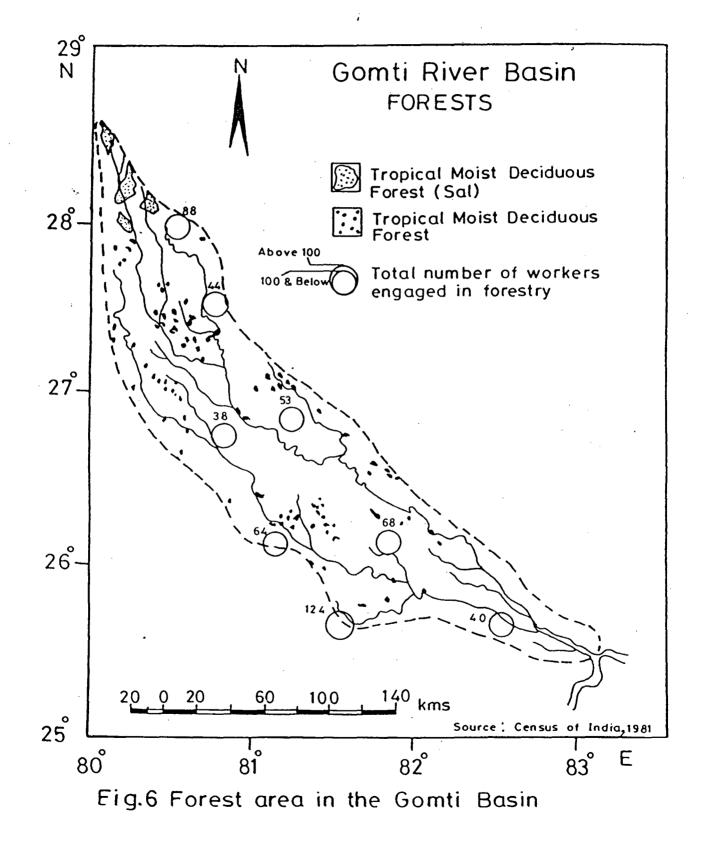


Figure 2: Sampling sites in Gomti River Basin









- Ustalps-Ochrepts-Orthtents(18) are shallow black brown and alluvial soils occurring in the eastern part of Varanasi, central Jaunpur and eastern Pratapgarh.
- Fluents-Psamments-Ochrepts(50) these soils are mostly brown to dark brown in color and loam to sandy loam in texture. These soils are found in the Ganga rivers in Ghazipur district (Gupta and Subramanian, 1994 and Census of India, 1991).

VEGETATION

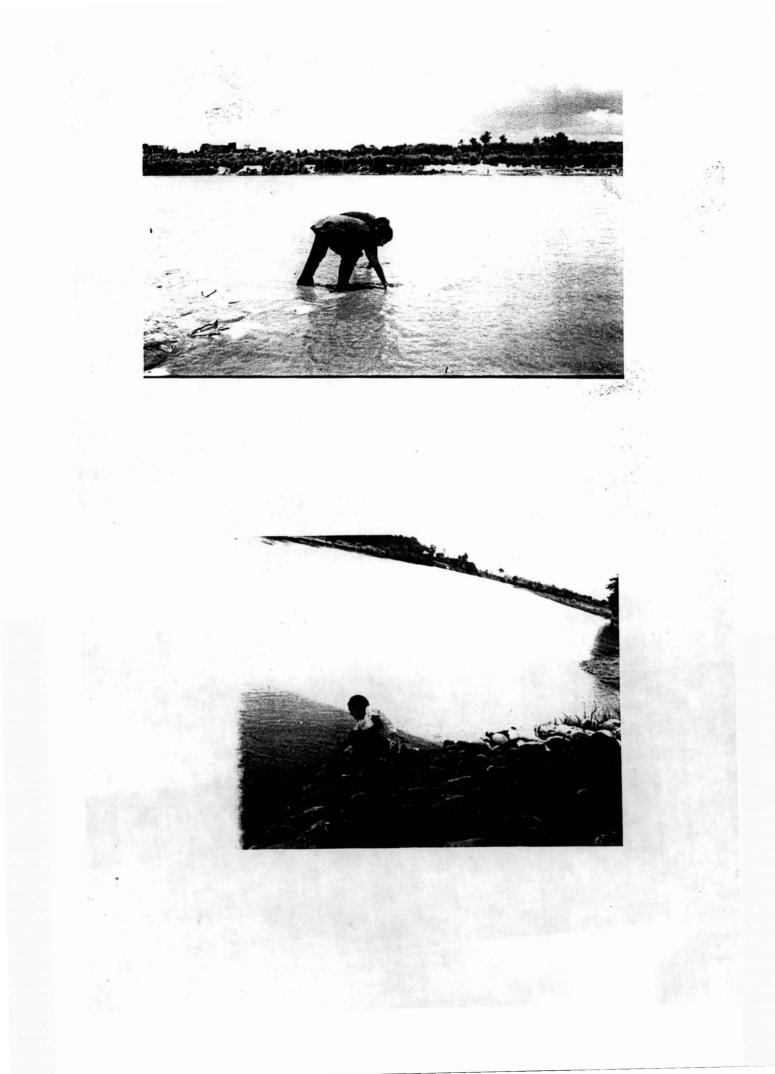
Apart from flowing through patches of tropical dry deciduous, tropical moist deciduous and dry deciduous forests and scrubs and grasslands, the river flows through the vast arable lands.

SAMPLING LOCATION

For the present work the whole stretch of river Gomti has been selected to study the transportation of organic and inorganic nutrients in it. In few decades the quality of river Gomti has been deteriorated because of pollution loads both from the point and non-point sources. It receives agricultural runoff from its vast catchment area spread over twelve districts directly or through its tributaries. Five major townships, Lucknow, Raibareli, Jagdishpur, Sultanpur, and Jaunpur are major pollution contributor both for domestic and industrial wastes directly to the river. Other pollution sources are washing of clothes and animals in river water. There are cremation ghats also on this river. Since there are several sugar mills, distilleries and breweries in several districts throughout Gomti basin, hence organic load is also high in this river.

The thick vegetation in the upper stream part of the river adds litter falls in the river which is the cause of organic nutrients like humic and fulvic acid in the Gomti. Temples at some location point like Madhotanda in Pilibhit, Nimsar in Sitapur, Belhatemple in Pratapgarh districts also contributes in organic load. On the basis of above sources of organic and inorganic nutrients, the samples have been collected from sixteen location point of ten districts, covering the whole stretch of Gomti river basin. Samples of river Ganges were also taken from two districts. One is from Saidpur district, after the confluence of Gomti with the Ganges, and other from Baluaghat, Varanasi before confluence of Gomti. The schematic diagram of study area showing sampling point locations in the fig Names of the sampling locations with their latitude and longitude position are given.





CHAPTER – IV

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MATERIALS & METHODS

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MATERIALS AND METHODS

FIELD METHODS

Water sampling

Running Water samples were collected in polypropylene bottles from sixteen location points covering ten districts of Uttar Pradesh during monsoon and post monsoon season. Collected water samples were brought to the laboratory and stored in cold room at 4°C temperature in order to avoid any major chemical alteration (APHA, 1995).

Water samples for the metal analysis were fixed with 4-5 drops of nitric acid and then filtered by 0.45µm membrane filter paper. The water samples for DOC and Humic acid were taken into brown bottle to avoid the decomposition of organic matter by the sun light. For the cations and anions the water samples were not fixed with acid for. The bicarbonate, pH, electric conductivity(EC) the unfiltered water was used.

Sediment Sampling

The top 5-7cm layer of the bed sediment was scooped out with a stain-steel vessel and immediately transferred into the polyethylene bags and stored in gold room at 4°C.

LABORATORY METHODS WATER ANALYSIS

pH and Conductivity

pH and conductivity was measured in unfiltered samples. The pH was measured by "CYBERSCAN 510". The glass electrode was conditioned (4M

KCI as filling solution) and calibrated with buffer solution of pH 4.7 and 9.2. The temperature knob was set in accordance with the temperature of the water samples. The samples were stirred continuously in order to maintain homogeneity before noting down the pH.

Conductivity was measured in micro-Siemens (μ S) using "Systronics Conductivity Meter (P602)". The instrument was caliberated and set for 0.01m KCl solution (1413 μ S at 25⁰C).

Bicarbonate (HCO₃⁻)

The bicarbonate content was determined following the potentiometric titration method (APHA, 1995). Bicarbonate standards ranging from 100-1000 mg/l was prepared from NaHCO₃. 50 ml sample and a series of bicarbonate standards were titrated against 0.02N HCl. The end point was noted at pH 4.5. A standard graph was plotted between bicarbonate standards and volume of acid consume. The readings of sample were noted down from this graph.

Phosphate (PO₄³⁻)

Phosphate was determined by the Ascorbic Acid Method (APHA, 1995).phosphate standards were prepared from KH_2PO_4 . 40 ml of each sample and standard solution was pipettes out in 50 ml volumetric flask and 5mlof molybdate antimony solution (prepared by dissolving 4.8 g of ammonium molybdate and 0.1 g potassium antimony tartar ate in 400ml 4N H_2SO_4 and making the total volume to 500 ml with the same acid) and 2 ml of ascorbic acid solution (2% w/v) was added and mixed well. The mixture was diluted to 50 ml and optical density was measured at 650 nm using "Cecil Spectrophotometer (Model no. 594)". A graph was plotted between standard concentration and optical density and sample concentration was recorded directly from the graph.

Dissolved Silica (H₄SiO₄)

The dissolved silica content was determined by the molybdo silicate method (APHA, 1995). Silica from sodium meta silicate. 20 ml each sample and standard pipette out in 50 ml volumetric flask and 10 ml of ammonium molybdate solution (prepared by dissolving 2 g ammonium molybdate in 10 ml of distilled water; 6 ml of concentrated HCl was added and final volume was raised to 100 ml by distilled water) and 15 ml of reducing reagent (prepared by mixing 100 ml metol sulphite solution, 60 ml 10% oxalic acid and 120 ml 25% sulphuric acid, and making the total volume 300 ml by adding distilled water) was added and mixed well (Metol sulphite solution was prepared by dissolving 5 g metol in 210 ml distilled water and 3 g sodium sulphite was added and the volume was made upto 250 ml by adding distilled water).

The samples were stirred properly and kept for 3 hrs to complete the reaction. The optical density was measured at 650 nm using "Cecil Spectrophotometer (Model no. 594)". Graph between standard concentration and optical density was drawn and concentration of samples was recorded from it.

ANIONS: Clorides (CI⁻), Fluoride (F⁻), Nitrate (NO₃⁻), and Sulphate (SO₄⁻⁻)

These were analysed using "Metrohm Ion Chromatograph" with "709 IC pump", "733.1 IC separations centre" and "732 IC Conductivity Detector". The column used for anion analysis was "IC anion column phenomex star ion A300 (6.1005.100)". The eluent used was 1.8 m mol / I sodium carbonate and 1.7m mol /I sodium hydrogen carbonate; conductivity after chemical suppression was 14 µmho/cm. The flow rate of 1ml/min was maintained during the analysis. The anions were eluted in order of fluoride, chloride, trace metals nitrate and sulphate. It took 20 min for each run.

CATIONS: Sodium (Na⁺), Potassium (K⁺), Calcium (Ca⁺⁺) and Magnesium (Mg⁺⁺) and TRACE METALS: Iron (Fe), Manganese (Mn), Copper (Cu), Zinc (Zn), Nickle (Ni), Chromium (Cr), Cadmium (Cd), Arsenic (As), Lead (Pb)

Cations and Trace metals analysis was done by using "Atomic Absorption Spectrophotometer, Shimadzu-AA-6800". First the instrument was calibrated by using known concentration of metal sample and a standard curve was drawn between absorbance and concentration, from this graph concentration of water sample was calculated. Flame used for metal analysis was Air -Acetylene.

