CHEMISTRY OF MAJOR ELEMENTS AND URANIUM-THORIUM SERIES NUCLIDES IN INDIAN RIVERS

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CERTIFICATE

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any degree or diploma by any University or Institution.

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Certified by:

Dr. S. Krishnaswami
Thesis Supervisor

December 1983.

DEDICATION

TO MY BELOVED FATHER

ABSTRACT

Surface water samples from the Ganga main channel, its tributaries and from the Brahmaputra River are collected during March, September and December 1982 representing the lean, peak and moderate flows occurring in these rivers. These samples have been analysed for dissolved major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, SO_4^{2-} and SiO_2^o), D/H and $^{18}O/^{16}O$ isotopic ratios, dissolved ^{238}U and $^{234}U/^{238}U$ activity ratio. The suspended sediments have been analysed for major and trace elements (Na, K, Mg, Ca, Al, Fe, Mn, Cr, Ni and Cu) and for U-Th isotopes (^{238}U, ^{234}U, ^{232}Th, ^{230}Th and ^{228}Th).

The rivers within the Ganga and Brahmaputra Basins have been broadly classified as 'highland rivers' , viz., Bhagirathi, Ganga (upto Hardwar), Yamuna (upto Saharanpur), Ghaghara, Gandak, Brahmaputra and Manas and 'lowland rivers', viz., Yamuna (at Allahabad), Chambal, Betwa, Ken, Son and Gomti. The abundances of major ions have been used to evaluate the major ion chemistry of the highland and lowland rivers in terms of chemical weathering of the rocks and soils of their drainage basins. In these river basins, the marine contribution of cyclic salts is insignificant relative to chemical weathering. In the highland rivers, Ca^{2+}, Mg^{2+} and HCO_3^- are the most abundant ions, $(Ca+Mg)/TZ^+$ ratio is about 0.9 and

HCO_3^-/TZ^- ratio varies between 0.8 to 0.9. This suggest that the chemistry of the highland rivers is dominated by weathering of carbonate rocks, an observation consistent with the regional lithologies. Further, the relatively low silica, Na^+ and K^+ abundances in these rivers and high (Ca+Mg): (Na+K) equivalent ratios (range between 5.2 to 11.5) lead to the conclusion that the silicate weathering in these drainage basins is of minor importance.

The abundances of major ions in the Yamuna, Chambal and Gomti Rivers (lowland rivers) is influenced by the weathering of carbonates, silicates and soil salts in varying proportions. The relative proportions vary seasonally there by providing a unique opportunity to study the weathering processes regulating the abundances of major ions in these river waters. During lean flow (summer months), the contribution from alkaline and saline salt-affected soils is more pronounced. This is reflected upon the high abundances of Na^+, Cl^- and SO_4^{2-} in these river waters during lean flow. Thus, in summer months the major ion composition of these rivers is more of 'evaporitic' nature. During peak flow, the chemical composition of these rivers closely follow that of 'rock-dominated' type of waters. Hence the major ion composition of these rivers show large seasonal variation. In Ken and Son Rivers the carbonate weathering dominates the major ion composition. Of all the rivers studied, the silicate weathering appears to be more pronounced in Betwa River.

The TDS content of the highland rivers ranges between 93 to 233 mg/l where as in the lowland rivers the TDS content varies between 130 to 460 mg/l, the higher values occur during lean flow. The downstream and seasonal variations in the major ion chemistry of the Ganga main channel are controlled by the chemistry of the tributaries and their mixing volumes. Also, the chemical transport of dissolved constituents is conservative within the Ganga River basin. The average annual fluxes of dissolved salts transported by the Ganga and Brahmaputra Rivers are $67X10^6$ and $50X10^6$ tons/yr, respectively. These two rivers transport 3 % of the global supply of water and salts to the oceans.

The regional and seasonal variations of δD and $\delta^{18}O$ have been studied, for the first time, in these river waters to delineate the relative contributions (to the river flow) from different hydrologic regimes. In all the rivers, δD and $\delta^{18}O$ values are higher during lean flow period compared to that during peak flow conditions. However, this seasonal variation is more pronounced in the lowland rivers. The linear relationship ($\delta D = 6.1\ \delta^{18}O - 4.5$) between δD and $\delta^{18}O$ values yield a slope of 6.1, significantly lower than the slope of meteoric water line. This seem to suggest that the isotopic enrichment in these river waters occurs as a result of evaporation losses from rivers and dams.

The regional variations in $^{234}U/^{238}U$ activity ratio of the river waters within the Ganga and Brahmaputra River basins seem to be dominated by the lithology of the terrains which they drain. In lowland rivers, draining through relatively fresh granite and gneissic rocks, the $^{234}U/^{238}U$ activity ratio varies between 1.16±0.03 to 1.84±0.03 which are significantly higher than those of the highland rivers, 1.02±0.02, consistent with the predominantly sedimentary geology of their drainage basins. The uranium concentration in these river waters show a linear relationship with ΣCations. The $^{238}U/\Sigma$Cations ratio in these river waters is very similar to that in the river suspended sediments suggesting congruent dissolution for major cations and uranium. The Ganga and Brahmaputra Rivers constitute the major source of dissolved uranium to the oceans. These two rivers transport annually 9.4×10^{8}g of uranium to the Bay of Bengal, about 10 % of the global river input to the oceans. The residence time of uranium in the Bay of Bengal relative to its supply via these rivers is only about 2×10^{4} years.

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CHAPTER I. INTRODUCTION

Rivers are the major pathways through which the end products of chemical and physical weathering on land are transported to the oceans. The transport of chemical constituents by rivers occurs via both dissolved and suspended load. The composition of precipitation falling on the drainage basin sets the initial chemical quality of the water but this is soon altered by chemical interaction with the vegetation, rocks and soils of the drainage basin. Although, chemical, biological and physical processes are all involved in rock weathering, by far the most important of these is the chemical process. The chemical reactions between rock minerals and soil waters produce dissolved constituents and solid residues. The dissolved constituents enter the groundwater system and eventually move into the rivers. Thus the study of the chemical composition of river waters and suspended sediments is most fundamental to our understanding of the geochemical cycle of elements in the continent - river - ocean system.

The chemical composition of the world rivers has been reviewed by Durum and Haffty (1963), Livingstone (1963), Turekian (1969, 1971), Meybeck (1976). These compilations provide a general idea of chemical composition of the rivers flowing through different geological terrains and climatic regimes. It can be seen from the data compiled by Livingstone (1963) and Meybeck (1976) that the ionic ratios in waters of the major rivers are fairly constant, Ca^{2+} and HCO_3^- are by far the most abundant. This is the case for more than 90 percent of the rivers which have the 'rock dominated type' of waters described by Gibbs (1970). For the remaining rivers Na^+, Cl^- or SO_4^{2-} are dominant, these waters are either of the 'rain dominated' type or of the 'evaporation-crystallisation' type (Gibbs, 1970; Feth, 1971). The rock-dominated type of waters reflect the weathering of minerals found in surface rocks, particularly the calcium carbonate minerals in sedimentary rocks.

Dissolved constituents of the rivers are highly variable. Many relationships between dissolved constituents of the rivers and environmental factors such as climate, relief and mineralogical composition of rocks and soils have been described by various authors. According to Durum and Haffty (1963) and Gibbs (1967) climate and relief are the major factors. Climate dictates the overall chemical composition of river waters and relief dominates the variations in the transport of dissolved constituents. For example, in temperate regions the major species present are usually calcium and bicarbonate ions, while the rivers draining arid regions usually contain relatively high sodium, chloride and sulfate. The importance of relief is reflected in the transport of dissolved constituents and their variations in the downstream areas. Gibbs (1970) finds that the chemistry of river waters is influenced by precipitation, rock interaction and evaporation. The recent study of Stallard (1980) shows that the geology and lithologies of the drainage basin are the prime factors controlling the chemistry of the Amazon River waters.

Because of the large temporal and geographical variability in the chemical composition of river waters, a number of systematic and detailed geochemical studies have been carried out during the last decade on some of the world's large and medium size river systems: Amazon (Gibbs, 1967; 1970; 1972; Stallard, 1980), the Mekong (Carbonnel and Meybeck, 1975), the Mackenzie (Hitchon et al. 1969; Reeder et al. 1972; Hitchon and Krouse, 1972), Susquehanna River (Lewis, 1976), Chinese Rivers (Hu Ming-hui et al, 1982) and African Rivers (Grove, 1972). The sediment yield of major rivers of the world has been documented by Holeman (1968), Jansen and Painter (1974) and Milliman and Meade (1983). The chemical composition of the river suspended sediments has been studied by Martin et al.(1970), Trefry (1977) and Martin (1979). However, our knowledge about the chemical composition of river waters and suspended sediments is still poor especially for the tropical rivers which are thought to provide an important part of the inputs to the world oceans. For example, the Ganga-Brahmaputra River System is one of the most poorly studied river systems of the world.

Holeman (1968) and Meybeck (1976) have clearly emphasized the global importance of the Ganga-Brahmaputra River system from the geochemical point of view. Ganga and Brahmaputra are two of the largest rivers draining the Indian subcontinent. These two rivers transport annually about 10^{15} liters of water (Milliman and Meade, 1983). Due to high gradients and tremendous velocities both these rivers are highly erosive while draining through the Himalayas. Thus huge amount of sediments, nearly two billion tons per year, are being dumped into the Bay of Bengal, ranking this system second in the world (Holeman 1968). The surface waters of the Ganga and Brahmaputra River basins offer ample opportunities for studying the physical and chemical weathering rates, representative of the tropical and semi-arid regions. The general characteristic features of their drainage basins are:

(i) these are made of a number of large tributaries which drain the areas that are characterised by distinct geology, soils, relief and to some degree climate and vegetation,

(ii) they are the major inland basins and hence the contributions from ocean derived cyclic salts by precipitation, are expected to be small, and

(iii) the upper reaches of these rivers are virtually unpolluted there by providing an opportunity to study the chemical weathering processes in natural environment.

Inspite of their geochemical significance, the data that have been collected specifically for geochemical purposes from these river basins are extremely scarce. In his compilation, Livingstone (1963) quoted the analysis of a single sample of Ganga water collected in 1940 near Calcutta. Holeman (1968) estimated the sediment yields of the Ganga and Brahmaputra Rivers based on a century old sediment discharge data. Raymahashay (1970) computed the transport rates of suspended sediments and dissolved solids carried by these two rivers using the discharge and sediment load data of the Government of India (1955). His computed data reveals that the ratio of physical to chemical erosion is 7:1 in the Ganga and 9:1 in the Brahmaputra River basin. A new estimate of the sediment yield of the Ganga and Brahmaputra Rivers made by Milliman and Meade (1983) has been derived from a sediment rating curve. Their estimate (1670×10^6 tons/yr) is considerably higher than the suspended load estimate (1180×10^6 tons/yr) quoted by Subramanian (1978).

Very little is known about the hydrogeochemistry of the Ganga and Brahmaputra River drainage basins. What little that is known about chemistry of the Indian River waters is from the compilation of the Central Water and Power Commission of India (CWPC, 1973). From time to time they had undertaken the chemical investigations of river waters in India primarily to evaluate the applicability of these waters for domestic, industrial and agricultural purposes. Although the data have been used for the assessment of water quality of the Indian Rivers, many of the chemical constituents have been analysed using mostly outdated techniques. Hence the data is of inferior quality for any quantitative geochemical interpretation. Moreover, the sample collection and their storage methods employed in the past do not meet the requirement for a rigorous geochemical investigation. The geochemical study of Ganga River reported by Handa (1972) suffers from insufficient spatial and seasonal coverage in sampling of many of the large tributaries which show large seasonal variations in flow and chemical composition. Furthermore, his study does not attempt to evaluate the relationship between river water chemistry and chemical weathering. For his geochemical study on Indian Rivers, Subramanian (1979) collected samples from five locations along the Ganga main stream, two samples from its tributaries and one sample from the Brahmaputra River. However, no samples were collected from the two largest tributaries namely Yamuna and Ghaghara which contribute nearly 50% of the annual flow in the Ganga River. Also, a close inspection of his data reveals that the charge balance between cations and anions is poor, the total cations to anions ratio varies from 0.7 to 1.7. Hence this meagre data is also of inferior quality for geochemical interpretation.

Thus I have observed that the geochemical studies carried out so far, on the Ganga and Brahmaputra River systems, are inadequate and the mechanisms that control the chemical composition of these river waters remain poorly understood. These considerations have led me to undertake a detailed geochemical investigation of these river systems with a view to understand some of the processes controlling the composition and flux of the dissolved and suspended material in the Ganga and Brahmaputra River drainage basins. The specific objectives of my investigation are:

(i) to evaluate the major ion chemistry of these rivers in terms of chemical weathering of the rocks and soils of their drainage basins, and

(ii) to determine the flux of dissolved chemical constituents transported by these rivers to their estuaries.

In addition, the ^{238}U concentrations and $^{234}U/^{238}U$ activity ratios were measured in water and suspended sediments in order to evaluate the geochemical controls regarding supply of ^{238}U and ^{234}U nuclides during chemical weathering. For the first time, the stable isotopes of Hydrogen (D,H) and Oxygen (^{18}O, ^{16}O) were measured in these river waters to delineate the contributions to the river flow from different hydrological regimes.

With these aims, samples were collected from several locations along the main streams of the Ganga and Brahmaputra Rivers and also from all the major tributaries of the Ganga River which drain a wide range of geological and climatic areas. The samples were collected during the typical pattern of annual flow, viz., lean, peak and moderate flows, in order to bring out the seasonal variations in the major ion chemistry of these rivers. All samples were filtered in the field to minimize the physicochemical changes on their storage. Prior to this, no detailed study of this kind for this large river system was undertaken. This study will be presented in five parts:

Chapter II describes the geological and hydrological regimes of the Ganga and Brahmaputra River basins.

Chapter III describes the sampling strategies and the analytical procedures adopted for the chemical and radiochemical analysis of water and suspended sediments.

Chapter IV is a presentation of the data on the major ion composition of the Ganga and Brahmaputra Rivers and of their major tributaries. The compositional variability of major ions in these river waters has been evaluated in terms of chemical weathering of the rocks and soils of their drainage basins. The seasonal and annual fluxes of dissolved major ions have been computed for the Ganga and Brahmaputra Rivers.

Chapter V discusses the D/H and $^{18}O/^{16}O$ isotopic variations in these river waters. The geochemical controls regarding supply of uranium isotopes (^{238}U, ^{234}U) during chemical weathering have also been evaluated.

Chapter VI summerizes the results of this study and evolution of the major ion geochemistry of the rivers within the Ganga and Brahmaputra Basins.

CHAPTER II. GEOHYDROLOGY OF THE GANGA AND BRAHMAPUTRA RIVER SYSTEMS

Miller (1961) has shown that under the same climatic conditions rocks of similar composition will weather to produce effluent waters of similar composition. Thus, under the uniform climatic conditions the variations in river water composition should reflect the influences of different rock types. In order to evaluate the river water chemistry in terms of chemical weathering of the rocks and soils of the drainage basin (the focus of this study) it is necessary to identify the regions of representative geology. Furthermore, the hydrologic response of the drainage basin is closely related to its geology. This chapter describes the geological, lithological and hydrological characteristics of the Ganga and Brahmaputra River drainage basins.

II.1. Ganga River system

The Ganga River system represents a large river catchment (Figure II-1), occupies about $10^6 km^2$ area of the Indian subcontinent (Rao, 1975). To the north are the Himalayas and to the south are the large Indo-Gangetic alluvial plains and the Vindhyan-Bundelkhand plateau. The climate of the Ganga River basin is considered to be humid tropical type. Most of the precipitation occur during south-west monsoon (July-September).

The Ganga at its origin is known as Bhagirathi which has its source in the Gangotri Glacier at an elevation of 7000 m, in the Kumaun Himalayas. Alaknanda is the major tributary of Bhagirathi, after their confluence at Devprayag, the river acquires the name 'Ganga'. The river descends into the plains after cutting across the Siwalik range at Hardwar and flows in the south-east direction. Along the course it receives a large number of tributaries, Figure II-1. The major tributaries of the Ganga are Gomti, Ghaghara and Gandak joining from the north and Yamuna and Son from the south. The Yamuna in turn receives Chmabal, Betwa and Ken, the major tributaries joining from its right bank (Figure II-1). The Yamuna, Ghaghara and Gandak also originate in the Himalayas, after draining through the southern slopes of the Himalayas these rivers descends into the Indo-Gangetic alluvial plains (Figure II-1). The major source of water to these rivers is the precipitation during south-west monsoon. During lean flow in summer months, the flow in these rivers is mainly sustained by snow/glacier melt waters. The Chambal, Betwa, Ken and Son originate in the Vindhyan-Bundelkhand plateau (Figure II-1). Though perennial, the peak flow in these rivers occurs during south-west monsoon (July-September). During lean flow these rivers receive considerable supply of water by effluent seepage of groundwaters. The hydrological characteristics of the Ganga and its tributaries are given in Table II-1. The total length of the Ganga from its source to its outfall into the Bay of Bengal is 2525 km. The average annual flow in the Ganga at Patna is 364×10^{12} L/yr (Rao, 1975). The largest contribution, nearly one-fourth, is from the Ghaghara. The next large contribution is by the Yamuna, then followed by the Gandak. Nearly 60 $^{o}/_{o}$ of the water flowing in the Ganga comes from the drainage areas north of the river (Rao,1975).

Figure II - 1.

Map of the Ganga and Brahmaputra River systems.

Figure II - 1

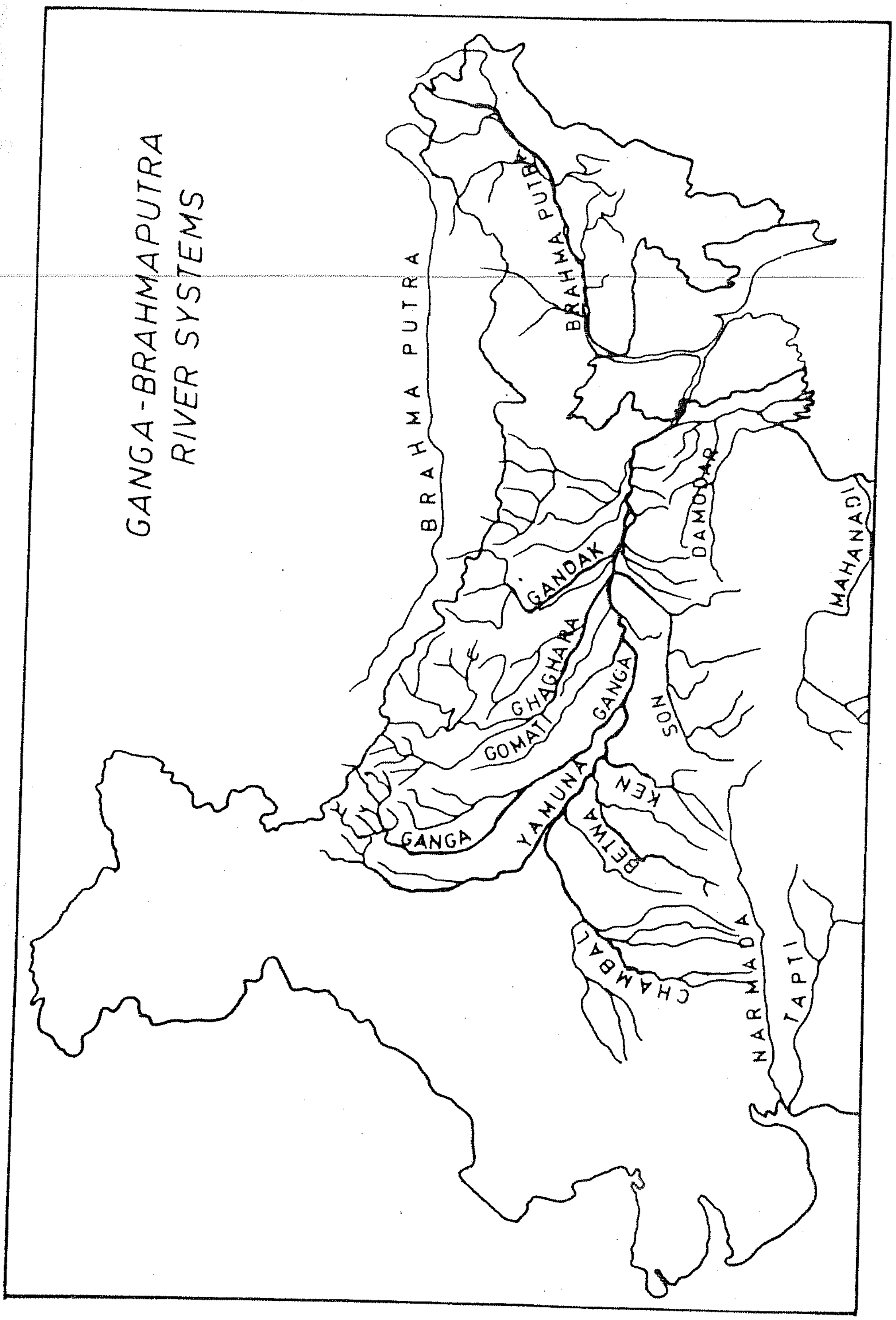

GANGA-BRAHMAPUTRA
RIVER SYSTEMS
BRAHMA PUTRA
BRAHMA PUTRA
GANDAK
GHAGHARA
GOMATI
GANGA
GANGA
YAMUNA
BETWA
KEN
SON
DAMODAR
MAHANADI
CHAMBAL
NARMADA
TAPTI

Table II-1. Hydrological Characteristics of the Rivers

River	Length[*1] (km)	Drainage Area[*1] ($\times 10^3$ km^2)	Average Annual discharge[*1] ($\times 10^{12}$ L)	Remarks
Ganga	1050	-	59	Ganga at Allahabad, before confluence with Yamuna
Yamuna	1376	139.5	93	Yamuna at Allahabad, before confluence with Ganga
Chambal	965		30	Tributary of Yamuna
Betwa	590	45.6	10	Tributary of Yamuna
Ken	360	28.2	11	Tributary of Yamuna
Gomti	940	30.4	7.5	Tributary of Ganga
Ghaghara	1080	128	94	Tributary of Ganga
Son	784	71.3	32	Tributary of Ganga

Table II-1. Contd.

River	Length[*1] (km)	Drainage Area[*1] ($\times 10^3$ km^2)	Average Annual discharge[*1] ($\times 10^{12}$ L)	Remarks
Gandak	-	46.3	52	Tributary of Ganga
Ganga[*2]	1600	861	364	Ganga at Patna, after confluence of Ghaghara, Son and Gandak
Manas	-	37.5	-	Tributary of Brahmaputra
Brahma-putra[*3]	2400	(187)	510	Brahmaputra near Goalpara, after confluence with Manas

*1. From Rao (1975)

*2. The total length, drainage area and average annual discharge of Ganga is 2525 km, 970×10^3 km^2, and 460×10^{12} L respectively.

*3. The total length and drainage area of Brahmaputra is 2900 km and 580×10^3 km^2 respectively, number in parentheses indicates the drainage area in India.

Figure II - 2.

Geologic and lithologic map of the Ganga and Brahmaputra River drainage basins (Reproduced from Singh, 1971).

Figure II - 2

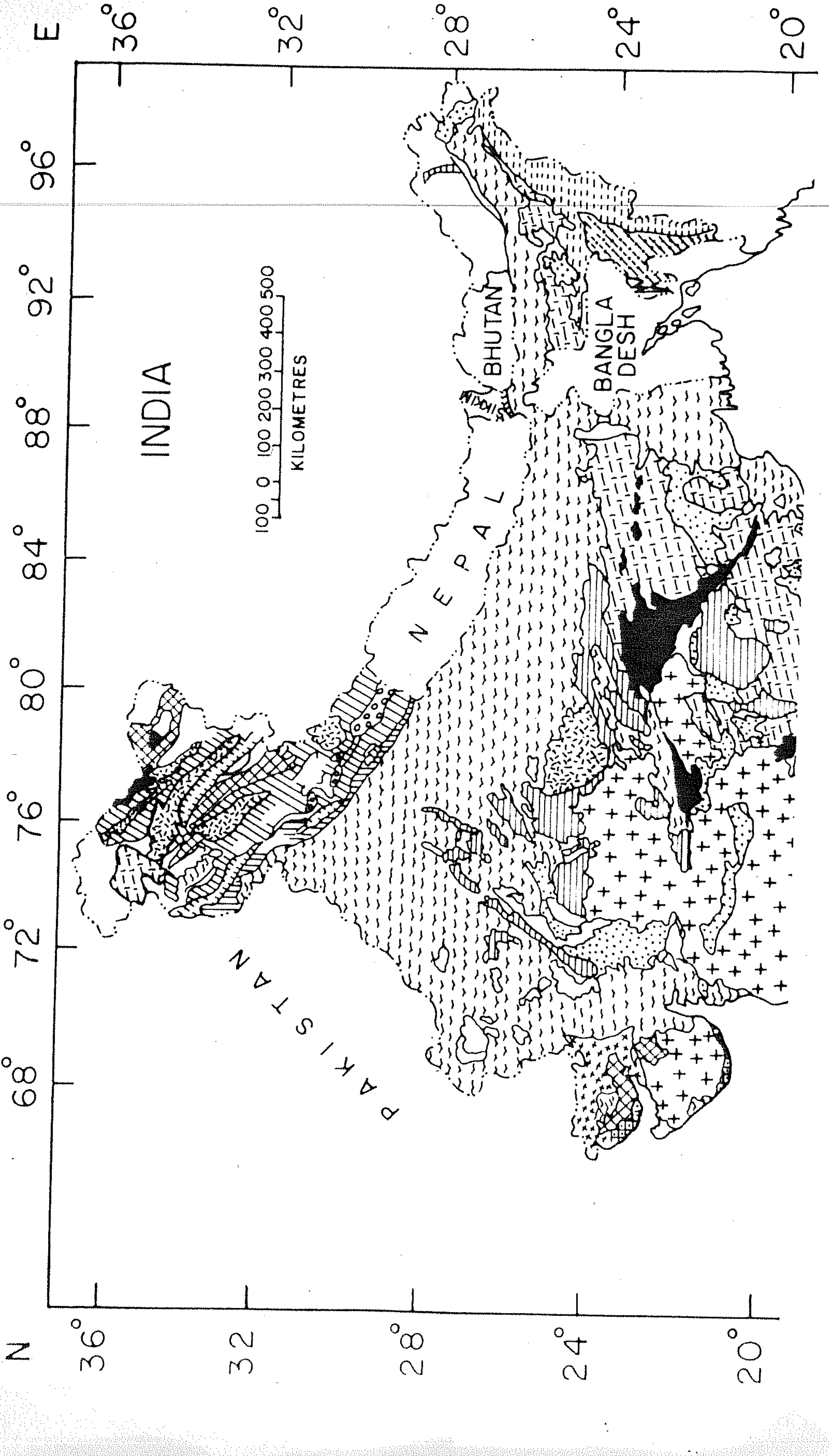

INDIA
PAKISTAN
NEPAL
BHUTAN
SIKKIM
BANGLA DESH
100 0 100 200 300 400 500
KILOMETRES
N
E
36°
32°
28°
24°
20°
68°
72°
76°
80°
84°
88°
92°
96°

Figure II-2. Symbol Key

〰	Pleistocene,	Younger and Older alluvium.
▥	Siwalik,	Coarsely-bedded sandstones, sandrocks, clays, conglomerates.
■	Gondwana and Upper Paleozoic	Paleozoic to Mesozoic sedimentary rocks: mostly sandstones, shales, carbonates.
▨	Lower Paleozoic	
▩	Mesozoic	
○	Mesozoic and Paleozoic windows	
▤	Vindhyan and Cuddapah system	Precambrian metamorphic rocks: mostly high grade gneisses, schists, quartzites and metamorphosed limestones.
●	Dharwar system	
▦	Unclassified crystallines	
⁖	Granites,	Intrusive, ingneous rocks of all ages.
▧	Malani volcanics	Extrusive igneous rocks ranging from Acid to Basic types with intertrapped sedimentary rocks like sandstones and shales.
+	Rajmahal and Deccan flows	

The drainage basin of Ganga (Figure II-1) lies within three major physiographic zones, the Kumaun Himalayas, the Indo-Gangetic alluvial plains and the Vindhyan-Bundelkhand plateau. These three zones are characterised by distinct geology (Figure II-2) soils, relief and to some degree climate and vegetation. The Kumaun Himalayas are subdivided into three broad stratigraphical zones (Gansser, 1964; Valdiya, 1980; Wadia, 1981):

(i) The Outer or Sub-Himalayan zone, composed of sediments mostly of Tertiary age. The foot-hill belt of this region is built entirely of Siwalik sediments. The Siwaliks constitute a great thickness of detrital rocks such as coarsely-bedded sandstones, sand-rocks, clays and conglomerates. Siwaliks are sub-divided in three stratigraphic units: Lower, Middle and Upper Siwaliks. The composition and characteristics of the Siwalik strata bear evidence of their very rapid deposition by the rejuvenated Himalayan rivers.

(ii) The Central or Lower Himalayan zone, the main structural features of this zone are: (a) the outer Krol belt of upper Carboniferous age, consisting mainly of dolomitic-limestones, calcareous shales and sand-stones. Gypsum occurs in large masses replacing Carboniferous limestones, (b) the inner sedimentary belt (Deoban-Tejam zone) which stretches across the Bhagirathi and the Alaknanda River basins. The major feature of its stratigraphy is the occurrence of lower Paleozoic carbonate series of enormously thick limestones and dolomites overlain by a sequence of shales and quartzites. The inner sedimentary zone is separated from the outer Krol belt by the Almora-Dudatoli thrust sheet which is a huge crystalline mass of metamorphic rocks.

(iii) The Higher Himalayan zone, the main rocks of this zone are quartzites, migmatites, gneisses, garnet-schists and dioritic amphibolites.