Dissolved Organic Carbon

The 100 ppm stock solution was prepared from potassium per thalate (C₈ H_5O_4) salt. Then standards ranges between 5 to 25 mg/l were prepared by serial dilution of stock solution. 10 ml of samples and standards were added to 50ml Erlenmeyer flask, 0.4 ml of buffer solution of pH 2 was added. Stired it at a moderate speed for 10 min. persulphate powder pillow was added to sample and to reagent blank vial.0.3 ml deionized water was added to reagent blank vial and 0.3 ml of prepared sample was added to the sample vial. Mixed it properly then blue indicator ampules was inserted in each vials. The vial assemblies were capped tightly and placed in the COD reactor for 2 hrs at 103 -105^oC. The vial assemblies were removed carefully from the reactor and placed them in a test tube rack.

The vials were allowed to cool for one hour for accurate results. The optical density of these vials were taken at 430 nm. (Hach process).

Dissolved Humic Acid

Standards of humic acid was prepared form the sodium salt of humic acid (sigma Aldrich) ranges between 0.1 to 10 mg/l. The water samples were

concentrated two times by rotavapour at 45°C. Then the optical density of standards and concentrated water samples were taken at 258 (U.V.) nm (Wang G.S. and Hsich S.T. (2001).

SEDIMENT ANALYSIS

Sediment analysis was analyzed for total carbon, total nitrogen, total phosphorus, humic acid and major and minor element. Samples were air dried and grounded for analysis.

Digestion method

Digestion Method for nitrogen and phosphorus analysis: Samples were digested by using digestion method of Anderson (1993). 0.2 g of finely grounded sample was taken in digestion tube and 4.4 ml of digestion mixture (prepare by dissolving 0.42g Selenium powder and 14g lithium sulphate in 350 ml 30%(v/v) H₂O₂ and mixed. In this mixture 420 ml H₂SO₄ was added carefully while cooling in ice bath) was added in each tube. This was digested at 90^{0} C till solution becomes colorless. The solution was added in each tube stirred the final volume was made up to 100 ml by adding distilled water. The clear solution was used for analysis.

Total nitrogen

Nitrogen was determined by Kjeldahl Method by using steam distillation. Free ammonia was liberated from the solution by steam distillation in the presence of excess alkali. The distillate is collected in a receiver containing excess boric acid indicator and nitrogen is determined by acid titration.

Distillation process was done by transferring 10ml aliquot to reactor chamber and adding 5ml alkali mixture (prepared by dissolving 500g NaOH and 25g sodium thiosulphate in water and final volume was made up to 1000ml with distill water) and starting distillation immediately. About 25ml of distillate was collected in 5 ml boric acid –indicator solution (prepared by 0.3 g bromocresol green and 0.165 g methyl red were dissolved in 500ml of 95% ethanol to make the indicator mixture. 20g of boric acid was dissolved in 700ml distilled water and cooled and 200ml of 90%ethanol was added. 20 ml of mixed indicator was added to it and mixed well by shaking. 0.05N NaOH was added to it till 1ml of indicator with 1ml distilled water changes color from pink to pale green (okalibo,1993) the solution was then made up to 100 ml).The distillate was titrated against N/140 HCl to a grey point using micro burette.

Kjeldahl Nitrogen was calculated using the following equation:

%N = <u>(a-b)*N of HCl*1.4</u> V*S

Total phosphorus

Total phosphorus in soil was determined by Ascorbic Acid Method. Standard phosphate solution ranging from 0.2 to 2.0 ppm was prepared using KH₂PO₄.5ml of digested samples and standard solution was pipette out in 50 ml volumetric flask and 20 ml distill water was added, then 10 ml of reducing agent (prepared by dissolving 2.108 g of ascorbic acid in 400 ml of ammonium molybdate –ammonium potassium tartarate solution (prepared by adding 12 g of ammonium molybdate in 250 ml of warm distill water.0.291 g antimony potassium tartarate was added in 100 ml distilled water and both solution were added to 1000ml of 5N H₂SO₄, final volume make up to 2000ml and mixed well) was added. The mixture was diluted to 50ml and optical density was measured at 880 nm using "Cecil Spectrophotometer(model no.594)". A graph was plotted between concentration of the standards and optical density and sample concentrations were obtained from this graph.

Humic Acid

<u>Method of extraction</u>: 10 g of air dry soil was weighed into a 200- ml propylene flask, 100ml of extractant was added (mixture of 0.1N NaOH and 0.1M $Na_4P_2O_7$), it was shaked for 24 hrs at room temperature. Then the dark colored supernatant solution from the residual soil was separated by centrifugation (preferably at 10,000 rpm for 10 min).

<u>Fractionation of sediment extracts</u>: The alkaline extract was acidified and washed to pH 2 with 2N HCI. Left it for over night then the soluble material (Fulvic Acid) is separated from the coagulate (Humic Acid) by centrifugation. Freezed dry both fractions and the weight of both fraction was taken. The percentage of humic acid was calculated.

Biogenic Silica

After extraction of sediment, the biogenic silica is determined by the modified molybdate – blue spectrophotometry method (strick land and parsons, 1968; Fanning and Pilson, 1973).

<u>Procedure</u>: 17.5 ml of molybdate working solution was dispensed into dry, clean plastic reaction vessel after 30 min. 125 µl of sample was pipetted out, standards and blank into each vessel and immediately mixed by swirling again after 20 min. 7.5ml of reducing working solution into each vessel, capped tightly and left it overnight (minimum 12 hrs) to complete the reduction of the silicomolybdate complex. The absorbance of the samples were taken at 812 nm by spectrophotometer (ECIL UV-VIS spectrophotometer UV 5704SS).

<u>Standards preparations</u>: Primary fused quartz silica standards were prepared as described in (Fanning and Pilson, 1973). Working silica standards (2, 4, 6 mg/l) were prepared by diluting the stock solution of sodium metasilicate with appropriate volumes of 2M Na₂CO₃. <u>Calculation</u>: The following algorithms were used to calculate the opal content of samples.

 C_{std} = silica concentration of the working standard (mM)

 C_s = silica concentration of the sample.

 A_{std} = absorbance of the standard

As = absorbance of the sample

F = F- factor (mM/abs). f= 1/s, where s is the slope of a linear regression through the standard curve; a plot of A_{std} Vs C_{std} for all standards

M = Sample mass in mg

The concentration of dissolved silica in each sample is determined by the equation

 $C_s = F \times As$

Weight percent silicon is calculated by the equation

%Si opal =112.4 × (Cs/ M)

GEOCHEMICAL PLOTS

Piper Diagram

Piper Diagrams were drawn by the help of "Gw_chart piper graph software" downloaded from USGS site.

Gibbs diagram

This diagrams were drawn by help of Waterclast software (DOS BASED).

Mineral Stability Diagram

Mineral stability diagrams were plotted using "Microsoft Excel X.P." and Waterclast software.

Line diagram

Line diagrams were plotted by using "Microsoft Excel X.P." showing downstream variation of major cations and anions.

STATISTICAL ANALYSIS

Correlation Matrix

Correlation matrix between various water quality parameter was constructed by using "Microsoft Excel X.P."

Factor Analysis

Factor analysis for water samples was done by using "Statistical Package for Social Sciences(SPSS), version-11.01".The extraction method for factor analysis was "Principal Component Analysis" and "Varimax Rotation" was used for deriving factors.

CHAPTER - V

RESULT AND DISCUSSION

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CHAPTER – V

RESULT AND DISCUSSION

WATER CHEMISTRY

Continental weathering, land run-off through vegetation and agricultural lands and human activities contribute the major part of nutrient input into the riverine environment, nutrient hydrochemistry, its biological utilization and regeneration by bacterial remineralization and geochemical recycling are important features of nutrient biogeochemistry in river waters (Gupta, R.S and Upadhayay, 1987).

Climate also plays an important role in the transportation of nutrients because the processes of rock weathering are strongly influenced by temperature and by amount and distribution of at some seasons of the year than at other seasons. Climates characterized by alternating wet and dry season may favour weathering reactions that produce considerably larger amounts of soluble inorganic matter climate may fluctuate greatly in volume of flow, and the water may have a wide range of chemical composition. (Hem J. D., 1991)

pH and EC

pH plays an important role in river water chemistry, as it decides the fate of various geo-chemical reaction of water body and it also controls the reactions involving trace metals.

The pH values of the surface water samples ranges from 7.06 to 8.49 in monsoon (table 4) and from 7.06 to 8.38 (table 5) during post monsoon season and indicating that the water of Gomti basin is neutral at some places and slightly alkaline at some locations.

The electrical conductivity is the ability of a substance to conduct an electric current and it indicates the amount of dissolve constituents present in water. As ion concentrations increases conductance of the solution increases. The EC values of the water sample ranges from 0.28 to 0.55 mS/cm in

Table2: Drinking water quality standards as recommended by WHO, 1996.

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Elements/radicals	Guideline values (mg/l)
Chloride	250
Sulfate	500
Nitrate	50
Fluoride	1.5
Iron	2
Manganese	0.5
Copper	2
Nickel	0.02
Lead	0.01
Zinc	3
Arsenic	0.01
Cadmium	0.003
Chromium	0.05
Mercury	0.001

Table 3: Drinking water Characteristics (IS:10500:1991) (BIS, 1991)

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S.No	PARAMETER	Desirable limit (mg/l)	Permissible limit (mg/l)				
1	рН	6.5 - 8.5	No relaxation				
2	Iron(Fe)	0.3	1.0				
3	Chloride(Cl)	250	1000				
4	Fluoride(F)	1.0	1.5				
5	Calcium(Ca)	75	200				
6	Magnesium(Mg)	30	100				
7	Copper (Cu)	0.05	1.5				
8	Mangnese(Mn)	.0.1	0.3				
9	Sulphate(SO ₄)	200	400				
10	Nitrate(NO ₃)	45	100				
11	Cadmiun(Cd)	0.01	No relaxation				
12	Zinc(Zn)	5.0	15				
13	Alkalanity	200	600				
14	Dissolve solid	500	2000				

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Table 4: Monsoon Water Analysis (All Values in mg/L Except pH and EC (mS/cm) and As in ppb)