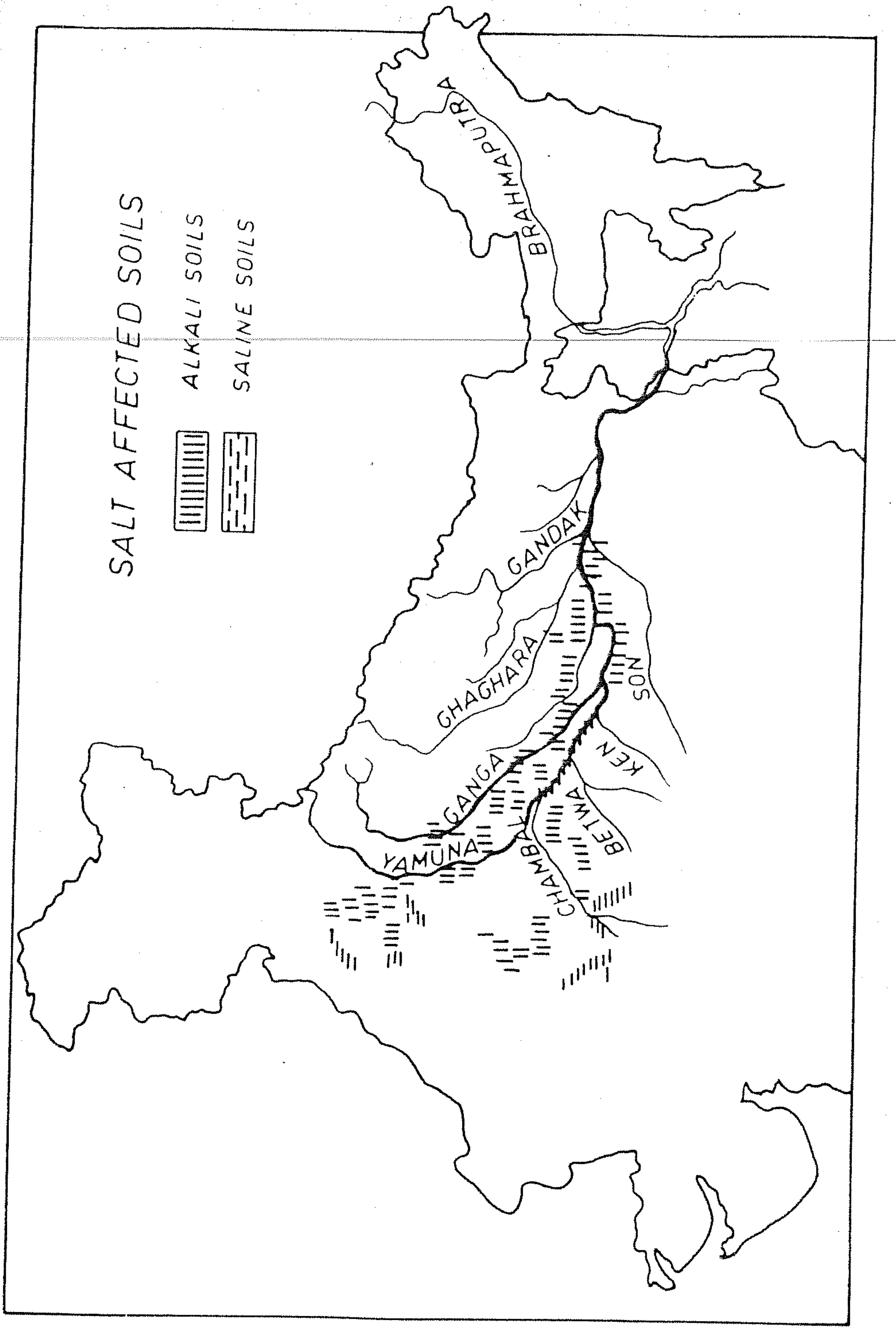
The Indo-Gangetic alluvial plains are formed by pre-Tertiary river-borne debris from the Indian Peninsula and post-Tertiary Himalayan debris brought by the present day major rivers, viz, Ganga, Yamuna, Ghaghara and Gandak. The area of these alluvial plains is about $7 \times 10^5 km^2$ (Wadia, 1981). The recent calculations from geodetic surveys estimate a thickness of more than 5000 m for these alluvial deposits resting on the pre-Tertiary bed rocks. The rocks are everywhere of fluviatile and sub-aerial formation - massive beds of clay, either sandy or calcareous, corresponding to the silts, mud and sand of the Himalayan rivers. A characteristic of the clayey part of the alluvial plains, particularly in the post-Tertiary deposits, is the abundant dissemination of impure calcareous matter in the form of irregular concretions 'Kankar'. The formation of Kankar concretions is due to the segregation of the calcareous material of the alluvial deposits into lumps or nodules. The alluvium of some places contains as much as 30 percent calcareous matter (Wadia, 1981).

A large part of the alluvial soils in the drier regions of the Indo-Gangetic alluvial plains is impregnated with alkaline and saline salts (Figure II-3). The characteristics and genesis of these alkaline and saline soils occupying the micro-depressions in the alluvial plains have been described by several workers (Abrol and Bhumbla, 1971, 1978; Raychauhdhuri and Govindarajan, 1971; Bhargava et al, 1980, 1981). Numerous torrents and seasonal streams originating in the Siwaliks debouch into the plains bringing in large quantities of runoff. Despite the perennial rivers, viz, the Ganga and the Yamuna, the Indo-Gangetic alluvial plain broadly constitutes an endoric inland area lacking a well-developed natural surface-drainage network (Wadia, 1981). In such circumstances the surface runoff laden with the weathering products (chiefly bicarbonates and carbonates of alkali and alkaline earths) brought by the Siwalik streams

Figure II - 3.

Salt affected soils in the Ganga River drainage basin, adopted from the map published by CSSRI, Karnal, 1975.

Figure II - 3


SALT AFFECTED SOILS
ALKALI SOILS
SALINE SOILS
BRAHMAPUTRA
GANDAK
GHAGHARA
GANGA
YAMUNA
CHAMBAL
BETWA
KEN
SON

cause intermittent flooding of the micro-depressions. In many parts of the hot alluvial plains, which have got no underground drainage of water, the bulk of the accumulated runoff is lost only through evaporation. Thus, the accumulation of the weathering products in the low-lying areas during the rainy season, evaporation in the post-monsoon months and the repetition of these flooding and evaporation cycles, appear to be the main factors that have resulted in the formation of these alkaline and saline salt-affected soils. Calcium and magnesium are the first to get precipitated as carbonates as the process of evaporation occurs and the soil solution gets increasingly concentrated with sodium. The lime concretions of finer sizes distributed in the upper 1 m depth result from this kind of pedogenic release of calcium and magnesium (Bhargava et al, 1981). Alkaline soils are concentrated in the zone of mean annual rainfall ranging from 50 to 100 cm (Bhargava et al, 1980). These soils are characterised by the dominance of sodium bicarbonate and carbonate among the soluble salts. In contrast, the saline soils tend to occur in regions with an annual rainfall of less than 50 cm, sodium chloride and sulfate are the main salt types. Groundwaters in these areas serve as the main source of soil salinization (Bhargava et al, 1980).

The headwaters of the Chambal, Betwa and Ken Rivers originate in the Vindhyan-Bundelkhand plateau. Geologically the region forms a part of the Archaean shield of the Deccan Peninsula. The main geological systems representative of this region are (Wadia,1981):

(i) The Archaean System, represented by 'massif Bundelkhand' which is largely composed of crystalline igneous and metamorphic rocks. Based on their texture and composition, several types of granites can be recognised in Bundelkhand.

(ii) Transitional System having been formed in the post-Aravalli or pre-Vindhyan period. The system represents sedimentary strata of sandstones and limestones in which lava intrusions had later penetrated. It also represent a contorated arrangement of very hard and soft rocks that are chiefly composed of massive quartzite sandstones and granitic sandstones.

(iii) The Vindhyan System forms a series of escarpments of massive sandstones and limestones which were originally deposited in a shallow but extensive basin.

(iv) Recent Deposits, which are represented by large scale alluvial deposits. The alluvial sediments are of fluviatile and subaerial formations of sand, silt and clay.

The lower Vindhyans of the Son River Valley are largely composed of limestones, shales and sandstones with interbedded porcellanites (silicified ash). The shales are sparsely developed and are of local occurrence only. They are often carbonaceous, siliceous or calcareous.

II. 2. Brahmaputra River

Brahmaputra rises in Chamyungdung Glacier in the Tibetan Himalayas, at an elevation of 5200 m. After flowing parallel to the main Himalayan Range it enters the Assam Valley. A number of small tributaries join the main river in Assam from the north and south. The hydrological characteristics of the Brahmaputra River are given in Table II-1. Ganga and Brahmaputra merge with each other in Bangaladesh and subsequently break into a number of estuaries before their outfall into the Bay of Bengal (Figure II-1).

The geological information on the Tibetan Himalayas is very restricted, vague and limited to its outermost part. The lithology, of the southern slopes of the Tibetan Himalays along the course of Brahmaputra River, is dominated by reduced shales, gneisses and volcanic rocks. Reduced shales, gneisses and granites are notably potassic (Gansser, 1964). The river drainage basin in the Assam Valley consists of recent and Pleistocene alluvium. In the middle part of the Valley, the river encounters the granite and gneiss projections of the Mikir Hills.

CHAPTER III. SAMPLE COLLECTION AND ANALYTICAL PROCEDURES

The geologic and hydrologic regimes of the Ganga and Brahmaputra River basins have been described in chapter II. These two river systems are too large to sample all the tributaries in detail. Therefore, a sampling scheme had to be designed which would be logistically feasible and would provide the relevant samples to achieve the specific objectives of this study. Because of their quantitative significance to the Ganga main stream, all the major tributaries draining large areas of distinctly different geology were sampled individually. One of the aim of this study is to determine the temporal variations in the major ion composition of these river waters. In order to achieve this aim samples were collected during lean, peak and moderate flows occurring in these rivers. Another important aspect of this study is that filtration of samples for dissolved constituents was carried out in the field within 5-6 hours of sample collection. The analytical procedures adopted for the chemical and radiochemical analysis of water and suspended sediments were selected from the literature and suitably modified for the wide range of concentrations encountered. This chapter describes the sampling strategies and the analytical procedures adopted for this study.

III.1. Sampling

Three sampling trips were undertaken, during March, September and December 1982, to collect water and suspended sediment samples from the Ganga main channel and its major tributaries, viz, Yamuna, Chambal, Betwa, Ken, Gomti, Son, Ghaghara and Gandak. These sampling periods were chosen to represent the typical pattern of annual flow occurring in these rivers, viz, lean, peak and moderate flows. Samples from the Brahmaputra and the Manas Rivers were collected during April and December 1982, representing their moderate and lean flows. Sample sites are shown in Figure III-1 and the relevant details of samples collection are given in Tables III - 1, 2 and 3. Sample sites along the Ganga main stream are spaced between Devprayag and Patna, a river length of about 1600 km. In order to obtain their representative samples, all the major tributaries were sampled within about 50 km upstream of their confluence with the Ganga main stream. Sample sites for the Brahmaputra River are spaced between Dibrugarh and Goalpara (a river length of about 700 km) and the Manas River was sampled about 500 m upstream of the confluence with the Brahmaputra River. Depending upon the location, access to the rivers were made either from highway bridges or by going into the rivers on small boats. The philosophy of sample collection was to obtain uncontaminated samples for:

(i) Suspended matter concentration,

(ii) D/H and $^{18}O/^{16}O$ isotopic ratios,

(iii) Dissolved major constituents: Na, K, Mg, Ca, HCO_3, Cl, SO_4 and SiO_2,

(iv) Dissolved ^{238}U and $^{234}U/^{238}U$ activity ratio, and

(v) Suspended sediments for major and trace elemental analysis and for U-Th decay series nuclides.

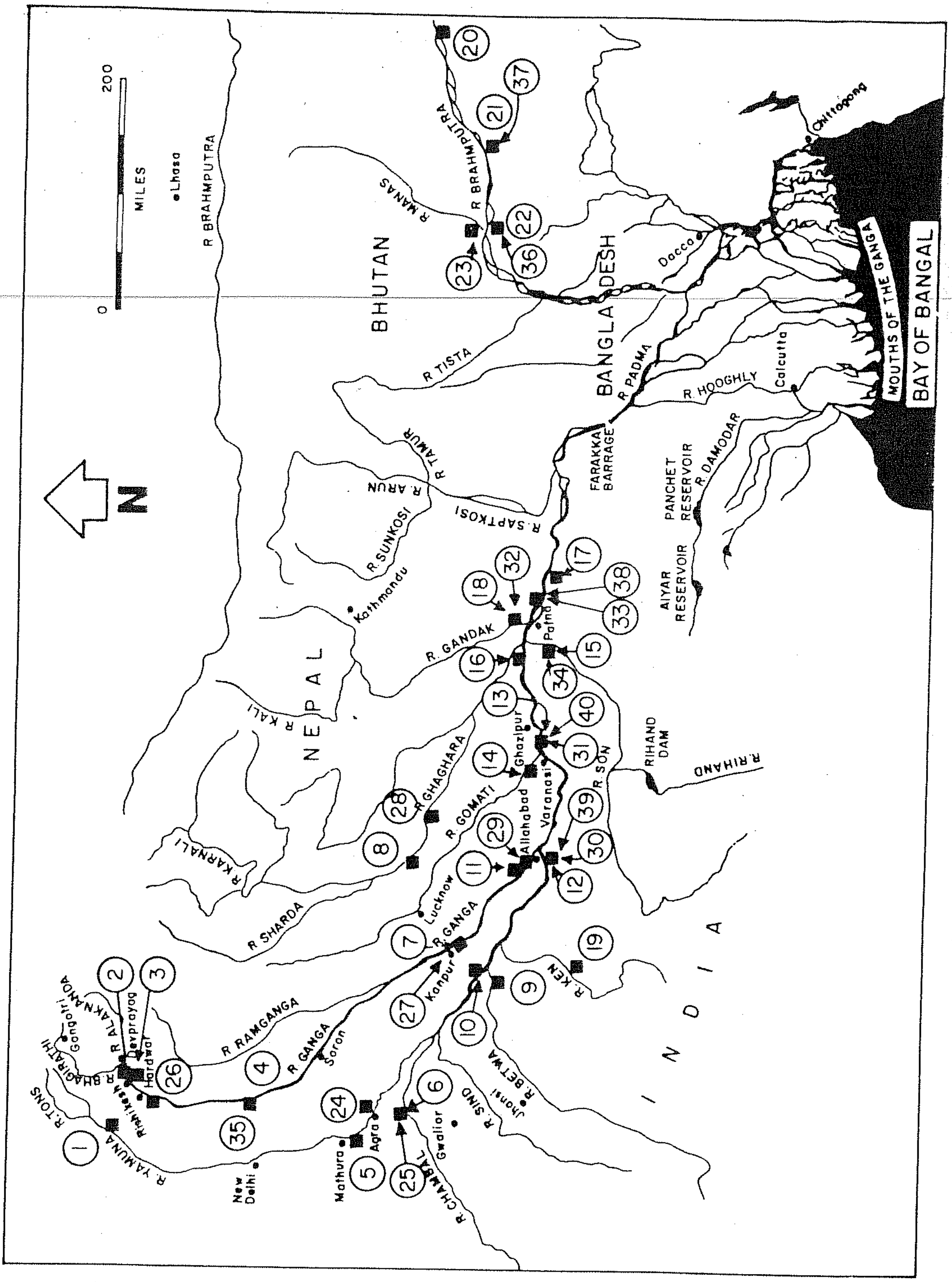
All are surface (0-2m) samples, collected from mid-channel of the rivers thereby avoiding local inhomogenities near the banks. All samples were collected and stored in polyethylene containers. Prior to their use in the field all containers were soaked in 1N nitric acid for 48 hours and rinsed several times with double distilled water. Samples from a highway bridge were collected in a plastic bucket with a nylon rope handle. The plastic bucket was rinsed repeatedly with ambient river water prior to collection of sample. The sub-samples for suspended matter concentration and for stable isotopes were immediately drawn from the bucket into 125 ml (or 250 ml) and 50 ml polyethylene bottles, respectively. The remaining sample was temporarily stored in precleaned jerrican (2.5 liters capacity) and was later split into different aliquots for the measurement of dissolved major constituents. Large volume samples for dissolved uranium isotopes were stored in 20 liters polyethylene carbouys. The general scheme for the subsampling is shown in Figure III-2. When sampling from a boat, jerricans and polyethylene carbouys were directly immersed and rinsed several times with ambient river water before collecting a sample. Samples for suspended matter concentration and stable isotopes were directly collected in their respective polyethylene bottles.

The measurements of pH, dissolved oxygen, conductance and bicarbonate were made in the field as described later in this chapter. An important aspect of the sub-sampling (Figure III-2) is that filtration of samples for dissolved major constituents was carried out in the field and in most cases it was completed within 5-6 hours of sample collection. An exploded view of the filtration system employed in the field of for filtration of small volume samples is shown in Figure III-3. About 500 ml of filtered unacidified samples were stored in polyethylene bottles until analysed in the laboratory for dissolved major ions. Large volume samples for uranium isotopes were filtered through Gelman cartridge filters (3.0 µm pore size) and uranium isotopes (^{238}U and ^{234}U) were extracted by coprecipitating with $Fe(OH)_3$ in presence of ^{232}U tracer and precipitates were brought to the laboratory for radiochemical purification. In all about 240 sample sets from 40 locations were collected for this study.

Figure III - 1.

Sample location map. Numbers correspond to the sample sites occupied during March September and December 1982. Relevant details are given in Tables III-1, 2 and 3.

Figure III - 1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200
MILES
Lhasa
R BRAHMPUTRA
N
BHUTAN
R MANAS
R BRAHMPUTRA
BANGLADESH
Dacca
Chittagong
MOUTHS OF THE GANGA
BAY OF BANGAL
Calcutta
R HOOGHLY
R PADMA
FARAKKA BARRAGE
R TISTA
R TAMUR
R ARUN
R SAPTKOSI
R SUNKOSI
Kathmandu
PANCHET RESERVOIR
R DAMODAR
AIYAR RESERVOIR
NEPAL
R KALI
R GANDAK
Patna
RIHAND DAM
R RIHAND
R SON
Ghazipur
Varanasi
Allahabad
R GOMATI
R GHAGHARA
R KARNALI
R SHARDA
Lucknow
R GANGA
Kanpur
R KEN
INDIA
R BETWA
Jhansi
R SIND
Gwalior
R CHAMBAL
Agra
Mathura
New Delhi
R YAMUNA
R TONS
R BHAGIRATHI
Gangotri
R ALAKNANDA
Devprayag
Rishikesh
Hardwar
R RAMGANGA
R GANGA
Soron
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Table III-1. Relevant Details of Sample Locations: Ganga Main Stream

Station No.	Location	Downstream (km)	Remarks
		Lean Flow, March 1982	
2.	River bank, Devprayag	180	Bhagirathi River, about 500 m upstream of the confluence with Alaknanda River, sampled by wading into the river
3.	River bank, Rishikesh	250	About 1 km upstream of Rishikesh, sampled by wading into the river
4.	Mid-channel, Garhmukteshwar	450	Near highway bridge, sampled by boat
7.	Mid-channel, Kanpur	850	About 10 km downstream of Kanpur, sampled from highway bridge
11.	Mid-channel, upstream Allahabad	1000	Near Kalakankar village, about 50 km upstream of Allahabad, sampled from bridge of boats

Table III-1. Contd.

Station No.	Location	Downstream (km)	Remarks
	(About 50 km downstream Yamuna joins the main stream)		
13.	Mid-channel, Varanasi	1200	About 2 km upstream of Varanasi, sampled from bridge of boats
	(Further downstream Gomti joins the main stream)		
16.	Mid-channel, upstream Patna	1470	Near Semariya village, about 70 km upstream of Patna, sampled by boat
	(Further downstream Ghaghara, Son and Gandak join the main stream)		
17.	Mid-channel, downstream Patna	1620	Near Pandarak village, about 80 km downstream of Patna, sampled by boat

Table III-1. Contd.

Station No.	Location	Downstream (km)	Remarks
		Peak Flow, September 1982	
26.	Mid-channel, Hardwar	250	Sampled from highway bridge
35.	Mid-channel, Garhmukteshwar	450	Near highway bridge, sampled by boat
27.	Mid-channel, Kanpur	850	About 10 km downstream of Kanpur, sampled from highway bridge
29.	River bank, Allahabad	1040	About 5 km upstream of Allahabad, before the confluence of Yamuna River, sampled by wading into the river
31.	Mid-channel, Varanasi	1200	About 2 km upstream of Varanasi, sampled by boat
33.	Mid-channel, Patna	1550	About 10 km downstream of Patna, after the confluence of Ghaghara, Son and Gandak Rivers, sampled from highway bridge

Table III-1. Contd.

Station No.	Location	Downstream (km)	Remarks
			Moderate Flow, December 1982
40.	Mid-channel, Varanasi	1200	About 2 km upstream of Varansi, sampled from bridge of boats
38.	Mid-channel, Patna	1550	About 10 km downstream of Patna, after the confluence of Ghaghara, Son and Gandak Rivers, sampled by boat

Table III-2. Relevant Details of Sample Locations: Tributaries of Ganga

Station No.	Tributary	Location	Remarks
		Lean Flow, March 1982	
1.	Yamuna	River bank, Yamunanagar	About 1 km upstream of Yamunanagar, sampled by wading into the river
5.	Yamuna	Mid-channel, Mathura	Sampled from highway bridge
		(Further downstream Chambal joins with Yamuna)	
10.	Yamuna	Mid-channel, Hamirpur	Before the confluence of Betwa River, sampled from bridge of boats
		(Further downstream Betwa and Ken join with Yamuna)	

Table III-2. Contd.

Station No.	Tributary	Location	Remarks
12.	Yamuna	Mid-channel, Allahabad	About 3 km upstream of the confluence with Ganga River, sampled by boat
6.	Chambal	Mid-channel, Dholpur	Sampled by highway bridge
9.	Betwa	Mid-channel, Hamirpur	Before confluence with Yamuna River, sampled from bridge of boats
19.	Ken	River bank, near Panna	Sampled by wading into the river
15.	Son	Mid-channel, Ara	Before confluence with Ganga River, sampled by boat
14.	Gomti	Mid-channel, Dobni	About 30 km north of Varansi, before confluence with Ganga River, sampled by boat

Table III-2. Contd.

Station No.	Tributary	Location	Remarks
8.	Ghaghara	Mid-channel, Elgin Bridge	About 75 km north-east of Lucknow, sampled from bridge of boats
18.	Gandak	Mid-channel, Hajipur	Before confluence with Ganga River, sampled by boat
		Peak Flow, September 1982	
24.	Yamuna	Mid-channel, Agra	Sampled from highway bridge
30.	Yamuna	Mid-channel, Allahabad	Before confluence with Ganga River, sampled by boat
25.	Chambal	Mid-channel, Dholpur	Sampled from highway bridge
34.	Son	Mid-channel, Ara	Before confluence with Ganga River, sampled from highway bridge

Table III-2. Contd.

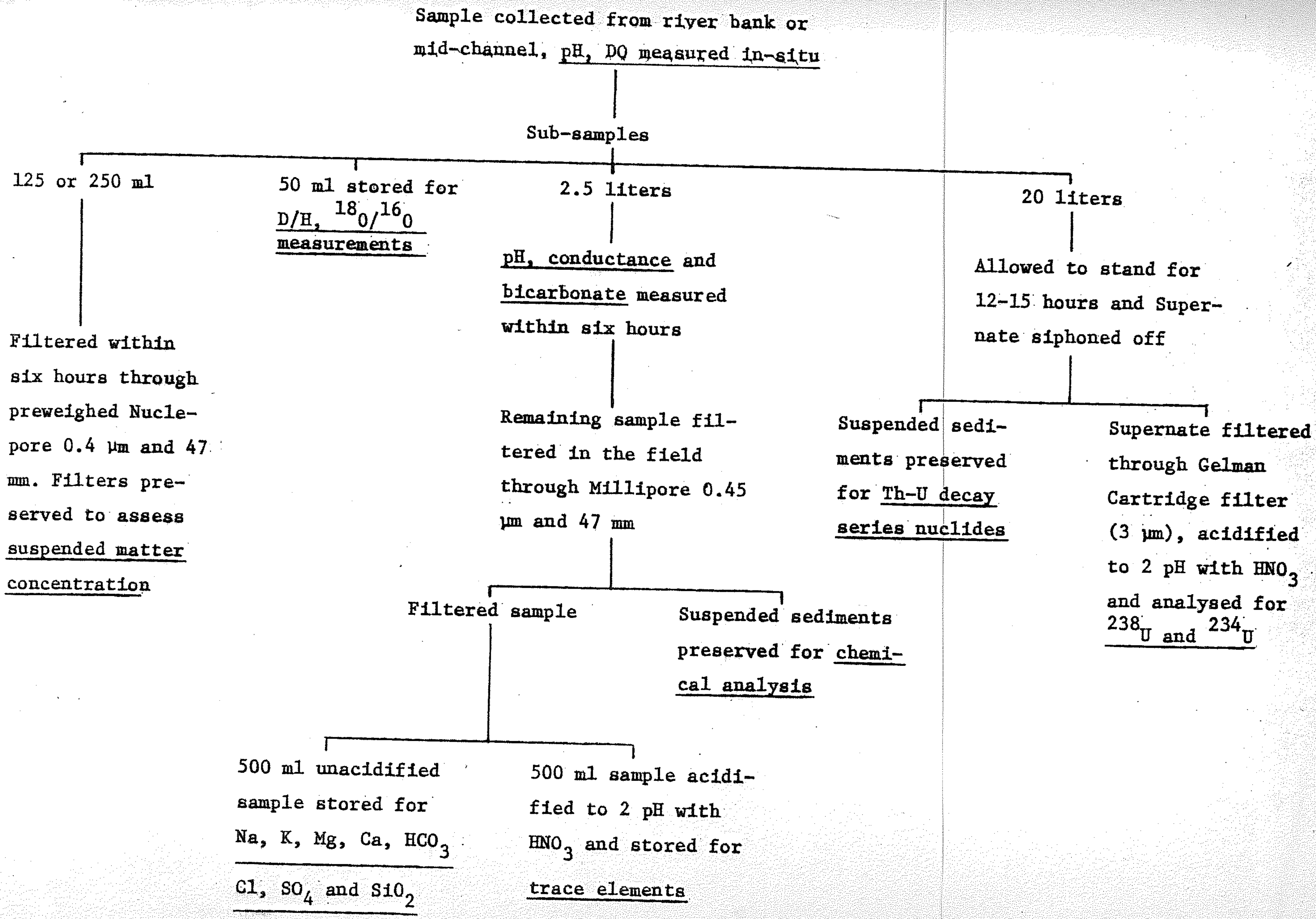
Station No.	Tributary	Location	Remarks
28.	Ghaghara	Mid-channel, Ayodhya	About 20 km from Faizabad, sampled from highway bridge
32.	Gandak	Mid-channel, Hajipur	Before confluence with Ganga River, sampled from highway bridge
		Moderate Flow, December 1982	
39.	Yamuna	Mid-channel, Allahabad	Before confluence with Ganga River, sampled by boat

Table III-3. Relevant Details of Sample Locations: Brahmaputra River

Station No.	Location	Remarks
		Moderate Flow, April 1982
20.	Mid-channel, Dibrugarh	Sampled by boat
21.	Mid-channel, Gauhati	Sampled by boat
22.	Mid-channel, Goalpara	About 500 m upstream of the confluence of Manas River, sampled by boat
23.	Mid-channel, Goalpara	Manas River, about 500 m upstream of the confluence with Brahmaputra main stream, sampled by boat
		Lean Flow, December 1982
37.	Mid-channel, Gauhati	Sampled by boat
36.	Mid-channel, Goalpara	About 500 m upstream of the confluence with Manas River, sampled by boat

Figure III - 2.

Schematic details of sample collection, subsampling and field measurements.

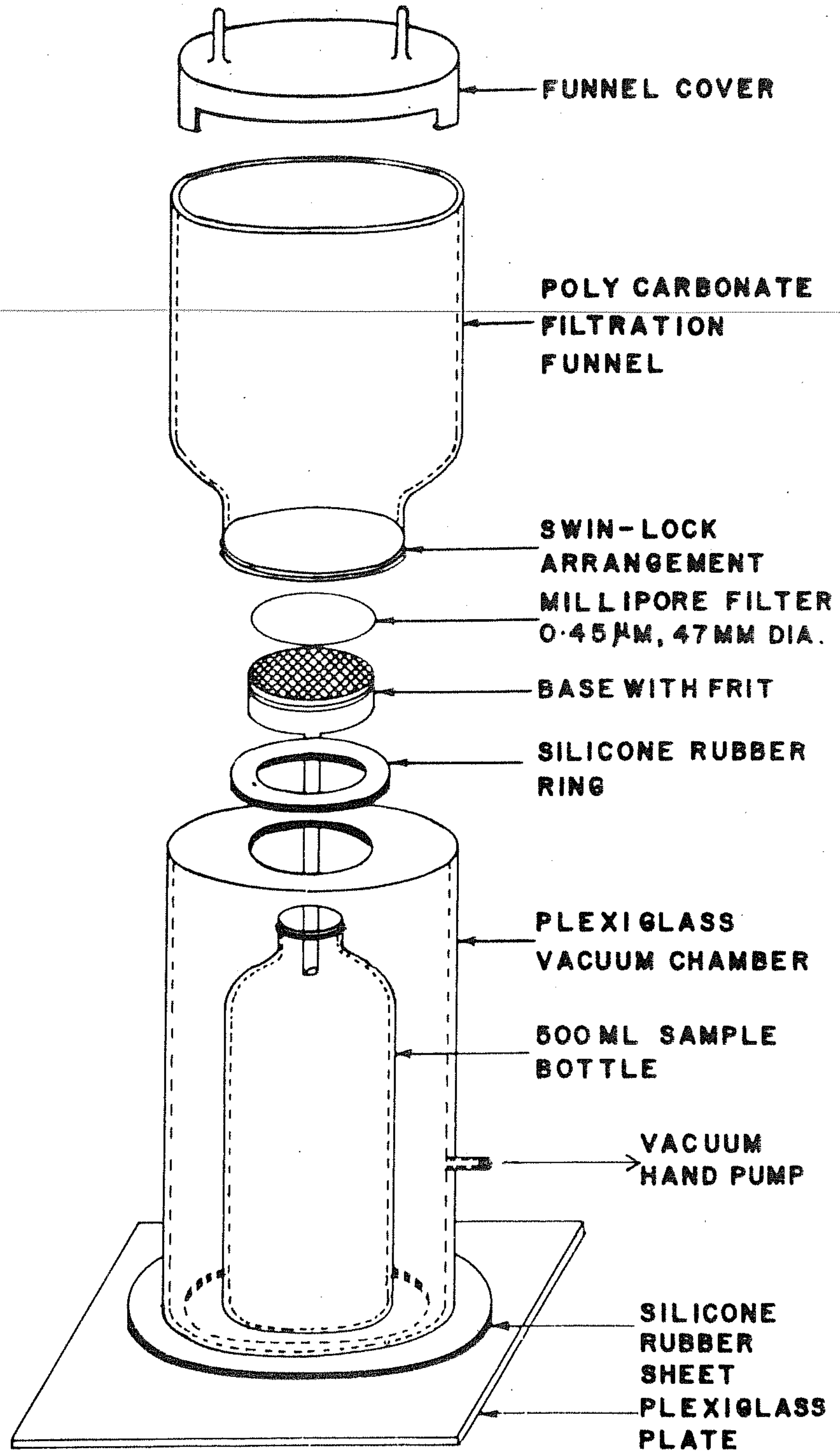


- Sample collected from river bank or mid-channel, pH, DO measured in-situ
  - Sub-samples
    - 125 or 250 ml
      - Filtered within six hours through preweighed Nuclepore 0.4 μm and 47 mm. Filters preserved to assess suspended matter concentration
    - 50 ml stored for D/H, $^{18}O/^{16}O$ measurements
    - 2.5 liters
      - pH, conductance and bicarbonate measured within six hours
        - Remaining sample filtered in the field through Millipore 0.45 μm and 47 mm
          - Filtered sample
            - 500 ml unacidified sample stored for Na, K, Mg, Ca, HCO_3 Cl, SO_4 and SiO_2
            - 500 ml sample acidified to 2 pH with HNO_3 and stored for trace elements
          - Suspended sediments preserved for chemical analysis
    - 20 liters
      - Allowed to stand for 12-15 hours and Supernate siphoned off
        - Suspended sediments preserved for Th-U decay series nuclides
        - Supernate filtered through Gelman Cartridge filter (3 μm), acidified to 2 pH with HNO_3 and analysed for ^{238}U and ^{234}U

Figure III - 3.

An exploded view of the filtration system employed in the field for small volume filtration.

Figure III - 3


FUNNEL COVER
POLY CARBONATE FILTRATION FUNNEL
SWIN-LOCK ARRANGEMENT
MILLIPORE FILTER 0·45 μM, 47 MM DIA.
BASE WITH FRIT
SILICONE RUBBER RING
PLEXIGLASS VACUUM CHAMBER
500 ML SAMPLE BOTTLE
VACUUM HAND PUMP
SILICONE RUBBER SHEET
PLEXIGLASS PLATE

III.2. Analytical Procedures

The analytical procedures adopted for the chemical and radiochemical analysis of water and suspended sediments are described here. The measurements of pH and dissolved oxygen were made in the field either *in-situ* or in a closed system on unfiltered samples. Conductance and bicarbonate measurements were also made in the field on unfiltered samples (Figure III-2) within 5 to 6 hours of sample collection.