LOCATION	pН	EC	HCO3	TSS	DOC	F	Cl	NO ₃	PO₄	SO4	Si	Na	ĸ	Ca	Mg	Cr	Fe	Mn	Ni	Cu	Cd	Zn	Pb	As	Charge
	-															•									balance
KIRAKAT	7.25	0.45	151.7	0.01	21.21	0.58	7.27	5.06	0.55	29.80	3.54	33.54	7.9	24.1	13.7	0.15	1.13	0.01	0.12	0.02	0.03	0.21	0.25	7.44	7.41
BALUAGHAT	7.35	0.39	167.9	0.00	4.77	0.10	11.56	3.51	0.42	24.34	0.36	52.40	11.9	24.2	10.6	0.18	0.72	0.03	0.09	0.03	0.02	0.02	0.22	6.41	12.02
BAZARSHUKLA	7.32	0.40	160.9	0.02	9.18	0.46	5.36	8.46	0.60	18.28	5.49	31.23	9.5	23.4	13.0	0.24	1.06	0.1	0.07	0.01	0.02	0.03	0.25	3.9	6.81
RAJGHAT	8.49	0.36	251.9	0.01	12.63	0.67	4.78	8.46	0.13	1.39	2.57	37.73	7.9	13.4	11.1	0.18	0.95	0.05	0.06	0.01	0.02	0.15	0.06	5.06	-13.16
RAJWARI	7.53	0.47	209.9	0.01	33.93	0.16	4.78	4.23	0.34	38.04	4.87	25.15	8.7	23.1	13.2	0.24	1.3	0.08	0.07	0.01	0.01	0.02	0.09	5.07	-11.16
SARAIN	7.06	0.35	174.9	0.01	17.39	0.14	5.90	20.06	0.63	3.28	2.48	27.67	11.9	14.8	11.4	0.25	1.63	0.12	0.09	0.01	0.02	0.04	0.16	3.12	-4.07
PIPRAGHAT	7.73	0.47	209.9	0.01	12.01	0.57	8.72	18.04	1.21	11.42	0.00	29.34	14.3	20.9	14.1	0.29	0.82	0.12	0.08	0.01	0.01	0.12	0.06	4.85	-5.38
GOLAGHAT	7.29	0.44	230	0.01	24.09	0.39	5.04	7.67	0.61	25.43	9.37	29.76	9.5	28.3	13.7	0.29	1.19	0.06	0.05	0.02	0.01	0.6	0.28	4.3	51.79
KHUTAR	7.20	0.29	146.9	0.00	14.80	0.39	2.61	1.57	0.43	2.78	10.34	18.86	11.9	19.7	10.9	0.27	0.47	0.1	0.07	0.03	0.01	0.11	0.41	4.57	7.27
NIMSAR	7.07	0.30	139.9	0.05	37.40	0.41	2.44	1.71	0.34	1.29	3.37	28.30	9.5	12.3	11.4	0.31	0.71	0.02	0.08	0.03	0.02	0.02	0.34	3.09	10.60
BHATPUR	7.12	0.32	146.9	0.01	9.45	0.56	4.08	11.06	0.72	3.87	3.37	29.34	11.9	13.2	12.7	0.32	2.91	0.08	0.11	0.03	0.02	0.03	0.31	3.62	7.31
JALALPUR	7.65	0.45	195.9	0.02	16.18	3.63	18.80	24.40	0.43	8.64	2.48	27.25	12.7	15.5	12.0	0.31	0.84	0.03	0.09	0.03	0.02	0.05	0.22	3.62	-16.06
MADHOTANDA	7.09	0.55	258.9	0.01	25.06	0.16	21.48	8.69	2.89	30.29	5.57	23.48	15.1	32.5	14.7	0.3	0.53	0.95	0.12	0.01	0.01	0.11	0.44	7.84	-14.83
BELHA	7.90	0.43	209.9	0.02	15.12	0.97	8.68	4.96	0.44	6.26	5.49	39.82	7.9	14.4	11.8	0.29	1.21	0.03	0.08	0.03	0.01	0.07	0.47	4.88	-4.49
SAIDPUR	7.02	0.41	153.9	0.01	8.48	0.41	8.62	6.53	0.60	27.51	2.48	35.00	9.5	22.0	11.8	0.3	1.22	0.05	0.09	0.03	0	0.04	0.53	6.17	4.79
PAKKAPUL	7.36	0.44	209.9	0.01	8.19	0.14	4.49	5.86	0.47	3.77	11.40	30.39	11.1	23.4	13.6	0.34	0.88	0.05	0.14	0.03	0.01	0.19	0.47	4.33	1.71
MEAN	7.4	0.41	189	0.01	16.87	0.61	7.79	8.77	0.68	14.77	4.57	31.2	10.7	20.3	12.5	0.27	1.1	0.118	0.09	0.02	0.02	0.113	0.285	4.892	
MINIMUM	7.02	0.29	139.9	0	4.77	0.1	2.44	1.57	0.13	1.29	0	18.86	7.93	12.3	10.6	0.15	0.47	0.01	0.05	0.01	0	0.02	0.06	3.09	
MAXIMUM	8.49	0.55	258.9	0.05	37.4	3.63	21.48	24.4	2.89	38.04	11.4	52.4	15. 1	32.5	14.7	0.34	2.91	0.95	0.14	0.03	0.03	0.6	0.53	7.84	
SD	0.39	0.07	38.56	0.01	9.333	0.84	5.421	6.613	0.634	12.61	3.321	7.663	2.22	5.91	1.27	0.06	0.57	0.225	0.02	0.01	0.01	0.144	0.15	1.427	

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LOCATIONS	pН	EC	HCO ₃	TSS	DOC	HA	F	CI.	NO ₃	PO4 3-	SO42-	Si	Na⁺	K ⁺	Ca ⁺⁺	Mg ⁺⁺	Ni ⁺⁺	Mn ⁺⁺	Charge
																	_		balance
KIRAKAT	8.23	0.40	216.91	0.01	6.03	1.42	0.36	6.88	3.98	0.45	30.99	4.51	32.32	6.53	58.33	7.51	0.08	0.00	3.28
BALUAGHAT	8.04	0.38	265.89	0.00	9.67	2.48	0.16	30.48	6.57	0.15	40.23	1.15	45.36	8.98	78.99	7.56	0.10	0.02	2.27
BAZARSHUKLA	7.80	0.42	272.88	0.00	6.71	1.15	0.4	7.8	0.37	0.79	20.26	6.01	29.48	6.53	56.65	7.51	0.21	0.01	-5.91
RAJGHAT	8.04	0.38	265.89	0.00	8.53	2.2	0.47	12.41	6.26	0.63	41.32	3.71	39.92	4.90	57.43	7.50	0.18	0.02	-6.27
RAJWARI	8.33	0.45	237.9	0.01	7.4	1.39	0.09	6.13	2.33	0.44	26.61	6.01	25.17	4.90	56.26	7.50	0.09	0.01	-3.79
SARAIN	8.30	0.30	349.85	0.00	11.72	2.26	0.13	6.15	7.41	0.71	21.65	2.74	27.44	8.98	81.98	7.65	0.20	0.03	-5.45
PIPRAGHAT	7.06	0.44	272.88	0.01	7.16	1.86	0.21	8.83	23.11	1.44	25.43	2.02	31.07	7.34	60.88	7.57	0.06	0.04	-7.44
GOLAGHAT	8.23	0.40	279.88	0.01	6.6	1.32	0.33	7.11	8.96	0.80	24.53	8.92	31.52	6.53	64.44	7.55	0.19	0.01	-3.95
KHUTAR	7.83	0.22	181.92	0.00	6.26	1.94	0.18	2.63	8.08	0.28	0.40	9.90	18.59	5.71	50.02	7.33	0.15	0.01	7.80
NIMSAR	8.16	0.24	293.87	0.01	14.45	2.22	0.63	3.4	0.97	0.19	7.94	4.51	28.35	5.71	54.44	7.53	0.23	0.02	-7.58
BHATPUR	8.33	0.30	293.87	0.01	5.92	1.21	0.43	2.87	1.37	0.22	16.19	4.23	31.07	6.53	61.45	7.64	0.08	0.01	-3.48
JALALPUR	7.83	0.43	174.93	0.01	8.08	3.15	0.3	6.88	0.16	0.09	34.56	3.36	27.44	4.90	45.86	7.44	0.21	0.01	1.48
MADHOTANDA	7.61	0.52	202.91	0.00	13.99	4.03	0.07	22.95	2.53	0.46	27.61	6.01	24.04	13.87	52.62	7.46	0.11	0.01	-3.01
BELHA	8.09	0.40	216.91	0.00	16.84	4.29	0.36	9.59	5.01	0.30	45.29	5.57	38.78	6.53	50.80	7.47	0.06	0.01	-1.87
SAIDPUR	8.38	0.38	258.89	0.01	8.19	2.58	0.24	15.62	3.74	3.07	33.77	4.60	35.61	6.53	58.46	7.54	0.03	0.02	-5.80
PAKKAPUL	7.85	0.41	244.9	0.01	7.51	1.51	0.13	7.44	3.9	0.41	21.06	11.75	30.16	6.53	55.48	7.60	0.16	0.00	-1.95
MEAN	8.01	0.38	251.89	0.01	9.07	2.19	0.28	9.82	5.30	0.65	26.12	5.31	31.02	6.94	59.01	7.52	0.13	0.01	
MINIMUM	7.06	0.22	174.93	0.00	5.92	1.15	0.07	2.63	0.16	0.09	0.40	1.15	18.59	4.90	45.86	7.33	0.03	0.00	
MAXIMUM	8.38	0.52	349.85	0.01	16.84	4.29	0.63	30.48	23.11	3.07	45.29	11.75	45.36	13.87	81.98	7.65	0.23	0.04	
STDEV	0.34	0.08	45.56	0.01	3.37	0.95	0.16	7.50	5.50	0.73	11.91	2.84	6.54	2.21	9.58	0.08	0.06	0.01	

 Table 5: Post Monsoon Water Analysis all Parameters are in mg/L except pH and EC (mS/cm)

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Table 6: Correlation Matrix of Water Samples During monsoon Season

<u> </u>	рН	EC	HCO ₃	TSS	DOC	F	CI.	NO ₃ [°]	P0₄	SO₄	Si	Na ⁺	κ⁺	Ca ⁺⁺	Mg ⁺⁺	Cr	Fe	Mn	Ni	Cu	Cd	Zn	Pb	As
рH	1.000					·			4	<u> </u>			l	I			<u> </u>	I					<u> </u>	<u> </u>
EC	0.116	1.000																						
нсоз	0.565	0.642	1.000																					
TSS	-0.062	-0.199	-0.200	1.000																				ľ
DOC	-0.161	0.113	0.115	0.541	1.000																			
F	0.310	0.118	0.046	0.221	-0.054	1.000																		
cr.	0.009	0.669	0.408	-0.114	-0.053	0.473	1.000																	
NO ₃	0.140	0.207	0.190	-0.038	-0.196	0.600	0.427	1.000																
PO₄ [—]	-0.294	0.590	0.413	-0.129	0.124	-0.165	0.652	0.158	1.000		-													
so₄-	-0.246	0.649	0.154	-0.291	0.242	-0.214	0.330	-0.228	0.326	1.000														
Si	-0.179	-0.007	0.141	-0.117	0.102	-0.198	-0.288	-0.405	-0.010	-0.079	1.000													
Na⁺	0.312	-0.011	-0.022	-0.121	-0.467	-0.084	0.059	-0.191	-0.307	0.095	-0.440	1.000		•										1
κ⁺	-0.302	0.228	0.135	-0.240	-0.176	0.105	0.553	0.487	0.673	-0.079	-0.118	-0.314	1.000											
Ca ⁺⁺	-0.319	0.686	0.337	-0.426	0.046	-0.341	0.374	-0.226	0.580	0.768	0.316	-0.062	0.255	1.000										ļ
Mg ⁺⁺	-0.146	0.744	0.410	-0.063	0.221	-0.125	0.251	0.120	0.613	0.463	0.230	-0.377	0.247	0.631	1.000									1
Cr	-0.299	0.039	0.049	0.315	0.062	0.188	0.093	0.207	0.254	-0.315	0.349	-0.464	0.407	-0.087	0.230	1.000								
Fe	-0.158	-0.262	-0.259	-0.075	-0.157	-0.062	-0.305	0.207	-0.164	-0.111	-0.160	0.014	-0.137	-0.365	0.030	0.132	1.000							
Mn	-0.229	0.520	0.483	-0.124	0.205	-0.186	0.630	0.051	0.950	0.303	0.087	-0.338	0.582	0.550	0.484	0.185	-0.232	1.000						
Ni	-0.370	0.279	-0.093	-0.099	-0.194	-0.055	0.309	0.041	0.376	0.018	0.078	-0.018	0.332	0.192	0.360	0.200	0.121	0.312	1.000					
Cu	-0.243	-0.383	-0.492	0.145	-0.220	0.268	-0.068	-0.272	-0.363	-0.297	0.192	0.221	-0.075	-0.285	-0.425	0.361	0.058	-0.392	0.243	1.000				Í
Cd	0.077	-0.261	-0.288	0.200	0.059	0.201	-0.058	0.153	-0.235	-0.181	-0.326	0.195	-0.163	-0.303	-0.148	-0.559	0.172	-0.219	0.133	-0.095	1.000			
Zn	0.050						-0.128				0.493							-0.019			-0.117			
Pb		-0.008															-0.079			0.622				
As	-0.025	0.579	0.255	-0.438	-0.050	-0.249	0.482	-0.331	0.501	0.680	<u>-0.1</u> 15	0.270	0.051	0.656	0.323	-0.429	-0.320	0.492	0.333	-0.143	-0.103	0.074	0.182	1.000