III.2.(a) pH

During the March 1982 sampling, pH measurements were done in a closed system on the field. About 50 to 70 ml of unfiltered water was drawn from a 2.5 liters sample (Figure III-2) into a glass cylinder fitted with a rubber cork through which a set of electrode (glass and calomal electrodes) were immersed in water, pH was read after two minutes of equilibration time. Prior to every measurement, the pH meter was calibrated with standard buffer solutions of 7.0 and 9.2 pH. During September 1982 and subsequent sampling trips, pH measurements were made *in-situ* by using a water quality meter (Ogawa Seiki Co. Ltd., Japan, model - OSK 3335) coupled with a throw away sensor. The unit was calibrated with 6.86 pH buffer solution supplied by the manufacturer, accuracy of the measurement is ± 0.1 .

III.2.(b) Dissolved Oxygen

Measurements for dissolved oxygen (DO) could be made only during the September 1982 sampling trip. These measurements were made *in-situ* by using a water quality meter (Ogawa Seiki Co. Ltd., Japan, model-OSK 3335). Manufacturer's specification were followed for the calibration and accuracy of the measurement was ± 5 %.

III.2.(c) Conductance

All conductance measurements were made in the field with a portable conductometer. Prior to every measurement, the conductometer was calibrated with standard 10^{-3}N potassium chloride solution. About 25 ml of untreated sample (Figure III-2) was used for the conductance measurement. The specific conductance (μmhos/cm) of sample was obtained by multiplying observed conductivity and cell constant. Precision of measurement was better than ± 3 °/o for the conductance range observed for all samples.

III.2.(d) Bicarbonate

Bicarbonate concentrations were measured in the field by acid titration. About 25 ml of unfiltered sample (Figure III-2) was titrated with standard solution of 10^{-2}N hydrochloric acid using methyl-orange indicator. Titration was done in duplicate or triplicate to get concordant burette readings. Carbonate concentration in all the samples was found to be extremely low and could not be measured unambiguously by HCl-tritration method using phenolphthalein indicator.

III.2.(e) Dissolved Major Constituents

In the laboratory, analytical procedures for the measurement of dissolved major constituents (Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^- , Cl^-, SO_4^{2-} and SiO_2) were selected from the literature and suitably modified (wherever required) for the wide range of concentrations encountered. All glass-wares were leached with 2N nitric acid and rinsed with double distilled water prior to their use.

III.2.e.(i) Sodium, Potassium, Magnesium and Calcium

Dissolved Na^+, K^+, Mg^{2+} and Ca^{2+} were determined (on filtered unacidified split, figure III-2) by flame atomic absorption spectrophotometry (AAS) using a Perkin-Elmer 305A model, following the procedures outlined in the Perkin-Elmer Handbook (1976). Wherever required samples were suitably diluted to bring the concentration to the linear portion of the absorbance curve. Chemical suppression on calcium and magnesium absorption in an air-acetylene flame was controlled by addition of lanthanum. Samples and working standards were prepared in 2000 ppm lanthanum. Based on replicate analysis the analytical precision for the measurement of these four cations is ± 5 %.

For Na^+, K^+, Mg^{2+} and Ca^{2+} the filtered unacidified samples were stable for several months. However, the stability of Ca^{2+} merits a brief discussion.

Since Ca^{2+} was measured in unacidified sample splits, and since in some of the samples HCO_3^- content was high, there was a concern about the possibility of loss of dissolved Ca^{2+} via $CaCO_3$ precipitation during storage of samples. In order to check on this, a time series analysis of Ca^{2+} in the unacidified and acidified samples were made. The results of these measurements (Table III-4) show that out of six samples four of them does not show any change in Ca^{2+} concentration in the unacidified samples when analysed after their storage for several months, and in these samples Ca^{2+} concentration in the unacidified and acidified splits was same within errors. However, in samples No.12 and 39 there was a significant decrease in Ca^{2+} concentration in the unacidified samples when analysed about four months after their collection. Also these two samples have the highest HCO_3^- concentration. Hence, this decrease in Ca^{2+} concentration during storage is not unexpected. However, the Ca^{2+} concentrations reported in this study are not expected to be affected by such losses since all the measurements were made within a period of one month after their collection. This is also demonstrated by the measurements made on acidified sample splits.

III.2.e.(ii) Chloride and Sulfate

The low concentrations of chloride and sulfate encountered in these river waters preclude the applicability of most of the classical titration methods

Table III-4. Reproducibility of calcium measurements

Sample Code*	Collection	Analysis+, Ca^{2+} conc. (µmole/l)			
		Unacidified Split			Acidified Split
		April 82	Oct 82	April 83	April 83
3.Ganga	March 82	398	-	371	371
12.Yamuna	"	**702**	-	297	753
25.Chambal	Sept 82	-	829	785	785
35.Ganga	"	-	471	435	435
36.Brahmaputra	Dec 82	-	-	531	531
39.Yamuna	"	-	-	337	967

* Sample Code indicates Station No. and River, Figure III-1

\+ These measurements also demonstrate the stability of Ca^{2+} on storage of filtered unacidified samples for several months, except for two samples No.12 and 39 because of their poor sensitivity. During initial stages of this study, preliminary chloride concentrations in March 1982 samples were obtained by silver nitrate titration method using sodium chromate indicator. At a later stage, chloride measurements were made on filtered unacidified samples (Figure III-2) by colorimetric mercuric thiocynate method (Florence and Farrar, 1971). Although the silver nitrate titration method could be satisfactorily used for the chloride concentration exceeding 150 μmole/l, the reliability of the method was doubted when the chloride content of the sample was found to be less than 150 μmole/l. Hence the mercuric thiocyanate method was suitably modified and adopted for all samples. The method is based on the displacement of thiocyanate ion (SCN^-) from mercuric thiocyanate by chloride ion (Cl^-) and the subsequent reaction of the liberated thiocyanate ion with ferric ion (Fe^{3+}) to form the coloured complex, ferric thiocyanate. This complex is proportional to the chloride concentration and is measured on a spectrophotometer at 480 nm.

Depending on the chloride concentration, sample volume ranging from 2-20 ml was taken in a 50 ml volumetric flask. To it 25 ml of saturated mercuric thiocyanate and 2 ml of 5 % ferric ammonium sulfate solutions are added and volume was made to 50 ml with distilled water. After 30 minutes, intensity of ferric thiocyanate complex was measured at 480 nm on a Beckman spectrophotometer, model 26. A number of blanks were run on distilled water using same quantity of reagents. Working standards for chloride were prepared by suitably diluting the stock solution of sodium chloride. Absorbance curve was found to be linear for the chloride concentration upto 80 μmoles/l. The precision of duplicate analysis was better than ±5 %.

Sulfate was determined on filtered unacidified samples (Figure III-2) by suitably modifying the titrimetric - barium chloride method (Analytical methods manual, Environment Canada, 1979). In this method, sulfate ion is titrated in an alcoholic solution under controlled acid conditions (pH = 3.8-4.0) with a standard barium chloride solution, using Thorin as the indicator. Thorin reacts with many cations, including

Ca^{2+}, therefore it is necessary to remove all the major cations prior to titration. The modified titration procedure adopted for this study is as follows:

1) The water sample, 10-15 ml at a time, was passed through a cation exchange column (Dowex-50X8 100-200 mesh, H^+ form) and effluent was discarded, this was repeated three times. A 10 ml aliquot of next effluent was pipetted into a small white porcelain dish.

2) To this aliquot 40 ml alcohol and 2 drops of Thorin indicator are added and pH adjusted to 3.8 - 4.0 by carefully adding NH_4OH (1:90 solution) until the solution just turns pink. Then HCl (1:90 solution) is added until the pink color disappears, 1 or 2 drops are usually sufficient.

3) This mixture was then titrated with barium chloride solution until the pink color reappears (barium chloride solution was pre-

pared by dissolving $BaCl_2 \cdot 2H_2O$ in distilled water and adjusted to pH 3.8 - 4.0). Working standard for sulfate were prepared by suitable dilution of stock standard solution of sodium sulfate. A number of blanks were run by titrating 10 ml aliquot of distilled water after passing through an ion-exchange column.

For chloride and sulfate, the filtered unacidified samples were stable for several months as demonstrated by the repeat measurements carried out on few samples after their storage for several months. The reproducibility of chloride and sulfate measurements is better than ± 5 $^{\circ}/_{\circ}$, Tables III - 5 and 6 respectively.

III.2.e.(iii) Silica

Dissolved silica was measured (on filtered unacidified split, Figure III-2) according to the molybolenum blue method of Strickland and Parsons (1968). A Beckman spectrophotometer, model 26, was used for absorbance measurements. Overall precision of the analysis is better than ± 5 $^{\circ}/_{\circ}$.

Table III-5. Reproducibility of chloride measurements by colorimetric mercuric thiocyanate method and intercomparision with silver nitrate titration method.

Reproducibility			Intercomparison		
Sample Code		Chloride*	Sample Code	Chloride*	
				A	B
7.Ganga	i)	162	5.Yamuna	414	400
	ii)	174	6.Chambal	594	594
			7.Ganga	172	168
16.Ganga	i)	620			
	ii)	594	10.Yamuna	769	775
			11.Ganga	287	291
			12.Yamuna	1076	1163
			15.Son	211	200
			18.Gandak	163	149

* Chloride concentration in units of µmole/l

A - Titration method, B - Colorimetric method

Table Reproducibility of sulfate measurements by titrimetric barium chloride method

Sample Code	Collection	Analysis*, SO_4^{2-} conc. (µmole/l July 82	Nov 82	May 83
3.Ganga	March 82	162	-	163
4.Ganga	''	190	-	190
8.Ghaghara	''	114	-	127
18.Gandak	''	264	-	245
21.Brahmaputra	April 82	99	-	109
26.Ganga	Sept 82	-	121	127
32.Gandak	''	-	103	127
35.Ganga	''	-	143	154

* These measurements also demonstrate the stability of SO_4^{2-} on storage of filtered unacidified samples for several months.

III.2.(f) D/H and $^{18}O/^{16}O$ Isotopic Ratios

The measurements of D/H and $^{18}O/^{16}O$ isotopic ratios (expressed as δD and $\delta^{18}O$, respectively) were made on unfiltered sample splits, see Figure III-2. The δD measurements were made following the procedures of Friedman and Hardcastle (1970). Briefly, about 10µl of water was sealed in a glass capillary and broken in vacuum. The water was quantitatively collected in a U-tube, then passed through uranium filings kept at 800°C, where it gets reduced to hydrogen. The hydrogen was then quantitatively absorbed on a uranium finger kept at 80°C. Subsequently, the uranium finger was heated to 700°C and the liberated hydrogen was measured on a manometer, the yield of hydrogen was 99 ± 1 $^{o}/_{o}$. The hydrogen was collected in a sample bottle and transferred to a VG Micromass 602D mass spectrometer where D/H ratio was measured against standard. The value is expressed as

$$\partial D = \left[\frac{(D/H)\ \text{sample}}{(D/H)\ \text{standard}} - 1 \right] X\ 10^3 \quad \text{per mil.}$$

All values are reported with respect to the SMOW standard. The reproducibility for the entire procedure was found to be ± 2 ‰.

Water samples for $\delta^{18}O$ measurements were processed using the H_2O-CO_2 equilibration method proposed by Epstein and Mayeda (1953). Briefly, 2 ml of water was taken in a bottle (approx. 8 ml capacity) and made free from dissolved gases by repeated freezing and thawing and allowed to equilibrate with CO_2 at 25 ± 0.1°C for over 60 hours. After equilibration, a small aliquot of the CO_2 was extracted, dried and measured in the mass spectrometer (VG Micromass 602D). All values are reported with respect to the SMOW standard, and reproducibility of the measurements was found to be ± 0.2 ‰.

III.2.(g) Dissolved Uranium and $^{234}U/^{238}U$ Activity Ratios

The dissolved uranium concentration and the $^{234}U/^{238}U$ activity ratios were measured in large volume samples (Figure III-2). In the field, about 20 liters sample was allowed to stand for 12-15 hours for settling out the suspended sediments. The supernate was siphoned off and filtered through Gelman cartridge filter capsule (3.0 µm pore size). The filtered water was then acidified to 2 pH with 8M HNO_3 and spiked with ^{232}U tracer (8.72 ± 0.18 dpm/ml) and 5 ml of iron carrier (equivalent to about 60 mg Fe_2O_3) was added. About one hour was allowed for equilibration during which sample was stirred vigorously to expel CO_2. Iron was then precipitated as $Fe(OH)_3$ at 6-7 pH with ammonia. The precipitate was allowed to settle for about three hours and the supernate was discarded by decantation. The precipitate was separated from the slurry by filtration through Whatman 54 filter and washed twice with 1:10 ammonia solution. The filters along with precipitate were returned to the laboratory. In the lab., $Fe(OH)_3$ precipitate was dissolved in 8M HNO_3 solution, U and Fe were separated on an anion exchange column (Dowex-1X8, 100-200 mesh). Uranium was radiochemically purified according to the procedure of Krishnaswami and Sarin (1976). The chemical yields ranged from 40 % to 70 %. The ^{238}U concentration and the $^{234}U/^{238}U$ activity ratios in samples were assayed by alpha-counting on an Ortec surface barrier detector coupled to a ND 100 pulse height analyser. The samples were generally counted for a period of 1-3 days so as to accumulate about 8000 to 10,000 counts under ^{238}U and ^{234}U peaks. The counting system had an overall efficiency of 27.2 ± 0.7 %. The background in the ^{232}U region varied from 6 to 9 counts per hour over the counting period of one year. A duplicate analysis done on sample No.38 (Figure III-1, Table III-1) indicate reproducibility to be better than ± 1 % for sampling and entire chemical procedure.

III.2.(h) Chemical analysis of suspended sediments

Suspended sediments for chemical analysis were recovered from 2.5 liter sample split (Figure III-2). A 2.5 liter sample was quantitatively filtered through preweighed millipore filters (0.45 µm, 47 mm). Depending on the suspended matter concentration in a river, 2 to 6 filters were required to filter the 2.5 liter sample. Filters were preserved in clean plastic boxes for return to the laboratory. The filters were dried in an oven at 110°C for 5-6 hours and reweighed to assess the suspended matter concentration. All filters were then combined and treated with acetone to dissolve the millipore filters. The suspended sediments thus recovered were preserved for chemical analysis.

Major and trace elements (Na, K, Mg, Ca, Al, Fe, Mn, Cr, Ni and Cu) in suspended sediments (recovered as above) were analysed by atomic absorption spectrophotometry (AAS) using a Perkin-Elmer 305A model. A known weight of oven dried sample (ranging from 50 to 400 mg) was digested in HF, $HClO_4$ and HNO_3 in a teflon beaker. The residue was finally dissolved in 10 ml of 4N hydrochloric acid and volume was made to 50 ml with distilled water. Elemental analysis by AAS was carried out according to the procedures of Sarin et al (1979). Along with the samples, USGS reference standard W-1 and reagent blanks were also analysed.

III.2.(i) Radiochemical analysis of suspended sediments

Gram quantities of suspended sediments were recovered in the field from large volume samples (Figure III-2). In the laboratory, samples were dried overnight at 110°C, powdered and preserved for the analysis of U and Th decay series nuclides (^{238}U,

^{234}U, ^{232}Th, ^{230}Th and ^{228}Th).

A known weight of sample was brought into solution by HF, $HClO_4$, HNO_3 and HCl treatments. Prior to the acid digestion, ^{234}Th and ^{232}U tracers were added to monitor the chemical yields of Th and U fractions, respectively. From the solution Th and U were separated on an anion exchange column (Dowex-1X8 100-200 mesh, Cl^- form) and purified following the procedures of Krishnaswami and Sarin (1976). Chemical yields for both Th and U fractions ranged from 50 % to 85 % . The concentrations of Th and U isotopes were determined by alpha-counting on a solid state dector coupled to a ND 100 pulse height analyser. The stability of the system was periodically checked by counting standard sources of U and Th. The overall counting efficiency of the system was 27.2 ± 0.7 % .