36

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 Table 7:
 Correlation Matrix of Water Samples during Post Monsoon

	pН	EC	HCO ₃	TSS	DOC	HA	F [.]	CI.	NO ₃ .	PO4 ³⁻	SO4 ^{2.}	Si	Na⁺	K	Ca ⁺⁺	Mg ⁺⁺	Ni ⁺⁺	Mn ⁺⁺
рН	1.000																	
EC	- 0.357	1.000																1
HCO ₃	0.281	-0.308	1.000															
TSS	0.129	0.059	0.020	1.000														
DOC	0.023	0.012	0.039	-0.396	1.000													
HA	-0.165	0.255	-0.393	-0.414	0.796	1.000												
F	0.227	-0.404	0.218	0.162	0.096	-0.144	1.000											
CL	-0.144	0.454	-0.084	-0.403	0.268	0.456	-0.373	1.000										
NO ₃	-0.582	0.050	0.186	0.020	-0.153	-0.093	-0.243	0.043	1.000									
PO4 3-	0.023	0.142	0.209	0.223	-0.172	-0.036	-0.122	0.144	0.284	1.000								
SO42-	0.068	0.607	-0.132	-0.152	0.244	0.474	-0.072	0.571	0.015	0.153	1.000							
Si	0.028	-0.058	-0.314	0.096	-0.190	-0.220	-0.169	-0.356	-0.177	-0.105	-0.441	1.000						
Na⁺	0.185	0.154	0.255	-0.129	0.150	0.152	0.250	0.549	0.096	0.155	0.754	-0.462	1.000					
K⁺	-0.279	0.359	0.053	-0.408	0.409	0.444	-0.482	0.623	0.085	0.005	0.077	-0.132	-0.054	1.000				
Ca ⁺⁺	0.253	-0.165	0.746	-0.210	-0.029	-0.237	-0.230	0.337	0.285	0.090	0.105	-0.423	0.388	0.313	1.000			
Mg ⁺⁺	0.234	-0.004	0.828	0.294	-0.060	-0.353	0.035	0.016	0.129	0.180	0.081	-0.282	0.356	0.132	0.678	1.000		
Ni ⁺⁺	0.005	-0.285	0.190	-0.149	0.035	-0.178	0.322	-0.314	-0.278	-0.421	-0.364	0.190	-0.293	-0.175	-0.009	-0.060	1.000	
Mn ⁺⁺	-0.341	-0.057	0.550	-0.039	0.061	0.000	-0.036	0.138	0.719	0.363	0.094	-0.622	0.201	0.116	0.490	0.377	-0.037	1.000

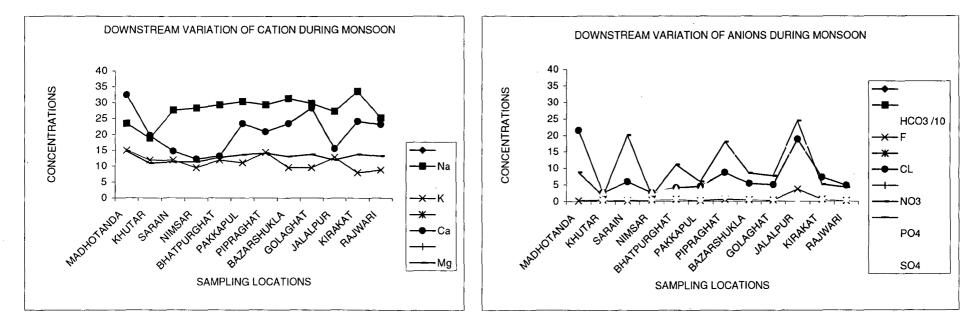


Figure 6: Downstream Variation of Cations And Anions During Monsoon Season

38

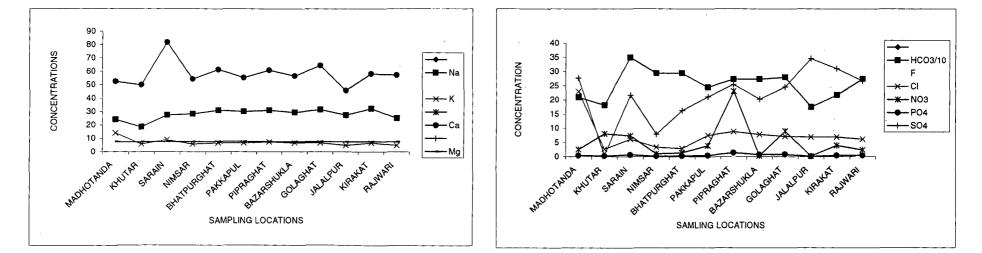


Figure 7: Downstream variation of Cations and Anions during Postmonsoon

39

monsoon season (table 4) and from 0.22 to 0.52 mS/cm in post monsoon season (table 5) the high value of in the monsoon may be due to high flushing of material with rain from the catchment area.

Bicarbonate (HCO₃⁻)

Bicarbonate is the major ion in water body. The source of bicarbonate is atmospheric CO_2 , which dissolves in water to form carbonic acid. Reaction of carbonic acid with limestone, certain mineral like albite (Garrel and Christ, 1965), from partial or complete decomposition of organic matter (Berner, 1971) give rise to bicarbonate ion in water body.

The concentration of bicarbonate values ranges between 139.94 mg/l to 258.88 mg/l during monsoon(table 4) and from 174.93 mg/l to 349.85 mg/l during post monsoon(table 5).

Dissolved Silica (H4SiO4)

The source of silica is from weathering of silicate rocks and minerals such as K-feldspar, Na-feldspar, Kaolinite, Montmorilonite and Illite etc. Silica occur as silicic acid (H₄SiO₄) in natural water at pH < 9.

The range of concentration of silica most commonly observed in natural water is from 1 to 30 mg/l. The mean value of silica for surface water is 14 mg/l Davis, (1964). The value dissolved silica ranges between 1.39 mg/l to 11.40 mg/l during monsoon(table 4) and from 1.15 to 11.75 mg/l during postmonsoon (table 5).

Chloride(Cl) and Fluoride (F)

The concentration of chloride ranges between 2.44 to 21.5 mg/l during monsoon season(table 4) and from 2.63 to 30.48 mg/l during postmonsoon and fluoride from 0.1 to 3.63 mg/l during monsoon(table 4) and from 0.13 to 0.63 mg/l during postmonsoon (table 5).

Nitrogen (NO₃⁻), Phosphate (PO₄³⁻) and Sulphate (SO₄⁻⁻)

Nitrogen occurs in water as nitrites or nitrate anions (NO_2^- and NO_3^-), serves as an essential nutrients for plant growth. Nitrates are readily transported in water and are stable over a considerable range of conditions. The concentration of nitrate above 45 mg/l is indication of pollution. Excessive concentration of nitrate in drinking water may cause methemoglobinemia in small children.

The source of nitrate into river is precipitation, nitrifying bacteria which convert reduced form of nitrogen into nitrate and nitrite. The concentration of nitrate in surface water samples varies from 1.57 to 24.4 mg/l during monsoon season (table 4) and from 0.16 to 23.11 mg/l during post monsoon (table 5).

Phosphorus is a common element in igneous rock, it is also fairly abundant in sediments, but concentrations present in solution in natural water are no more than a few tenths of a milligram per liter. The ortho phosphate ion (PO_4^{3-}) is the final dissociation product of phosphoric acid and aquatic biota use this ion as a nutrient. Major sources of phosphate in water are phosphatic minerals, sedimentary phosphate beds, and decay of organic material, agriculture fields discharges and domestic and industrial wastes. Excess of PO_4^{3-} gives rise to algal bloom i.e. excessive growth of blue green algae, which disrupts the food chain of that water body, finally leads to death and decay of aquatic life. Phosphorus availability is generally believed to be a critical factor in eutrophication of water bodies, as the nutrient in shortest supply will tend to be the control on production rates.

The concentration of phosphate in surface water samples varies from 0.13 to 2.89 mg/l in monsoon period(table 4) whereas from 0.09 to 3.07 mg/l in post monsoon period (table 5). The higher concentration of PO_4^{3-} in Madhotanda during monsoon season is mainly attributed to the discharge of agricultural runoff from the nearby agricultural fields.

The geochemical cycle of sulfur is characterized by a rapid recycling of solute forms in water and of gases and aerosols in the atmosphere, sulfide minerals the reduced form of sulfur is relatively immobile. Sulfate occurs in certain igneous-rock minerals of the feldspathoid group, but the most extensive sediments and important occurrences are in evaporate sediments. The principal natural sources of dissolved sulfur in river water include rock weathering, input from volcanoes, and input from biological or biogeochemical processes. An additional major source is anthropogenic activities and precipitation.

The sulfate concentration ranges between 1.29 to 38.04 mg/l during monsoon period(table 4) and between 45.29 mg/l to 0.40 mg/l during post monsoon (table 5). The higher concentration of $SO_4^{2^-}$ during monsoon may be attributed to discharge.

Sodium (Na⁺) and Potassium (K⁺)

The sodium ion is transported in river mainly by the weathering of plagioclase, pyroxene and hornblende, it ranges between 18.59 to 45.36 mg/l. higher values of sodium is due to conservative nature of element as it is not used up in the biological processes or clay mineral formation (Subramanian & Saxena, 1983), also there are no important precipitation reactions that can maintain low sodium concentration in water and sodium is retained by adsorption on mineral surfaces, especially by minerals having high cation- exchange capacities such as clays.

Potassium is slightly less common than sodium in igneous rock but more abundant in all the sedimentary rocks. The principal potassium minerals of silicate rocks are the feldspar orthoclase and microcline (KAlSi₂O₈), the micas, and the feldspathoid leucite (KAlSi₂O₆).

The potassium concentration varies from 7.93 to 15.06 mg/l during monsoon (table 4) and from 4.896 to 13.876 during post monsoon(table 5). The lower values during post monsoon is due to dilution and the lower values for potassium ion as compared to sodium ions is due to high degree of

stability of potassium bearing alumino-silicate minerals also the biological factors may be important in controlling the availability of potassium for solution in river water and ground water.

Calcium (Ca²⁺) and Magnesium (Mg²⁺)

Calcium is an essential constituent of many igneous-rock minerals, especially of the chain silicates pyroxene and amphibole, and the feldspars. It is an essential element for plant and animal life forms.

The concentration of calcium ranges between 12.31 mg/l in monsoon(table 4) and between 45.86 to 81.98 mg/l in post monsoon(table 5). The permissible limit of Ca for drinking water is 200 mg/l given by BIS (table). All the water samples have Ca concentration well with in the permissible limit.

In Igneous rock magnesium is typically a major constituent of the dark colored ferromagnesium minerals. These include olivine, the pyroxenes, amphiboles, and the dark colored micas, calcite, dolomite and magnesite are also source of magnesium in water.

The values of magnesium ranges between 10.55mg/l to 14.10 mg/l in monsoon period(table 4) and between 7.65 to 7.33 mg/l in post-monsoon season(table 5).

Iron and Managnese

The chemical of iron and its solubility in water depends strongly on the oxidation intensity in the system in which it occurs; pH is a strong influence as well.

Iron is an essential element in the metabolism of animals and plants. Iron may be present in natural sources in igneous rocks, amphiboles, ferromanganate soils and in combined from that is as iron oxide etc.the concentration of iron in the surface water samples varies from 0.53 to 2.91 mg/l during monsoon season. (table 4). Manganese is an essential element in plant metabolism. Many igneous and metamorphic minerals contain divalent manganese as a minor constituent. It is a significant constituent of basalt and many olivines and of pyroxene and amphiboles. When divalent manganese is released to aqueous solution during weathering, it is somewhat more stable towards oxidation than ferrous ion.

The concentration of manganese in surface water ranges between 0.01 to 0.95 mg/l during monsoon season(table 4) and between 0.003 to 0.043 mg/l during post monsoon(table 5).

Nickel and Copper

Nickel is one of the ubiquitous elements and may be present in soil in mainly sulphide and oxide forms and its concentration may vary according to mineral composition of soil. Nickel enters the environment through natural process like weathering of minerals and rocks, geothermal emissions. Its main anthropogenic sources in the environment are electroplating, Ni-Cd batteries, steel production and alloy manufacture etc. Nickel in general is relatively non-toxic, through oral route, due to its nickelsubsulphides and nickel oxides can cause lung cancer and cancer of nasal sinus.

The concentration of Ni in surface water varies from 0.05 mg/l to 0.14 mg/l during monsoon(table 4) and from 0.03 mg/l to 0.23 mg/l during post monsoon (table 5).

Arsenic and Cadmium

These both metals are toxic in nature and they are present in surface water in very trace amounts. The permissible limit for arsenic given by W.H.O. is 0.01 mg/l and for cadmium it is 0.003 mg/l. and data of monsoon season(table 4) for arsenic 4.89 ppb shows that they are well below their permissible limits but the values of cadmium 0.02 mg/l shows that they are present in significant amount i.e. above their permissible limit.

Zinc and lead

Zinc is an essential micronutrient and beneficial element for human bodies. The metallic element present abundantly in natural sources, soil etc. the zinc is also contributed with discharge from municipal and industrial waste water treatment plant

The values of zinc vary from 0.02 to 0.6 mg/l during monsoon season(table 4).

The major source for lead is atmospheric precipitation and dust fall. The other sources are batteries and insecticides.

The value of lead in water samples ranges between 0.06 to 0.53 mg/l during monsoon season(table 4).

Dissolved organic carbon (DOC) and humic acid

Concentration of DOC in rivers ranges from less than 1 mg/l in alpine streams to more than 20 mg/l in some tropical or polluted rivers and rivers draining swamps and wetlands. DOC inputs to rivers are generally subdivided into allochthonous carbon, which is produced on land and autochthonous carbon which is produced in river, reservoirs and lakes.

The value of DOC ranges between 4.77 to 37.4 mg/l during monsoon(table 4) and from 5.92 to 16.84 mg/l during postmonsoon(table 5). Higher value of DOC in Madho Tanda, Belha Temple and Nimsar is attributed to thick vegetation and litter fall and also due to wastes coming from the temple which is located nearby and these wastes mainly consists of organic wastes.

Aquatic humic substances constitute 50% of DOC and are largest fraction of natural organic matter in water. Out of this 50% of aquatic humic substances 40% is humic acid and approximately 10% is fulvic acid. The value of humic acid ranges between 1.15 to 4.29 mg/l. during postmonsoon season(table 5). Again the higher values of humic acid in Belha Temple,

MadhoTanda, and Nimsar indicating high organic loads in water samples of these locations.

DOC has a strong correlation with humic acid indicating that they are originated from the same source.

TRANPORATION OF NUTRIENTS AS SOLUTE LOAD

Nutrient transported from continents to oceans via rivers is one of the important processes regulating biogeochemical cycling of elements. Chakrapani.G.J. (2005). Transportation of major nutrients in Gomti basins as solute load are calculated and results are given in table no: below

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TRANSPORTATION OF NUTRIENTS IN DISSOLVED FORM

PARAMETERS	DISSOLVED (10 ³ * ton/yr)
HCO3-	1631.29
TSS	0.074
DOC	95.96
HA	16.19
NO3-	52.04
PO4	4.92
SO4	151.27
Na+	230.21
K+	65.26
Ca++	293.43
Mg++	74.08
Si	36.56

FACTOR ANALYSIS

Factor analysis aims to explain observed relation between numerous variables in term of simpler relations. It is also a way to classifying manifestation of variables (Cattel, 1965). For the water chemistry of Gomti river five factors are identified in monsoon season (table)

Factor 1: This factor has an Eigen value of 5.949 and accounts 24.788% variance in the data. The variables present in this factor are EC, SO₄, Ca and Mg and As. Thus this factor can be considered due to contribution from soil media.SO4 is may be coming from soil media by the action of Reverse ion-exchange and also through atmospheric precipitation.

Factor 2: This factor has an Eigen value of 3.649 and accounts for 15.204% variance in the data. The variables are K, PO4, Mn and Ni. This factor may be attributed to anthropogenic acitivity including agriculture field runoff and domestic waste.

Factor 3: This factor has an Eigen value of 3.205 and account 13.354% variance in the data. The variables are Si, Cr and Pb.

Factor 4: This factor has an Eigen value of 2.294 and accounts 9.558% variance in the data. This factor shows positive loading for F and NO₃, which may be attributed to natural process of weathering supplemented by anthropogenic discharge.

Factor 5: This factor has an Eigen value of 1.872 and accounts 7.802% variance in the data. This factor shows positive loading for TSS and DOC.

	1	2	3	4	5	Communalities
PH				.518		.637
EC	.844					.854
HCO3						.561
SPM					.501	.489
DOC					.789	.678
F				.733		.596
CL		.590				.759
NO3				.862		.815
PO4	.565	.717				.898
SO4	.772	-				.700
SI			.742			.690
NA					742	.719
К		.718				.676
СА	.887					.911
MG	.688					.713
CR			.744			.894
FE						.111
MN	.531	.685				.822
NI		.690				.556
CU	532		.540			.745
CD			788			.663
ZN		511				.734
РВ			.690			.868
AS	.722	1				.878
% of Variance explained	24.788	15.204	13.354	9.558	7.802	
Cumulative Variance%	24.788	39.991	53.345	62.903	70.705	
Eigen values	5.949	3.649	3.205	2.294	1.872	

 Table 8: Factor analysis of water sample for Monsoon season

	1	2	3	4	5	Communalities
PH					855	.838
EC			.653			.601
НСО3	.921					.921
SPM		742				.705
DOC		.662				.744
НА		.717				.866
F			584	.517		.819
CL		.682				.809
NO3					.819	.807
PO4			.538			.374
SO4			.525	.722		.880
SI				687		.653
NA				.788		.834
к		.829				.848
СА	.913					.892
MG	.854					.766
NI			720			.563
% of variance explained	18.345	18.188	14.574	14.269	10.618	
Cumulative % of variance explained	18.345	36.533	51.107	65.375	75.993	
Eigen values	3.119	3.092	2.478	2.426	1.805	

Table 9: Factor analysis of water samples for Post- monsoon season

Factor analysis for Post-monsoon season identified five factor (table):-

Factor 1: This factor has an Eigen value of 3.119 and accounts for 18.345% variance in the data. The variables are Ca, Mg and HCO₃. Thus this factor can be attributed to carbonate weathering process taking place in the study area.

Factor 2: This factor has an Eigen value of 3.092 and accounts for 18.188% variance in the data. The variables are DOC, HA, CI and K.

Factor 3: This factor has an Eigen value of 2.478 and accounts for 14.574% variance in the data. The variables are EC and PO₄. So, this factor can be attributed to anthropogenic process taking place in the study area.

Factor 4: This factor has an Eigen value of 2.426 and accounts for 14.269% variance in the data. The variables are Na, F and SO₄. So, this factor can be attributed to natural geochemical process taking place in the area.

Factor 5: This factor has an Eigen value of 1.805 and accounts for 10.618% variance in the data. This factor is showing positive loading for NO₃ but negative loading for pH.

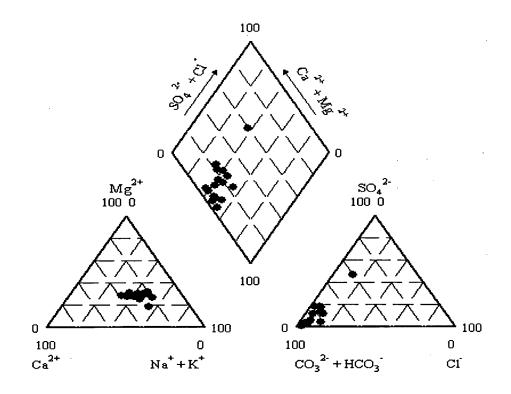
GEOCHEMICAL DIAGRAMS

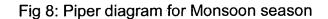
Trilenear Diagram and Hydrochemical facies of Water samples

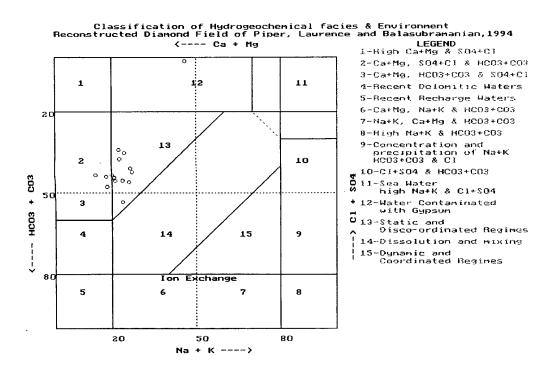
Trilinear diagram (Hill Piper) which adds to the original two triangles, is a diamond shaped area shaped area in which two points plotted with triangles are projected into diamond and plotted as a single point.

The piper diagram and its hydrochemical facies for Monsoon season are shown in fig 8:-

From the figure 8, it is clear that HCO_3 is the dominant anion and Na, and Ca constitute the dominant cations.