CHAPTER IV. MAJOR ION GEOCHEMISTRY OF THE GANGA AND BRAHMAPUTRA RIVERS

A river derives its chemical load (the dissolved constituents) mainly via chemical weathering of the rocks and soils of the drainage basin and through atmospherically cycled salts. The main objective of this study is to understand the major ion chemistry of the rivers, within the Ganga and Brahmaputra Basins, in terms of the chemical weathering of their terrains. However, the atmospheric contribution of chemical constituents has also been evaluated in order to establish a meaningful relationships between river water chemistry and chemical weathering.

Relief provides the logical basis for the separation of the discussion on the chemical weathering processes within the Ganga and Brahmaputra River basins. Thus, the rivers within the Ganga and Brahmaputra Basins have been broadly classified as 'Highland' and 'Lowland' Rivers. The classification, as shown below, is to be used in conjunction with Figure III-1 and Tables III - 1, 2 and 3.

Highland Rivers : Bhagirathi, Ganga (upto Hardwar), Yamuna (upto Saharanpur), Ghaghara, Gandak, Brahmaputra (upto Goalpara) and Manas.

Lowland Rivers : Yamuna (at Agra), Yamuna (at Allahabad), Chambal, Betwa, Ken, Son and Gomti.

IV.1. Experimental Results

The water temperature, pH, dissolved oxygen (DO) and conductance measurements were made either *in-situ* or in the field in order to characterise the river conditions at the time of sampling. The data for the Ganga main stream, its tributaries and for the Brahmaputra River are given in Tables IV - 1, 2 and 3 respectively. The water temperature varied from 13-30°C during the three sampling trips. Lower values are typical of the samples from the upper reaches of the Ganga and the Yamuna Rivers, consistent with that expected from their proximity to the glacier sources and local climate.

The pH values of the Ganga River waters and its tributaries range between 7.6 to 8.4 (Tables IV - 1, 2 and 3), similar to those reported by Central Water and

Table IV-1. Ganga main stream: Temperature, pH, DO and Conductance

Sample* Code	Temperature °C	pH	DO mg/l	Conductance µMhos/cm
	Lean Flow, March 1982			
2. Devprayag	13	7.8	-	107
3. Rishikesh	20	8.0	-	142
4. Garhmukteshwar	21	8.1	-	231
7. Kanpur	24	8.3	-	326
11. Upstream Allahabad	27	8.1	-	360
13. Varanasi	26	-	-	540
16. Upstream Patna	30	8.2	-	524
17. Downstream Patna	28	8.3	-	441
	Peak Flow, September 1982			
26. Hardwar	16.5	7.6	6.0	110
35. Garhmukteshwar	23	7.6	6.2	147
27. Kanpur	22	8.2	6.2	196
29. Allahabad	24	7.7	5.4	188
31. Varanasi	21	7.9	5.6	211
33. Patna	24	8.1	6.4	196
	Moderate Flow,			
40. Varanasi	-	-	-	517
38. Patna	21	7.6	-	368

* Sample Code indicates Station No. and Locations See Figure III-1 and Table III-1

Table IV-2. Tributaries of Ganga: Temperature, pH, DO and Conductance

Sample* Code	Temperature °C	pH	DO mg/l	Conductance µMhos/cm
Lean Flow, March 1982				
1.Yamuna	16	-	-	222
5.Yamuna	20	8.1	-	315
10.Yamuna	25	8.1	-	494
12.Yamuna	26	8.1	-	626
6.Chambal	23	8.1	-	473
9.Betwa	25	8.2	-	515
19.Ken	-	-	-	333
15.Son	29	8.3	-	255
14.Gomti	27	8.1	-	440
8.Ghaghara	26	8.4	-	294
18.Gandak	26	8.3	-	275
Peak Flow, September 1982				
24.Yamuna	22.5	7.1	6.8	489
30.Yamuna	24	7.9	5.6	220
25.Chambal	20.5	8.1	6.2	350
34.Son	24	8.3	7.0	151
28.Ghaghara	22	7.9	6.4	161
32.Gandak	23	8.2	6.8	196
Moderate Flow, December 1982				
39.Yamuna	-	7.8	-	622

*Sample Code indicates Station No. and Tributary, see Figure III-1 and Table III-2

Table IV-3. Brahmaputra River: Temperature, pH and Conductance

Sample* Code	Temperature °C	pH	Conductance µMhos/cm
	Moderate Flow, April 1982		
20.Dibrugarh	20	-	137
21.Gauhati	22	7.4	118
22.Goalpara	23	7.6	118
23.Goalpara+	23	-	142
	Lean Flow, December 1982		
37.Gauhati	-	7.2	170
36.Goalpara	-	7.5	185

* Sample Code indicates Station No. and Location, see Figure III-1 Table III-3

\+ Manas River at Goalpara

Power Commission of India (CWPC, 1973). No seasonal trends are observed regarding pH variations in these river waters. However, the relatively high pH values are typical of the rivers draining the alkaline and saline salt-affected soils of the Indo-Gangetic alluvial plains (Bhargava et al, 1981). In case of the Brahmaputra River the pH values are slightly more acidic, varying from 7.2 to 7.6. Both in the Ganga and the Brahmaputra River basins, the pH values are higher than the global average river water pH of 6.1 (Livingstone, 1963).

The specific conductance of these river waters has a wide range, 107-622 µmhos/cm, the low values occurring during peak discharge conditions (Figure IV-1 and Tables IV-1, 2 and 3). In the Ganga and Yamuna main channels, during lean flow conditions, conductivity increases downstream due to the contribution from soil salts, which are mainly sodium bicarbonate, chloride and sulfate. The dissolved major ions, viz, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and SiO_2 (silica), were measured in the laboratory on filtered unacidified samples whereas HCO_3^- was measured in the field on untreated samples. The total dissolved solids (TDS) were estimated by summing up the measured concentrations of cations, anions and silica. During

Figure IV - 1.

The geographical and temporal variations in conductivity and total dissolved solids (TDS) in the Ganga main channel and its tributaries. Arrows along the X - axis indicate the confluence point of the tributaries (represented by the numbers in parentheses) with the main channel.

Figure IV - 2.

The linear relationship between TDS and specific conductance in samples from the Ganga main channel, highland rivers, lowland rivers and Brahmaputra River. Regression statistics for the linear relation are given in Table IV-4.

Symbol key used for Figures 1 and 2:

● Lean flow, March 1982

O Peak flow, September 1982

▲ Moderate flow, December 1982

Figure IV - 1

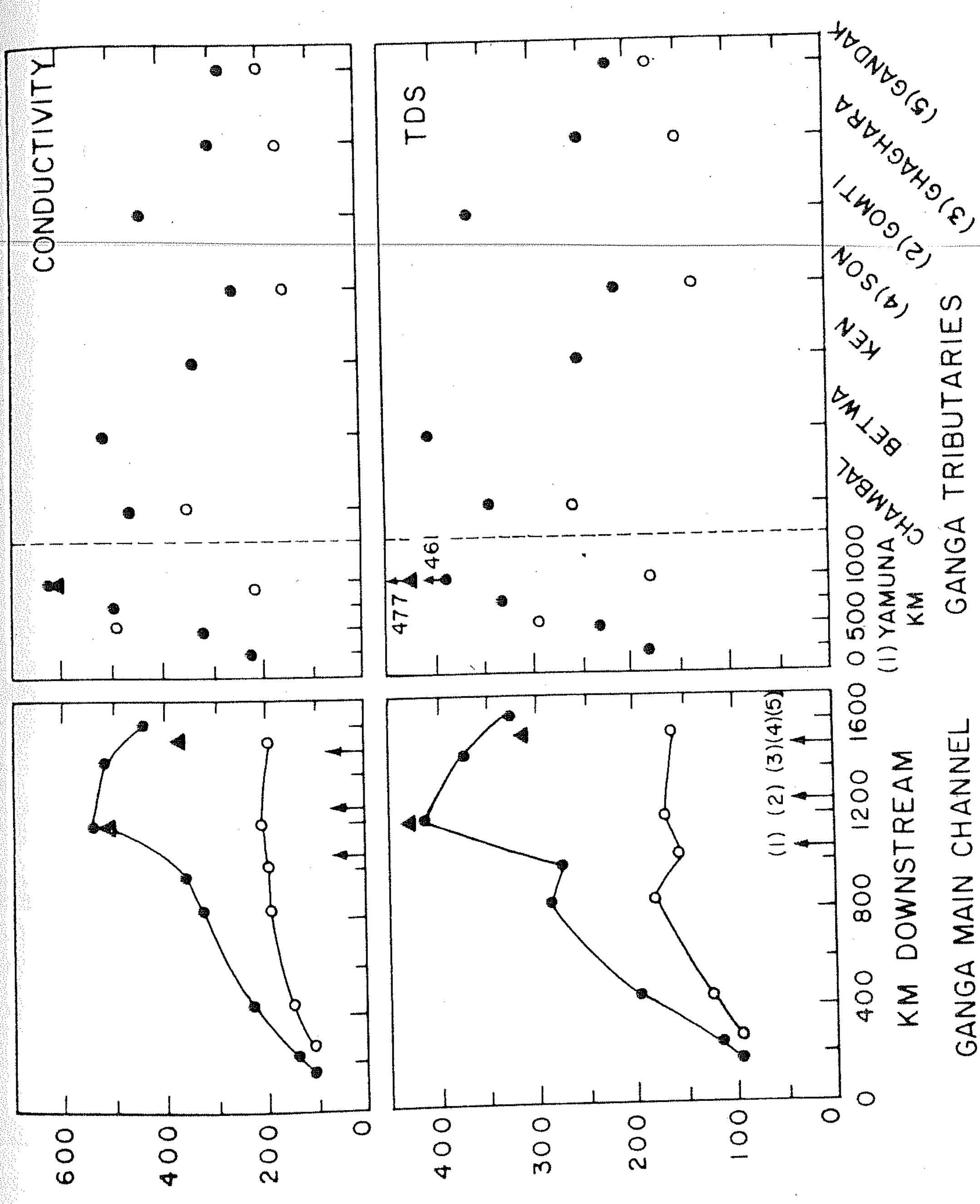
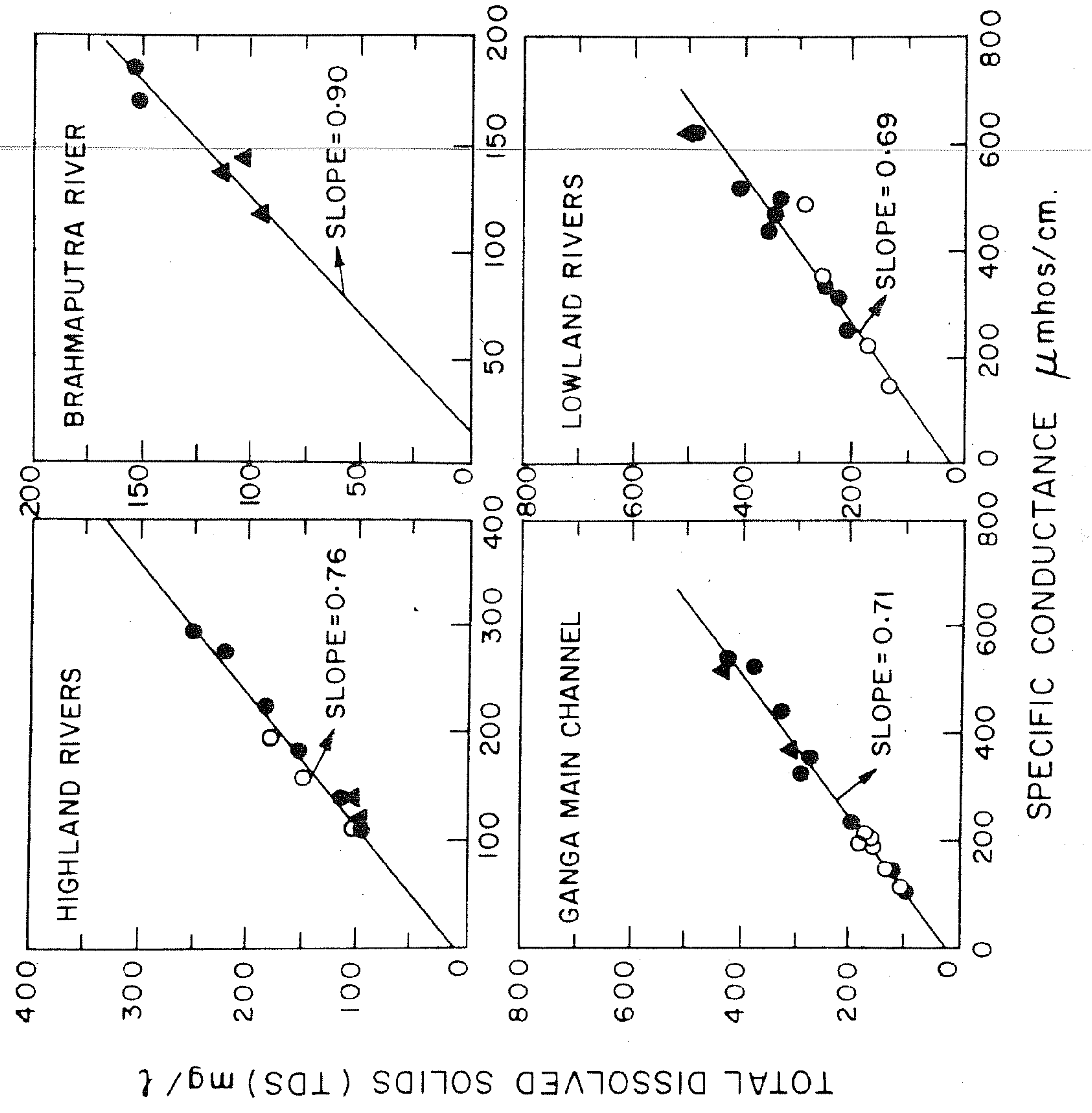

CONDUCTIVITY
μ mhos/cm
600
400
200
0
TOTAL DISSOLVED SOLIDS
mg/ℓ
400
300
200
100
0
0
400
800
1200
1600
KM DOWNSTREAM
GANGA MAIN CHANNEL
(1) (2) (3)(4)(5)
CONDUCTIVITY
TDS
477
461
0 500 1000
(1) YAMUNA
KM
CHAMBAL
BETWA
KEN
(4)SON
(2)GOMTI
(3)GHAGHARA
(5)GANDAK
GANGA TRIBUTARIES

Figure IV - 2



HIGHLAND RIVERS
SLOPE=0·76
BRAHMAPUTRA RIVER
SLOPE=0·90
GANGA MAIN CHANNEL
SLOPE=0·71
LOWLAND RIVERS
SLOPE=0·69
TOTAL DISSOLVED SOLIDS (TDS) mg/ℓ
SPECIFIC CONDUCTANCE μmhos/cm.
0
100
200
300
400
0
50
100
150
200
0
200
400
600
800

lean flow, the high concentration of TDS (Figure IV-1), is reflected in high conductivity of these river waters. Furthermore, the TDS content of the rivers within the Ganga and Brahmaputra Basins show a linear relationship with specific conductance (Figure IV-2). The statistical parameters of the regression line, for the relation:

$$\text{TDS (mg/l)} = m \times \text{Conductance } (\mu\text{mhos/cm}) + C,$$

are given in Table IV-4. The non-zero intercept could be due to the presence of non-ionic dissolved species such as silica which is perhaps not sensed by the conductance measurements. Since the TDS content is estimated by summing up cations, anions and silica, the non-zero intercept is not unexpected. It is observed that the individual cation or anion do not correlate well with specific conductance in the samples from the Ganga and Yamuna main streams, which implies that the rivers are fed by waters with different ionic ratios over the annual discharge cycle. The input from soil salts being more significant during lean flow as discussed later in this chapter.