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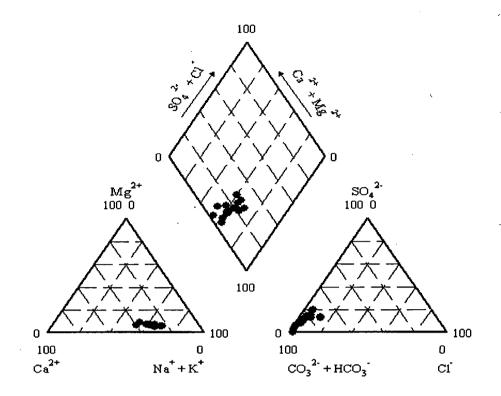
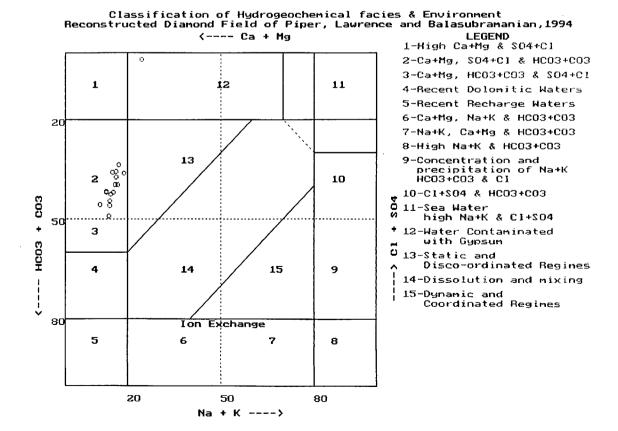


Fig 9:- Piper diagram for post-monsoon



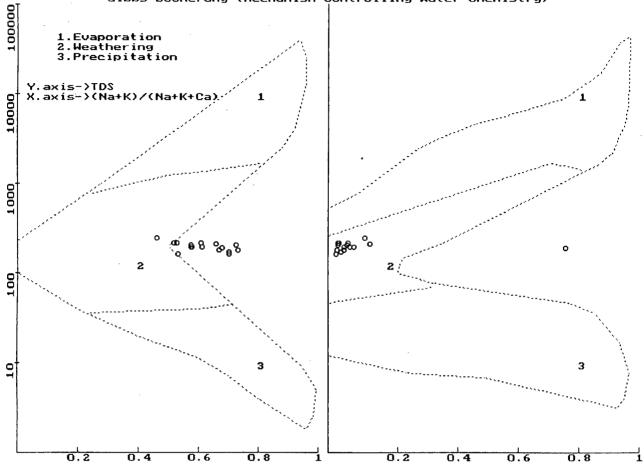
52

Most of the samples are showing Static and Disco-ordinated regimes. Few samples are also showing Ca+Mg, SO_4+CI and HCO_3+CO_3 type hydrochemical facies.

The piper diagram and its hydrochemical facies for Post- Monsoon season are shown in fig 9 .The post-monsoon samples are showing high seasonal variation as majority of samples are showing Ca+Mg, SO_4 +Cl and HCO_3+CO_3 type hydrochemical facies in contrast to monsoon sample where were showing Static and Disco-ordinated regimes.

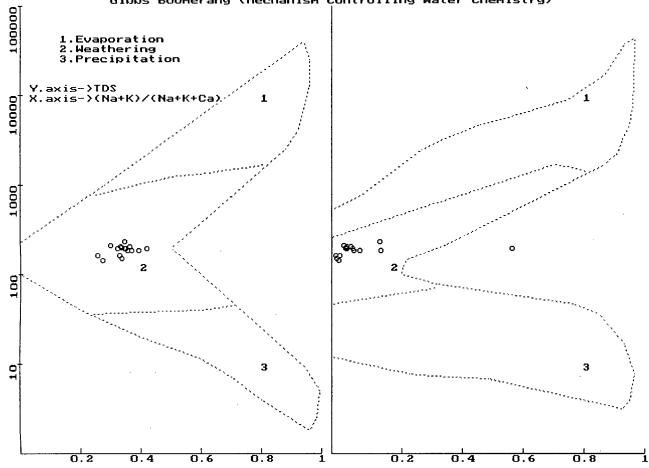
Gibbs Diagram

The ratio Na/(Na+Ca), in mass units, plotted against TDS gives a characteristics boomerang-shaped plot depicting the major factors operating behind the water chemistry of the major aquatic system of the world (Gibbs1970). This plot (fig 10&11) places the Gomti in the region of rock dominance during both monsoon and post-monsoon, which is consistent with the observation that the dissolution of various minerals in water is a prime factor operating behind the chemistry of water in the river Gomti.



Gibbs Boomerang (Mechanism Controlling Water Chemistry)

Fig10: Gibbs diagram for Gomti water samples during Monsoon season.



Gibbs Boomerang (Mechanism Controlling Water Chemistry)

Fig 11: Gibbs diagram for Gomti water samples during Post-Monsoon season.

MINERAL EQUILIBRIUM IN CARBONATE AND SILICATE SYSTEM

The mineral stability in water can be predicted by the application of thermodynamic concepts of chemical equilibrium of Water (Karmer, 1967). It is based on the concept, that the water derives its composition from the parent rocks in the weathering region.

From the Fig 12 & 13 it is clear that samples are falling in the Dolomite region of the stability graph during all seasons with some samples are in augite region in monsoon season.

The Dolomite weathering reaction can be summarized as:

$$2H_2CO_3 + CaMg (CO_3)_2$$
 $Ca^{++} + Mg^{++} + 4HCO_3$

Fig (14.a,b,.c,d&15.a,b,c,d) shows the thermodynamic stability relationships of water chemistry in Na, K, Ca and Mg silicate system (Garrel & Christ, 1965) during monsoon, Monsoon and post-monsoon season respectively. There is contribution of Chlorite, Kaolinite, Ca-Montmorllionite,Gibbsite.

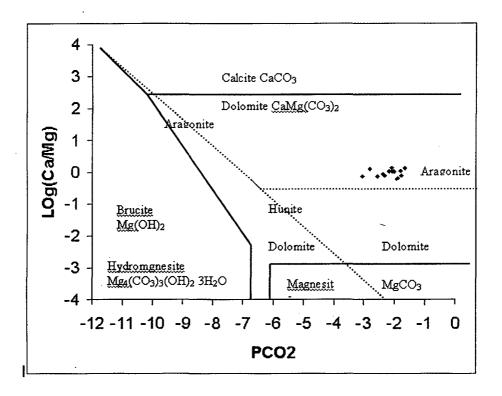


Fig 12 : $\log PCO_2$ vs $\log (Ca / Mg)$ during monsoon

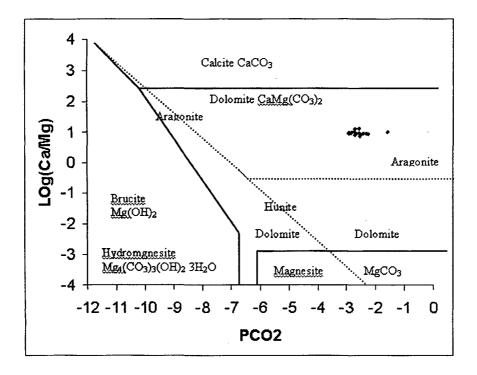


Fig 13: log PCO₂ vs log (Ca / Mg) during Post-monsoon

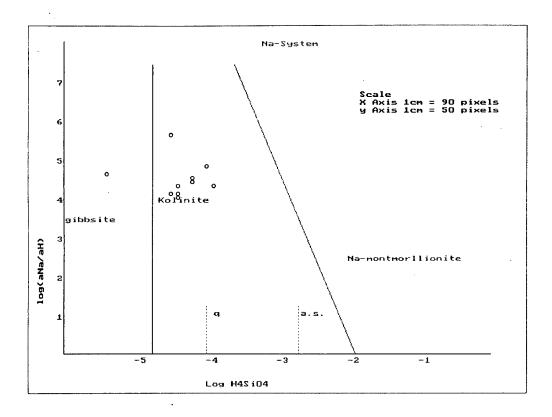


Fig 14.a : Log (Na/ H) vs Log H4SiO4 for monsoon season.

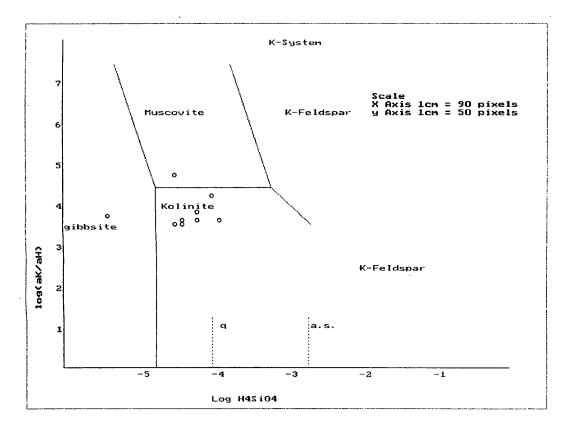


Fig: 14.b : Log (K/ H) vs Log H4SiO4 for monsoon season

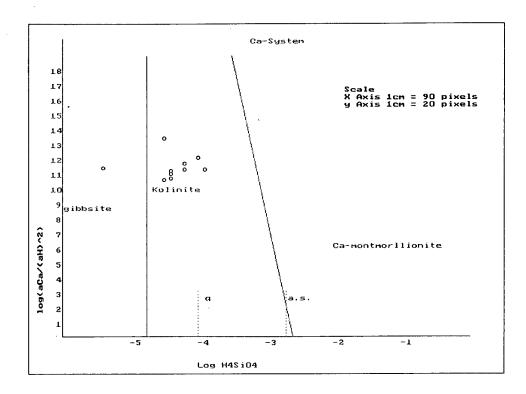


Fig: 14.c : Log (Ca/H) vs Log H4SiO4 for monsoon season.

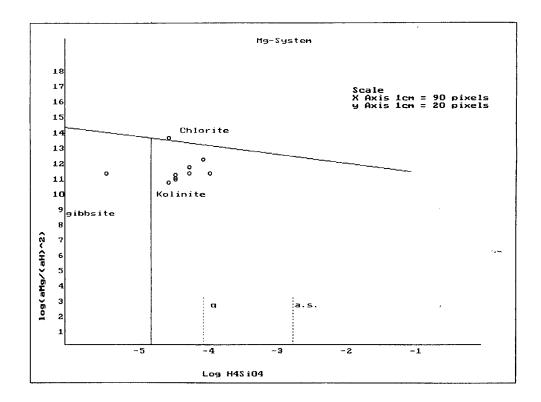


Fig 14.d : Log (Mg/H) vs Log H4SiO4 for monsoon season.

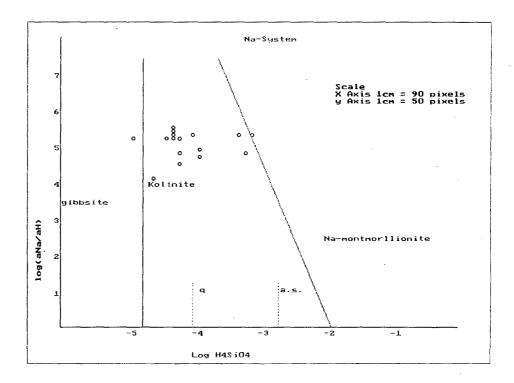


Fig 15.a: Log(Na/H) vs Log H₄SiO₄ for post-monsoon season

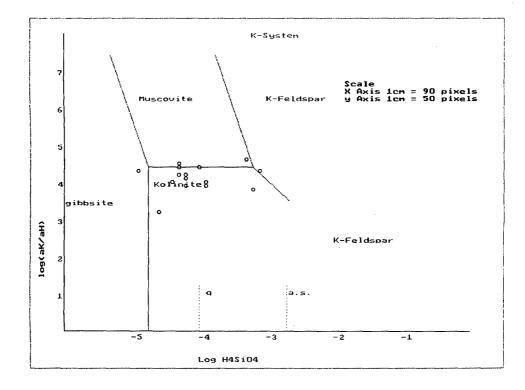


Fig15.b : Log (K/ H) vs Log H4SiO4 for Post-Monsoon

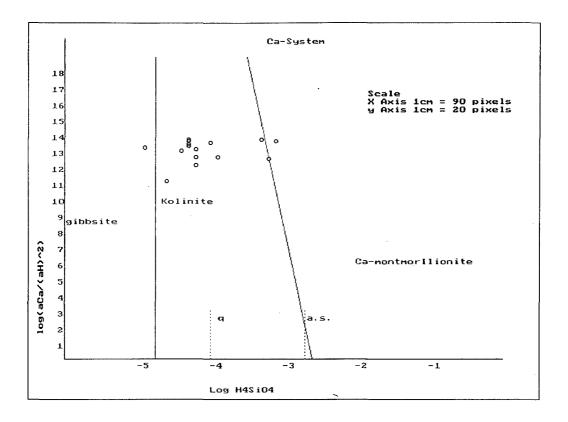


Fig i5.c: Log(Ca/H) vs Log H₄SiO₄ for post-monsoon season

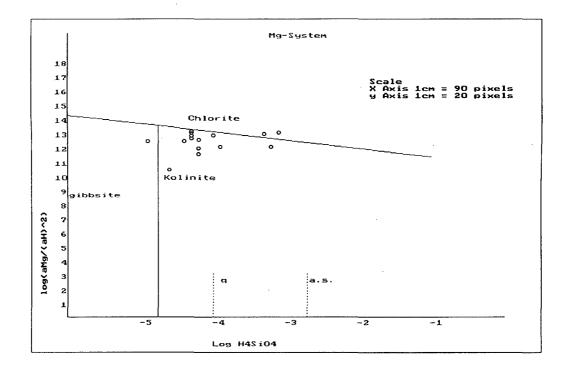


Fig 15.d : Log(Mg/H) vs Log H₄SiO₄ for post-monsoon season

SEDIMENT CHEMISTRY

Total sixteen sediment samples were collected from different part of river basin and analysed for nutrients. Sediment derives its constituents from rock weathering, precipitation and dry deposition and anthropogenic activity.

Carbon (TC, OC and IC)

Carbon inputs to rivers are generally subdivided into allochthonous carbon, which is produced on land and autochthonous carbon which is produced in river, reservoirs and lakes. After death and decay they settled down and deposited as organic load in bed sediment. Besides these sources the other main sources are atmospheric co_2 which react with water to form HCO_3^- and CO_3^- ions and these ions under suitable condition of Eh and pH combines with divalent cations to form carbonate minerals which are deposited in the sediment.

The total carbon values vary from 0.24% to 1.57% during monsoon(table 10) and from 0.21% to1.53 % during post monsoon(table11). The values of inorganic carbon varies from 0.13 % to 0.73 % during monsoon(table 10) and from 0.13 % to 0.62 % during post monsoon(table11) and organic carbon shows 0.02 % to 1.08 % during monsoon(table 10) and from 0.04 % to 0.94 % during post monsoon(table11).

Total Nitrogen (TN)

Nitrogen is mostly present in organic form but in small amount as nitrates and ammonium. The source of nitrogen in the sediments are biologically fixed nitrogen in the form of nitrate, death and decay of organic matter and also input from fertilizers.

The value of TN varies from 0.05 % to 0.65 % during monsoon(table 10) and from 0.05 to 0.60 during post monsoon(table11). The values of total nitrogen showing very less seasonal variation.

LOCATION	ТС	IC		BSI		Na	K	HA	TP	AI	Tsi	Ni	C/N
KIRAKAT	0.83			0.0025	0.05				288.39				16.6
BALUAGHAT	0.3	0.17	0.12	0.0022	0.35	18.532	5.712	5.33	1057.43	98462.6	301173	0.481	0.85
BAZARSHUKLA	1.01	0.45	0.56	0.0031	0.1	10.848	13.056	12	1490.02	128388	200499	0.681	10.1
RAJGHAT	0.24	0.18	0.07	0.0021	0.1	15.594	9.792	3.999	144.195	205613	166059	0.421	2.4
RAJWARI	1.14	0.4	0.74	0.0038	0.15	16.272	10.608	5.33	1153.56	197649	294991	0.762	7.6
SARAIN	1.57	0.49	1.08	0.0017	0.4	15.82	15.504	5.33	1153.56	161450	210214	0.601	3.93
PIPRAGHAT	0.29	0.35	0.06	0.0033	0.25	18.08	12.24	3.99	769.04	111494	189902	0.742	1.16
GOLAGHAT	1.03	0.73	0.3	0.0032	0.65	13.108	15.504	3.99	961.3	139006	109540	0.521	1.58
KHUTAR	0.27	0.19	0.07	0.0018	0.25	18.532	12.24	3.99	817.105	136110	264966	1.083	1.08
NIMSAR	0.48	0.33	0.17	0.0028	0.45	19.662	13.872	6.665	1441.95	140454	218161	0.501	1.066
BHATPUR	0.71	0.56	0.16	0.0049	0.1	14.012	16.32	5.33	961.3	159278	114839	0.32	7.1
JALALPUR	0.41	0.29	0.12	0.0022	0.15	25.312	9.792	3.99	1153.56	117286	180188	0.742	2.73
MADHOTANDA	0.79	0.13	0.65	0.0031	0.15	14.69	8.976	23.994	1009.37	113184	275563	0.481	5.26
BELHA	0.91	0.28	0.62	0.0029	0.05	21.922	13.872	6.665	1201.63	109322	260550	0.401	18.2
SAIDPUR	0.38	0.19	0.19	0.002	0.1	17.854	4.896	1.333	1057.43	143109	232291	1.042	3.8
PAKKAPUL	0.71	0.56	0.16	0.0049	0.1	16.498	16.32	5.33	961.3	159278	114839	0.32	10
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MEAN	0.6919		0.33438	0.00291	0.2125	17.1375	11.832	6.32913	976.32	142943	197960	0.622563	5.841
MINIMUM	0.24	0.13	0.06	0.0017	0.05	10.848	4.896	1.333	144.195	98462.6	33593.5	0.32	0.85
MAXIMUM	1.57	0.73	1.08	0.0049	0.65	25.312	16.32	23.994	1490.02	205613	301173	1.083	18.2

Table	10:	Chemical	Charecteristics	of	Sediment sam	ple oʻ	fmonsoon	period	

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 MAXIMUM
 1.57
 0.73
 1.08
 0.0049
 0.65
 25.312
 16.32
 23.994
 1490.02
 205613
 301173
 1.083
 18.2

 STDEV
 0.3815
 0.17712
 0.30248
 0.00098
 0.1698
 3.44784
 3.4875
 5.20977
 353.517
 30873.1
 75847.2
 0.235951
 5.469529

TC =TOTAL CARBON in % IC = INORGANIC CARBON in % OC = ORGANIC CARBON in % Bsi = BIOGENIC SILICA in % TN = TOTAL CARBON in % Na = SODIUM in mg/l K = POTASSIUM in mg/l Ha = HUMIC ACID in % TP = TOTAL PHOSPHRUS µg/g Tsi =TOTAL SILICA µg/g

 Table 11:
 Chemical Characteristics of Sediment Samples during Post Monsoon

LOCATION	TC	IC	00	Bsi	На	TP	Al	Tsi	Na	К	TN	Ni	C/N
KIRAKAT	0.73	0.52	0.21	0.002	2.67	1356.5	78432.3	38955.1	16.69	9.79	0.10	0.79	7.30
BALUAGHAT	0.72	0.21	0.51	0.002	4.00	1808.6	77225.6	103421.4	18.20	4.12	0.35	0.45	2.05
BAZARSHUKLA	`0.98	0.39	0.59	0.003	10.66	1492.1	82052.2	43370.6	0.99	13.68	0.10	0.66	9.80
RAJGHAT	0.21	0.17	0.04	0.002	2.67	1401.7	71916.3	46903.0	14.99	9.65	0.10	0.40	2.10
RAJWARI	0.43	0.23	0.1	0.004	4.00	1582.6	99669.3	73396.0	15.79	10.60	0.15	0.70	2.87
SARAIN	1.12	0.39	0.73	0.002	4.00	1537.3	112218.5	51318.5	14.88	14.90	0.40	0.59	2.80
PIPRAGHAT	1.53	0.59	0.94	0.003	4.00	1627.8	104978.6	68980.5	18.06	11.65	0.25	0.79	6.12
GOLAGHAT	0.93	0.62	0.31	0.003	5.33	1446.9	109322.5	46019.9	12.93	12.50	0.65	0.51	1.43
KHUTAR	0.22	0.13	0.09	0.002	2.67	1627.8	54299.3	55734.0	17.90	11.85	0.25	0.97	0.88
NIMSAR	0.48	0.31	0.17	0.003	5.33	1537.3	108357.2	60149.5	19.89	18.98	0.45	0.45	1.07
BHATPUR	0.68	0.47	0.3	0.005	5.33	1446.9	107633.2	55734.0	13.79	14.61	0.10	0.23	6.80
JALALPUR	0.53	0.31	0.22	0.002	2.67	1401.7	110046.5	42487.5	24.88	9.66	0.15	0.68	3.53
MADHOTANDA	0.71	0.13	0.58	0.003	20.00	1446.9	61297.8	71629.8	15.95	8.91	0.15	0.58	4.73
BELHA	0.9	0.26	0.64	0.003	6.67	1356.5	82052.2	53084.7	20.78	13.79	0.05	0.46	18.00
SAIDPUR	0.75	0.6	0.15	0.002	1.33	1899.1	58643.2	122597.3	18.90	4.87	0.10	0.88	7.50
PAKKAPUL	0.52	0.41	0.11	0.002	2.67	1989.5	88326.8	72512.9	15.99	9.90	0.05	0.68	10.40
MEAN	0.72	0.36	0.36	0.003	5.25	1560.0	87904.5	62893.4	16.29	11.22	0.21	0.61	5.46
MINIMUM	0.21	0.13	0.04	0.002	1.33	1356.5	54299.3	38955.1	0.99	4.12	0.05	0.23	0.88
MAXIMUM	1.53	0.62	0.94	0.005	20.00	1989.5	112218.5	122597.3	24.88	18.98	0.65	0.97	18.00
STDEV	0.34	0.17	0.27	0.001	4.50	191.1	19998.6	22766.2	5.03	3.70	0.17	0.19	4.53

TC =TOTAL CARBON	in %
IC = INORGANIC CARBON	in %
OC = ORGANIC CARBON	in %
Bsi = BIOGENIC SILICA	in %
TN = TOTAL CARBON	in %
Na = SODIUM	in mg/l
K = POTASSIUM	in mg/l
Ha = HUMIC ACID	in %
TP = TOTAL PHOSPHRUS in µg/g	48/g
Tsi =TOTAL SILICA	48/9

	TC	IC	OC	BSI	TN	Na	K	Ha	TP	AI	Tsi	Ni
TC	1											
IC	0.566925	1										
loc	0.897466	0.15352	1									
BSI	0.210117	0.424351	0.048477	1								
TN	0.182697	0.295891	0.071947	-0.092939	1							
Na	-0.395931	-0.418045	-0.254687	-0.370073	-0.11315	1						
ĸ	0.512836	0.676325	0.274385	0.42627	0.311153	-0.263345	1					
Ha	0.240813	-0.26798	0.43025	0.222816	-0.082621	-0.314952	-0.022115	1				
TP	0.287404	0.08357	0.293251	0.146323	0.164198	0.036453	0.177803	0.194484	1			
AI	0.230411	0.246653	0.136395	0.084905	-0.149698	-0.321525	0.132527	-0.291351	-0.440981	1		
Si	-0.090372	-0.643066	0.229141	-0.182656	-0.014343	0.192353	-0.339789	0.290055	0.494166	-0.306295	1	
Ni	-0.196235	-0.134553	-0.164373	-0.443709	-0.163639	0.178122	-0.371091	-0.327351	-0.070131	0.035535	0.029003	1

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TABLE 12: Correlation Matrix of Sediment Samples During Monsoon Season all values in % expect TP, Tsi, Al IN µg/g AND Na, K IN mg/l