The analytical precision of data collected in this study has been discussed in Chapter III. An independent estimate of the precision can also be deduced from the

Table IV-4. Regression statistics for the linear relationship[*] between TDS and specific conductance

River	Conductance		TDS		Corr. coeff.	Slope (m)	Y-intercept (c)
	Max.	Min.	Max.	Min.			
Ganga main channel	540	107	415	93	0.99 (N=16)[+]	0.71 ±.03	20.5
Lowland Rivers	626	151	477	129	0.97 (N=13)	0.69 ±.05	14.7
Highland Rivers	294	107	233	92	0.98 (N=11)	0.76 ±.05	7.5
Brahmaputra River	185	118	147	91	0.96 (N=6)	0.90 ±.12	-17.8

[*] TDS (mg/l) = m X Conductance (μmhos/cm) + C

[+] N = number of samples

charge balance between cations and anions. The scatter diagram of TZ^+ (total cations) and TZ^- (total anions) is shown in Figure IV-3. As evident, the charge balance is quite good and can be expressed by the relation :

$$TZ^+ (\mu Eq/l) = 0.96\ TZ^- (\mu Eq/l) + 24.7$$

and the correlation coefficient for this linear relation is 0.998 for 40 data points. The greatest deviation from charge neutrality is less than 5 percent and is more pronounced at higher concentrations of cations and anions. The cause for the data to fall below the 1:1 (i.e. $TZ^- > TZ^+$) is not clear. A likely possibility is a small systematic error in the measurements of HCO_3^- which were made in the field by acid titration method whereas all the other major ions were analysed in laboratory, and hence better precision. Loss of cations on storage, could be ruled out as has been demonstrated in Chapter III (see Table III-4) by the replicate measurements of calcium made on samples after their storage for several months. In the above discussion it is implicit that the concentrations of the ions other than those measured, for the cation and anion charge balance, are insignificant. This assumption appears to be valid in light of the water quality data reported by Central Water

Figure IV - 3.

Charge balance between total cations (μEq/l) and total anions (μEq/l).

Symbol key:

Ganga main channel:

● Lean flow

O Peak flow

+ Moderate flow

Ganga Tributaries:

▲ Lean flow

△ Peak flow

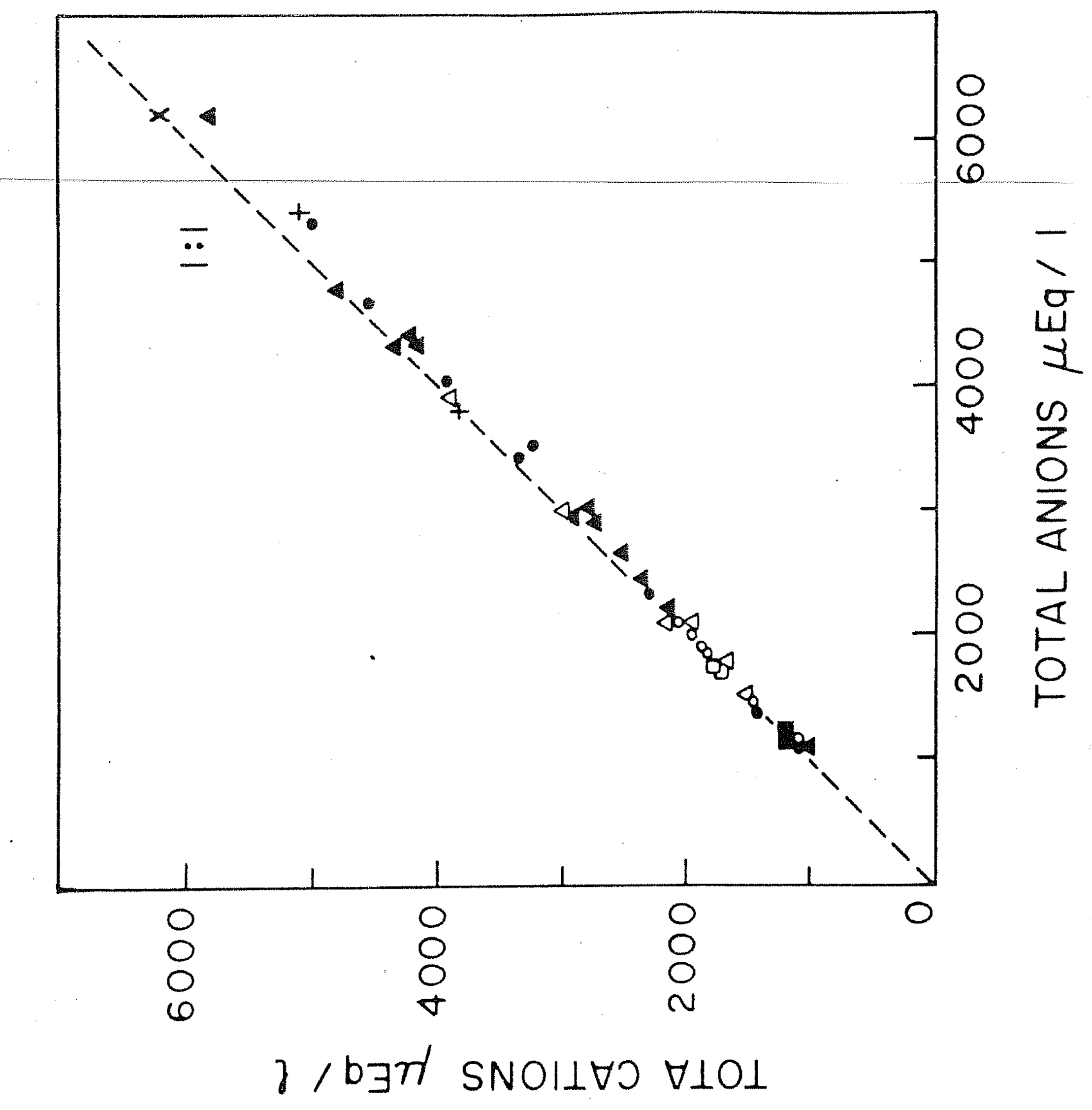
X Moderate flow

Brahmaputra River:

■ Moderate flow

□ Lean flow

Figure IV - 3


1:1
TOTAL ANIONS μEq / l
0
2000
4000
6000
TOTA CATIONS μEq / l
0
2000
4000
6000

and Power Commission of India (CPWC, 1973) which show that the concentrations of the ions such as NO_3^- and PO_4^{3-} in these river waters is very low.

IV.2. Atmospheric contribution to river water chemistry

Several studies (Eriksson 1955, 1960; Cleaves et al 1970; Garrels and Mackenzie 1971; Holland 1978; Meybeck 1979) have shown that the atmospheric supply of chemical constituents to the river waters can be substantial and correction for this input is required to establish a meaningful relationship between river water chemistry and chemical weathering in the drainage basin. The flux of atmospherically derived materials consists of three principal components: marine, terrestrial and anthropogenic inputs. The marine component consists of Na, K, Mg, Ca, Cl and SO_4 in approximately sea-salt proportions. The terrestrial and anthropogenic components make a significant contribution of K, Ca and SO_4 which can be related to vegetation, soil dust and human activities (industrial effects). The most common approach to the problem of determining these atmospheric inputs to the river water is based on the 'best' estimate of the chemical composition of rain water. Marine component is fairly well characterised whereas it is difficult to derive reasonable estimates of terrestrial and anthropogenic components, which are considered to be of local origin. The atmospheric contribution from these sources is highly variable and great uncertainties exist in the analytical procedures that are employed. Conway (1942) estimated that atmospherically derived chloride constitutes 44 percent of the annual river flux of chloride. Livingstone (1963a) estimated that 46 percent of the annual river flux of sodium is atmospherically cycled. Several estimates of the net contribution of atmospherically derived materials to the Amazon River basin have been published. Gibbs (1970) suggests that 81 % of the Na, K, Mg, and Ca in the dilute lowland rivers of the Amazon basin are cyclic. Stallard (1981) based on the analysis of precipitation and surface waters in the Amazon Basin, has demonstrated that the cyclic salts make only a minor contribution, relative to terrestrial inputs, to the chemistry of the Amazon Basin rivers. He estimated that, during peak discharge, 17.6 % Cl, 6.9 % Na, 0.4 % K, 1.3 % Mg, 0.1 % Ca and 3.6 % S of the dissolved load at Obidos is cyclic.

In this study the chemical analysis of rain water has not been done. However, some studies on the chemistry of monsoon rain water over India have been reported by

Handa (1968), Sequeira and Kelkar (1978) and Subramanian and Saxena (1980). Their data has been used to assess the atmospheric contribution of major ions, relative to chemical weathering, in the Ganga River drainage basin. The data of Subramanian and Saxena (1980) on the chemistry of monsoon rain water at Delhi suffer from a major drawback. Although, they measured all the major cations and anions in the rain samples the charge balance between cations and anions is very poor, in some samples it is offset by a factor of about ten, anions being more than cations. Hence this data looses its validity for any geochemical implications. Sequeira and Kelkar (1978) have analysed rain water samples from ten coastal and inland stations over India during the entire monsoon period of 1975. Their data for the coastal stations and for Delhi (an inland station) is given in Table IV - 5. Data on the chemical analysis of rain water samples from Hardwar and Dehra Dun (the inland stations) has been taken from Handa (1968), Table IV - 5.

The atmospheric contribution reflecting mainly the marine component, in the Ganga River drainage basin, has been estimated from the data of Sequeira and Kelkar (1978). Their data show that the chloride concentration decreases for the inland stations with increasing

Table IV-5. Weighted mean composition of monsoonal rain water over India, June-September 1975*

Location	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}
	µmole/l					
			Coastal Stations			
Thumba	207	5.6	19.3	23	228	6.8
Kallianpur	74	3.6	8.2	17.5	90	5.5
Bombay	115	3.6	12.3	17.8	138	5.3
Tarapur	222	6.9	25	55	270	18.8
(Average)	154	4.9	16.2	28.3	182	9.1
			Inland Stations			
Delhi	30	5.9	3.7	28.8	18	4.4
Hardwar+	42	12	9.9	20	23.9	30.2
Dehra Dun+	31.7	12.8	22.4	62.5	41.3	39

* Sequeira and Kelkar (1978)

\+ Handa (1968)

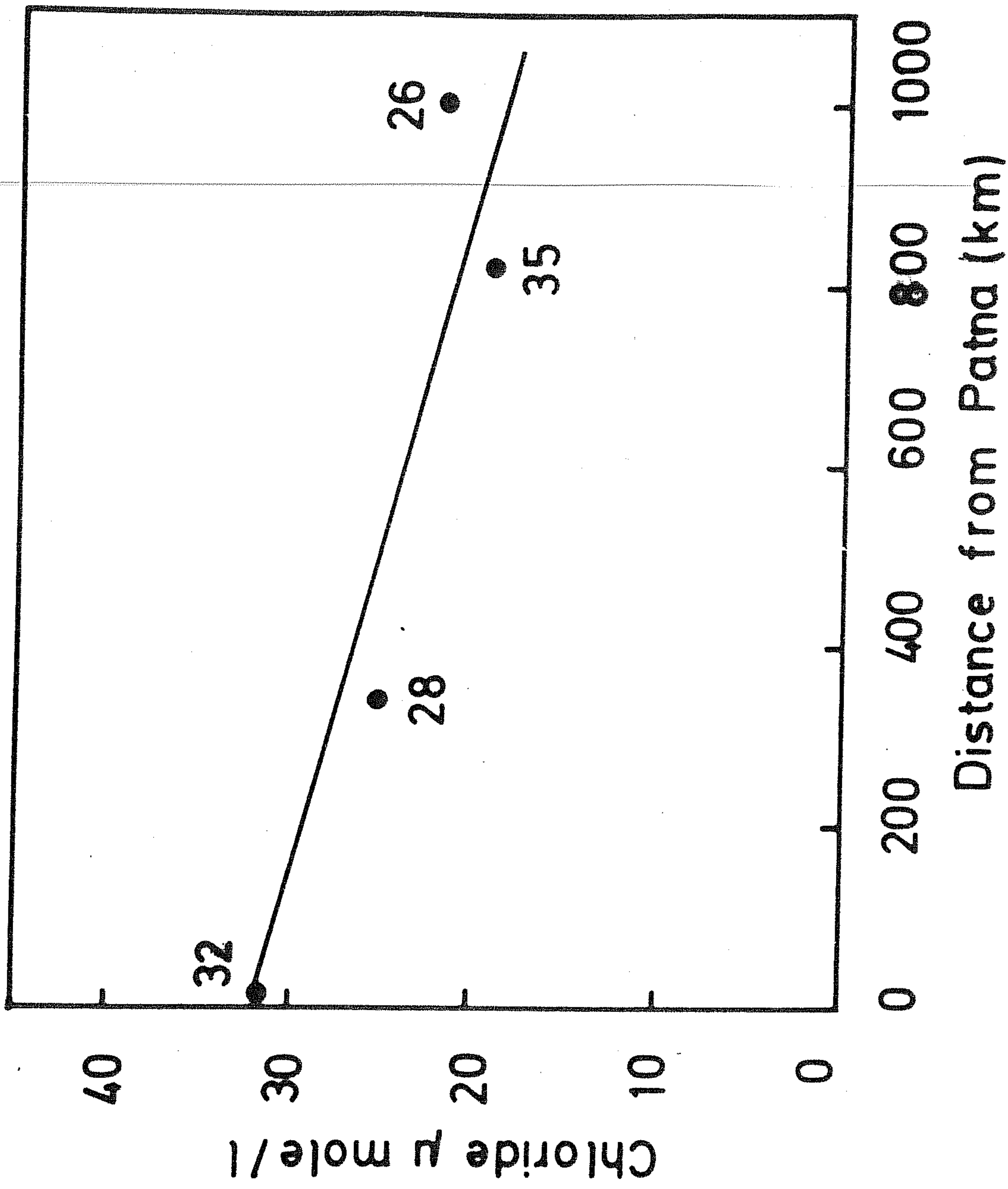
distance from the coast. This is a reflection of the loss of chloride from marine air masses moving inland, a mechanism proposed by Eriksson (1960). I have used chloride as the reference to estimate the marine cyclic component of river waters in Ganga Basin. The estimate of the cyclic component is based on the assumption that all the chloride in highland rivers, during their peak flow, is of marine origin derived via local precipitation. The observation that the abundance of chloride in highland rivers (average, 25 µmole/l) is very similar to that in the rain waters of inland stations, (18-41 µmole/l, Table IV - 5), lends credence to this assumption. The absence of chloride bearing rocks and halite deposits in the drainage basins of the highland rivers, further supports this assumption.

In order to calculate the cyclic component, a reference line is drawn at Patna parallel to the east-coast of India and perpendicular to the average wind direction. This reference line is used to determine the distances of the highland and lowland river basins from the moisture front assumed at Patna. A plot is then constructed (Figure IV - 4) between the chloride concentration (assumed to be all cyclic) in the highland rivers and

Figure IV - 4

Concentration of chloride in the highland rivers plotted as a function of distance from the moisture front assumed at Patna. Numbers along the data points indicate the sample code for the highland rivers to be used in conunction with Figure III - 1.

Figure IV - 4


Chloride µ mole/l
40
30
20
10
0
0
200
400
600
800
1000
Distance from Patna (km)
32
28
35
26

their distances from the moisture front. It can be seen from this reference plot (Figure IV - 4) that the chloride concentration in the highland rivers decreases with increasing distance from the moisture front (at Patna). Based on their distances from the moisture front, the marine component of chloride in the lowland rivers has been estimated from this linear plot. Thus, using cyclic chloride as a reference, the marine contribution of Na, K, Mg, Ca and SO_4 has been calculated using their observed abundance ratios in the samples collected from the coastal stations, Table IV - 5.