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	TC	IC	00	Bsi	На	TP	AI	Tsi	Na	ĸ	TN	Ni
TC	1.000									• • • • • • • • • • • • • • • • • • • •		
IC	0.608	1.000									•	
oc	0.880	0.172	1.000									
Bsi	0.212	0.173	0.175	1.000								
Ha	0.169	-0.319	0.411	0.351	1.000							
ТР	-0.030	0.149	-0.144	-0.216	-0.311	1.000						
AI	0.361	0.383	0.218	0.413	-0.201	-0.233	1.000					
Tsi	0.026	0.064	-0.026	-0.086	-0.087	0.776	-0.377	1.000				
Na	-0.208	-0.151	-0.173	-0.274	-0.346	0.069	0.047	0.229	1.000			
κ	0.120	0.047	0.144	0.287	0.107	-0.458	0.557	-0.633	-0.197	1.000		
TN	0.215	0.191	0.142	-0.108	-0.051	-0.037	0.426	-0.065	0.012	0.279	1.000	
Ni	0.039	0.140	-0.092	-0.427	-0.216	0.358	-0.396	0.196	0.100	-0.316	-0.142	1.000

Table13 : Correlation Matrix of Sediment Samples during Post Monsoon Season (all values in % except TP, Tsi, Al in µg/g and Na, K in mg/l)

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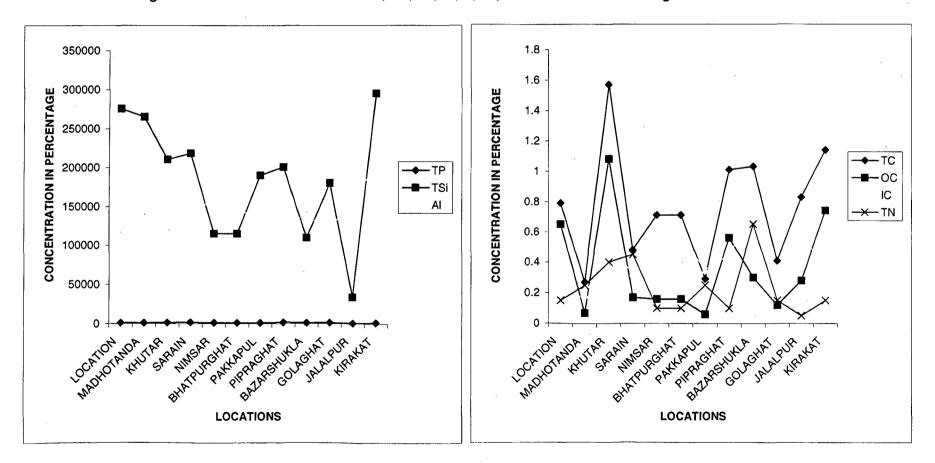


Figure 16: Downstream variation of TP,Tsi , AI ,TC,IC,OC,TN in Bed sediment during Monsoon

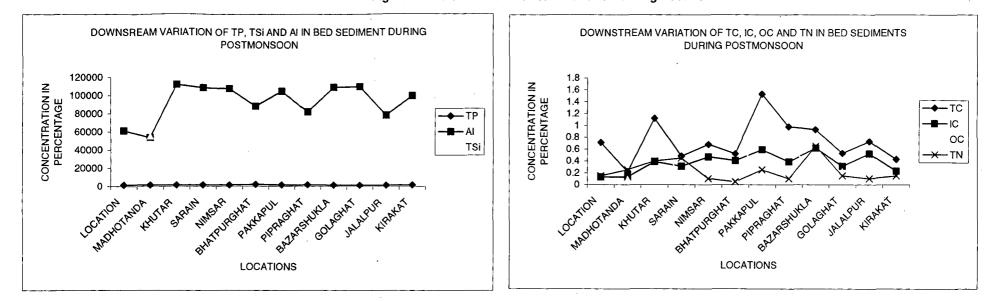


Figure 17: Data For Dowmstream Variation During Postmonsoon

The C/N ratio varies from 0.85 to 18.2 during monsoon(table 10) and from 0.88 to 18.0 during post monsoon(table11). The C/N ratio of soil decides the availability of nitrogen for the plant growth.

Total Phosphorus

Phosphorous is present predominantly in inorganic form as calcium phosphate minerals, the most common being apatites, and as aluminum and iron phosphate minerals. Organic phosphorus compounds present usually in soil humus are inositol phosphate, nucleic acid nucleotides and phospholipids. Beside this input from fertilizers and domestic waste discharge is also there.

The phosphorus content of the soil in their natural state varies considerably, depending on the nature of the parent material, degree of weathering and extent to which P lost through leaching. The usual range of TP in soils is of the order of 500 to 800 μ g/g Stevenson, (1986).

The concentration of TP varies from 144.20 to 1490.02 μ g/g during monsoon season(table 10) and from 1356.48 to 1989.50 μ g/g in post monsoon(table11).

Alumina (Al)

Aluminium is a major and chemically unreactive constituent of clay minerals, which are the dominant component of river-borne particles. It also is usually nonanthropogenic in origin and exhibits a good positive correlation with decreasing grain size (Belkin and Sparck, 1993). Alumina is showing good correlation with potassium (table).

The value of alumina varies from 98462.6 to $205613\mu g/g$ during monsoon(table 10) and from 54299.25 to $112218.50 \mu g/g$ during post monsoon season(table11).

Total Silica (TSi)

Silicate minerals, except quartz are, in general, not resistant to weathering, although they do not weather rapidly. the concentration of total silica in gomti varies from 33593.5 to $301173.0 \ \mu$ g/g during monsoon(table 10) and from 38955.1 to $122597.3 \ \mu$ g/g, during post monsoon(table11).

Biogenic Silica

Biogenic silica, better known as opal, is one of the three biogenic components of pelagic sediments, along with carbonate and organic matter, and it is a power tool for understanding the carbon cycle of the present and the past. Aquatic organisms such as diatoms, silicoflagellates, and radiolarians build up their skeleton by taking up silicic acid from water. When these organisms are dead the biogenic silica accumulated in them becomes dissolved. The portion of biogenic silica that escapes dissolution either in the surface or in deeper part, settles downward eventually reaching the sediments.

The value of biogenic silica varies from 0.0017 to 0.0049% during monsoon(table 10) and from 0.0016 to 0.0045% during post monsoon(table11) in the sediment samples of Gomti river.

Humic Acid

Humic substances comprise a general class of biogenic, refractory, yellow black organic substances that are ubiquitous, occurring in all terrestrial aquatic environments. Humic acid (HA) is that fraction of humic substances which is soluble in basic solution but insoluble in acidic solutions. Humic acids are very active chemically and they are a kind of brownish black, multiphenolic, large molecule polymer composed mainly of C,N,H and O. The values of humic acid varies from 1.333 to 19.995 % during monsoon(table 10) and from 1.333 to 23.994 % during post monsoon(table11).

Sodium (Na) and Potassium

The sodium ion is transported in river mainly by the weathering of plagioclase, pyroxene and hornblende, the concentration of sodium ranges between 10.84 mg/l to 25.31 mg/l during monsoon season(table 10) and it varies from 0.987 to 24.878 mg/l during post monsoon season(table11) in sediment samples.

Potassium is slightly less common than sodium in igneous rock but more abundant in all the sedimentary rocks. The principal potassium minerals of silicate rocks are the feldspar orthoclase and microcline (KAlSi₂O₈), the micas, and the feldspathoid leucite (KAlSi₂O₆). The values of potassium in sediment samples ranges between 4.89 to 16.32 mg/l during monsoon(table 10) and from 4.122 to 18.97 mg/l during postmonsoon(table11).

Nickel (Ni)

Nickel is one of the ubiquitous element and may be present in sediment in mainly sulphide and oxide forms and its concentration may vary according to mineral composition of sediment. Nickel enters the environment through natural process like weathering of minerals and rocks, geothermal emissions.

The concentration of nickel in sediments varies from 0.23 mg/l to 0.967 mg/l during postmonsoon season(table11).

TRANPORATION OF NUTRIENTS AS BED LOAD

Nutrient transported from continents to oceans via rivers is one of the important processes regulating biogeochemical cycling of elements.Chakrapani.G.J. (2005). Transportation of major nutrients in Gomti basins as solute load are calculated and results are given in table no: below

PARAMATERS	BED LOAD IN 10 ³ *TON/Yr					
тс	5.15					
IC	2.65					
ос	2.51					
ТР	9473.11					
AI	849950.9					
TSi	884919.5					
TN	1.561					
Na⁺	123.67					
K+	84.14					

CHAPTER - VI

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CONCLUSION

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CONCLUSION

The main conclusions of this study are as follows.

- pH value shows that water samples of Gomti river are neutral to slightly alkaline in nature. Low to moderate EC value of river samples indicating that the concentration of free ions is not much high.
- The decreasing order of anions in river water samples as follows $HCO_3 > SO_4 > NO_3^- > CI^- > PO_4^{3-} > F^-$. The major source for bicarbonates is exchange reaction with atmospheric CO_2 and microbial decomposition of dead organic matter
- The dominant cation is calcium followed by sodium, magnesium and potassium due to carbonate and silicate weathering taking place in the area.
- Gomti River also shows high concentration of dissolved organic carbon and humic acid which is due to discharge from anthropogenic activities and high litter falls from densely vegetated areas.
- The concentration of all the metal ions are below their permissible limits except Lead (Pb) and Cadmium, which indicates that there is no major source of metals in the river basin
- Factor analysis of water samples show that major factor controlling water chemistry is weathering process i.e. both

silicate and carbonate weathering. This is also indicated by the Gibbs diagram. Other important factor includes ion exchange process taking place in sediments media and anthropogenic activity taking place in the study area.

Geochemical diagrams (piper diagrams) indicate the importance of weathering process taking place in the area which is inferred by the dominance of sodium, calcium and bicarbonate ion.

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- Stability diagram for carbonate system indicates the presence of dolomite as mineral assemblage in both season and in case of silicate system minerals like Kaolinite, gibbsite, montmorillonite are present.
- Bicarbonate (1631.29 ×10³ T/yr) and organic carbon (95.96×10³ T/yr) are the major species transporting in dissolved form. In bed load the major proportion is of silica (884919.46 ×10 ³ T/ yr) and alumina (849950.86 × 10 ³ T/yr). Phosphate also present in significant amount which is due to its tendency to bind in solid medium.
- Total carban value is low to moderate in sediment samples, IC constitutes the important proportion out of it, which indicates the importance of water sediment interaction taking place. Total nitrogen also indicates low values due its uptake as nutrient by biota.
- The C/N ratio showing low values which indicates that it is having freshly deposited organic matter.
- Silica and Alumina are the major constituents of bed load, high silica Vs alumina ratio suggests addition of silica from detrital quartz, which is in abundance in river sediment.

Total phosphorus is also showing higher value which indicates extra input from anthropogenic activity taking place in basin area.

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APPENDIX

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APPENDIX – III

Calculation of Log p CO₂

(Adopted after B.C.Raymaheshay, 1986)

Example:

pH = 8.2

 $HCO_3 = 98 \text{ ppm}$

So,

 $mHCO_3 = 98/(1000 \times 61) = 1.60656 \times 10^{-3}$

and $\log mHCO_3 = -2.7941$

Using the formula

 $\text{Log pCO}_2 = 7.9 + \text{Log mHCO}_3 - \text{pH}$

 $Log pCO_2 = 7.9 - 2.7941 - 8.2$

 $Log pCO_2 = -3.0941$

Calculation of meq/l values for ion from mg/l values.

Concentration (mg/l)

Concentration of ions (meq/l) =

Equivalent weight of ion (Molecular Wt./ valency)

Example:

Ca = 80ppm, equivalent weight of Ca = 20

Ca (meq/l) = 80/20Ca = 4 meq/l.