Data on the calculated marine cyclic salts contribution, during peak discharge conditions, to the highland and lowland rivers in the Ganga River drainage basin, are presented in Table IV - 6. In the highland rivers about 30 % of the sodium is cyclic. The marine contribution of K, Mg, Ca and SO_4 is insignificant relative to chemical weathering in their drainage basins. Among lowland rivers, only Son River has a 45 % and 11 $^{o}/_{o}$ contributions of marine cyclic chloride and sodium respectively. The abundance of other major ions in the lowland rivers is dominated by inputs from chemical weathering. These observations lead to the conclusion that the marine cyclic salts

Table IV-6. The predicted cyclic salts contribution to the Ganga River drainage basin

River (Location)*	Measured Cl^-	Cyclic Cl^-	Cl^-	Na^+	K^+	Mg^{2+}	Ca^{2-}	SO_4^{2-}
	µmole/l		Percentage Cyclic					
			Highland Rivers$^+$					
Ganga (Hardwar)	22.6	22.6	100	27	1.3	2.2	1.7	1.6
Ghaghara (Ayodhya)	25.8	25.8	100	23	1.2	2.0	1.5	3.4
Gandak (Hajipur)	32.3	32.3	100	37	1.0	2.2	1.5	3.1
(Average)	-	-	(100)	(29)	(1.2)	(2.1)	(1.6)	(2.7)

Table IV-6. Contd.

River (Location)*	Measured Cl^-	Cyclic Cl^-	Cl^-	Na^+	K^+	Mg^{2+}	Ca^{2-}	SO_4^{2-}
	µmole/l		Percentage Cyclic					
			Lowland Rivers⁺					
Yamuna (Agra)	1172	23	2	1.4	0.5	1.0	0.9	0.6
Yamuna (Allahabad)	222	29	13	4.4	1.4	2.7	1.6	4.3
Chambal (Dholpur)	284	23.5	8	3.4	1.2	1.2	0.9	3.1
Son (Ara)	71	32.3	45	11	2.3	3.5	2.3	14

* For Location refer to Figure III-1 and Tables III-1 and 2

\+ Predicted contribution during peak flow conditions.

Figure IV - 5.

Scatter diagram of sodium (µEq/l) and chloride (µEq/l). Note that all the samples fall above the 1:1 trend, and the Na:Cl equivalent ratio in all samples is about 3.

Symbol key:

Ganga main channel:

● Lean flow

O Peak flow

\+ Moderate flow

Ganga Tributaries:

▲ Lean flow

△ Peak flow

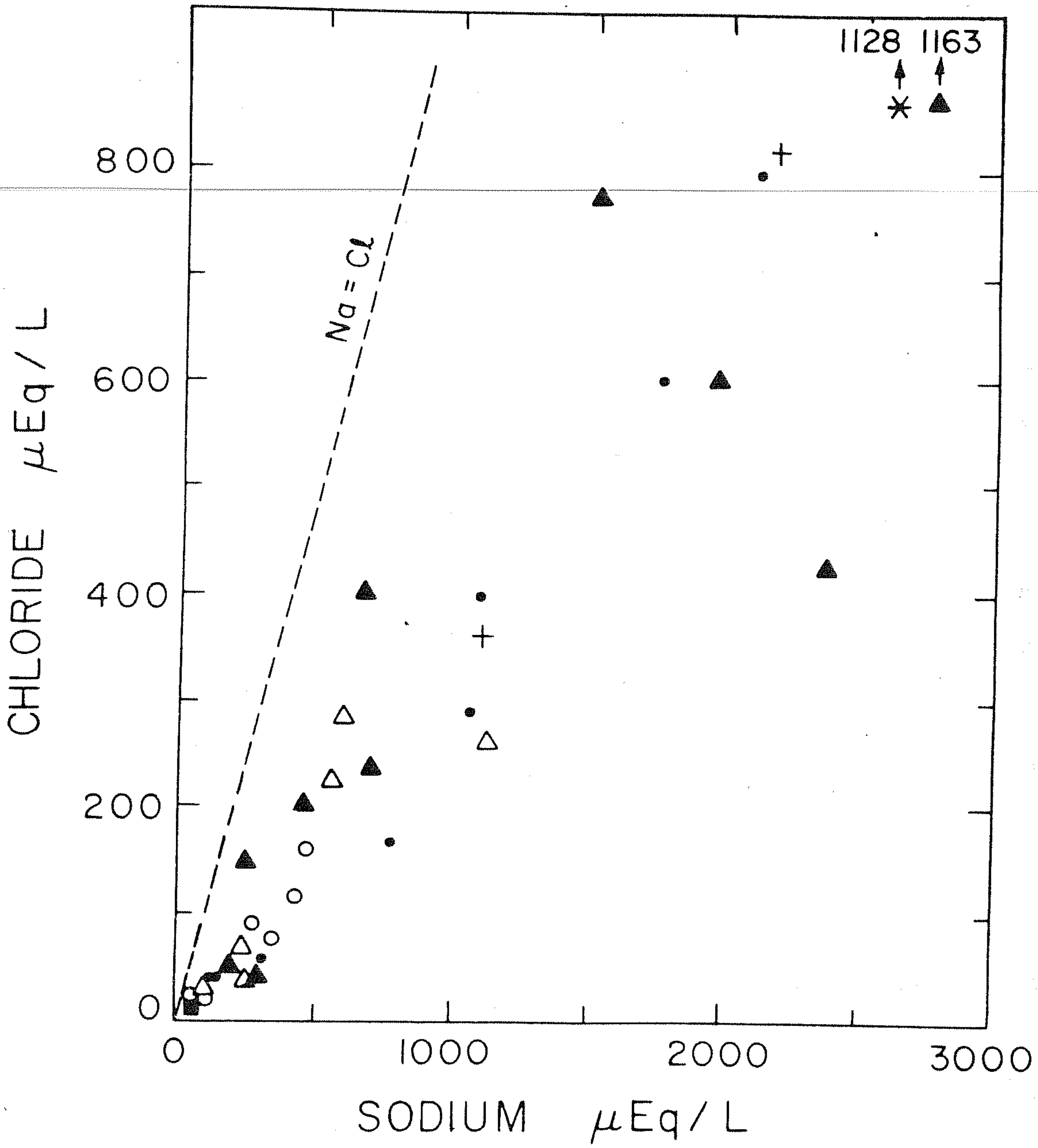
* Moderate flow

Brahmaputra River:

■ Moderate flow

□ Lean flow

Figure IV - 5



CHLORIDE μEq/L
800
600
400
200
0
Na = Cl
1128
1163
0
1000
2000
3000
SODIUM μEq/L

contribution is insignificant, relative to chemical weathering, in the Ganga River drainage basin. This inference is also borne out from the plot of Na versus Cl, Figure IV—5. The Na:Cl equivalent ratio in all samples is about 3, much higher than that observed for the rain water samples from inland stations (Table IV-5).

IV.3. Chemical weathering processes

The chemical controls on the abundances of dissolved major cations (Na, K, Mg and Ca) and anions (HCO_3, SO_4 and Cl) in river waters can be modelled in terms of weathering of various mineral phases of the rocks of the drainage basin. Some of the weathering reactions for carbonate minerals such as calcite ($CaCO_3$), dolomite [$CaMg(CO_3)_2$] and gypsum or anhydrite ($CaSO_4.2H_2O$, $CaSO_4$) associated with the sedimentary rocks are as follows (Garrels and Christ,1965; Garrels and Mackenzie,1971; Holland, 1978):

1. $CaCO_3 + H_2CO_3 == Ca^{2+} + 2HCO_3^-$
2. $CaMg(CO_3)_2 + 2H_2CO_3 = Ca^{2+} + Mg^{2+} + 4HCO_3^-$
3. $CaCO_3 + H_2SO_4 = Ca^{2+} + SO_4^{2-} + H_2CO_3$
4. $CaMg(CO_3)_2+2H_2SO_4 = Ca^{2+} + Mg^{2+} + 2SO_4^{2-} + 2H_2CO_3$
5. $CaSO_4 = Ca^{2+} + SO_4^{2-}$

All these minerals weather congruently, Thus, the equivalent ratio of Ca:HCO_3 in the effluent waters resulting from calcite weathering is 1:2 whereas that from dolomite weathering is 1:4. A source of protons is necessary for the rapid weathering of these carbonate minerals. The most common sources of protons are carbonic acid (H_2CO_3, reactions 1 and 2) and sulfuric acid (H_2SO_4, reactions 3 and 4). The sulfuric acid is mainly derived from the oxidation of sulfate minerals (pyrites) and from anthropogenic sources (Holland,1978, Jickells et al, 1982). Pyrite that is oxidised in a carbonate environment yields H_2SO_4 which is neutralised largely by Ca^{2+} and Mg^{2+} carbonates, whereas pyrite that is oxidised in a schist or gneissic environment yields H_2SO_4 which is used for the weathering of silicates, yielding Ca^{2+}, Mg^{2+}, Na^+ and K^+ in solution. The relative proportions of the various ions in solution depend on their relative abundances in the host rocks.

The solution products of silicate weathering are not as well defined because the degradation of silicates generates a variety of solid phases (mostly clays) along with the dissolved species. Thus the weathering of silicase rocks with carbonic acid is written as:

$$(Na, K, Mg, Ca)\ Silicate + CO_2 + H_2O = H_4SiO_4 + HCO_3^- + Na^+ + K^+ + Mg^{2+} + Ca^{2+} + \text{solid products}$$

Thus, the abundances of cations and anions released to solution are determined by the bulk composition of the parent rock and the availability of protons for rock weathering. For example, the relative proportions of Ca^{2+} and HCO_3^- released during the weathering of calcium silicate (Ca - feldspar) can be same as that resulting from calcite dissolution (Garrels and Mackenzie 1971). Therefore, it is difficult to speculate on the origin of Ca in the water based on the water chemistry alone. Additional information on the geology of the terrains is required to distinguish the relative inputs of Ca and Mg from weathering of cabonates and silicates. Furthermore, in addition to the inputs of calcium, magnesium and bicarbonate, there are other reaction products such as SiO_2, Na and K which are released to solution during silicate weathering.

IV.4. Major ion chemistry of the rivers within the Ganga and Brahmaputra Basins

Despite the complexity of the weathering environment, by studying the abundance ratios of various cations, anions and silica in river waters and with a knowledge of the regional lithologies it is possible to evaluate the major ion chemistry of the rivers in terms of chemical weathering of their terrains. Thus, based on the weathering reactions and the observed geographical variability of the dissolved major constituents, the major ion chemistry of the 'Highland' and 'Lowland' Rivers (within the Ganga and Brahmaputra River basins) has been evaluated in terms of chemical weathering in their drainage basins. The Ganga main stream (downstream of Hardwar) receives large number of tributaries from north and south. Hence the variations in major ion composition along the course of the Ganga main stream have been discussed separately.

IV.4.(a) Highland Rivers

The major ion chemistry of the Bhagirathi, Ganga (upto Hardwar), Yamuna (upto Saharanpur), Ghaghara, Gandak, Brahmaputra (upto Goalpara) and Manas Rivers has been described here. All these rivers rise either in the Higher or Lower Himalayas and then drain through the southern slopes of the Himalayas. The regional lithologies of their drainage basins have been discussed in detail in Chapter II.

The salient features of the major ion chemistry of these highland rivers are: (i) Calcium and magnesium are the major cations, together they account for 84 to 92 % of the cations (Figure IV-6, Table IV-7), Mg:Ca equivalent ratios vary from 0.4 to 0.6 . During lean flow conditions the contributions from sodium and potassium to the cation balance are relatively higher than that during peak flow conditions. This trend is evident from the plot of (Ca:Mg) versus total cation (TZ^+) (Figure IV - 7) which shows that at high TZ^+ concentrations (typical of lean flow) the (Ca+Mg) fall below the 1:1 trend reflecting increased contributions of sodium and potassium. The K:Na ratios vary from 0.2 to 0.6, the low values occurring during lean flow. (ii) Among anions, bicarbonate is the most dominant and accounts for 73 % to 81 % of the anions, sulfate accounts for most of the remainder. In the Ghaghara and Gandak Rivers bicarbonate accounts for as much as 90 % of the anions. The SO_4:Cl equivalent ratios range between 3.5 to 10.7, the higher values are typical of peak flow. (iii) The silica concentrations of these rivers range between 114 to 204 µmole/l and the molar ratio of silica to bicarbonate concentrations is about 10 % .

Table IV-7 Major ion composition of Highland Rivers

Sample Code*	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	TDS
	µmole/l								mg/l
					Lean Flow, March 1982				
2.Bhagirathi	141	36.6	160	300	854	42	95	157	92.7
3.Ganga	145	40.4	239	398	1004	42	162	152	114
1.Yamuna	203	45.4	329	590	1677	51.7	251	168	176
8.Ghaghara	299	70.2	453	729	2637	42	114	172	233
18.Gandak	251	88.4	411	682	2013	149	264	166	210
36.Brahmaputra**	164	58	214	553	1406	40	148	204	147

Table IV-7 Contd.

Sample Code*	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	TDS
	µmole/l								mg/l
				Peak Flow, September 1982					
26.Ganga	59.4	38.2	153	353	894	22.6	121	109	94.2
28.Ghaghara	96	59.4	232	528	1601	25.8	76	114	144
32.Gandak	74	84.3	259	649	1860	32.3	103	143	170
22.Brahmaputra⁺	80	46.2	148	318	884	29	99	118	91.5
23.Manas⁺	94	42	181	348	930	25.8	113	131	98.5

* Sample Code indicates Station No. and River, see Figure III-1

**Sample collected during Lean Flow, December 1982 (Table III-3

\+ Sample collected during Moderate Flow, April 1982 (Table III-3

The scatter diagram of (Ca+Mg) versus bicarbonate (Figure IV - 8) shows that almost all of the (Ca+Mg) in the highland rivers can be balanced by bicarbonate. This observation, coupled with the characteristic features of these waters presented above and the weathering reactions discussed earlier, leads to the conclusion that chemistry of the highland rivers is dominated by weathering of carbonates. The regional lithologies dominated by limestones and dolomites support the above contention. A closer look at the scatter diagram (Figure IV - 8) shows that most of the samples collected during the lean flow fall above the equiline of (Ca+Mg):HCO_3. This requires that, a small fraction, about 10 % of the (Ca+Mg) in these waters has to be balanced by another anion, likely to be sulfate, which is next in abundance. The sulfate in waters mainly originates through dissolution of gypsum and anhydrite or through weathering of carbonates by sulfuric acid produced via pyrite reduction (Holland, 1978). In the Kumaon Himalayas gypsum has been reported as a common accessory mineral (Valdia, 1980) and the published stratigraphy (Gannser, 1964) shows pyrite sediments in the Brahmaputra River drainage basin.

The relative importance of silicate weathering to the major ion composition of these rivers can be deciphered from the abundances of sodium, potassium and silica in these waters. As mentioned earlier, (Na+K) account for less than 15 % of the total cations. The (Na+K):Cl ratio is about 4:1 suggesting that about 75 % of the (Na+K) in these waters has a source other than marine cyclic salts and halite deposits. The $(Na^* + K):TZ^+$ equivalent ratios (Na^* signifies sodium corrected for chloride) range between 0.06 to 0.12 suggesting that the contribution of sodium and potassium in these river waters from silicate weathering can account for less than about 12 % of the total cations (in equivalent units). In using the $(Na^* + K)$ as an index of silicate weathering it is assumed that sodium and potassium are supplied to the water mainly by silicate weathering and they behave conservatively during their aqueous transport.

IV.4.(b) Seasonal Variations in Highland Rivers

Samples from the Ganga (upto Hardwar), Ghaghara and Gandak Rivers were collected during lean and peak flow conditions whereas that from Brahmaputra River were collected during lean and moderate flows. These samples have been used to evaluate the seasonal variations in the major ion composition of these rivers. The data are presented in Table IV-7 and in Figures IV-9 through IV-13. The salient features of the seasonal variations in these rivers are:

(1) The (Ca+Mg):(Na+K) equivalent ratios are higher in peak flow relative to that in lean flow, Figure IV-9. During peak flow the ratios for the Ganga, Ghaghara and Gandak are 10.4, 9.8 and 11.5 respectively whereas during lean flow the ratios for all these rivers are nearly the same and decrease to about 6.5. This decrease in the ratios during lean flow is mainly caused by a disproportionate increase in sodium content compared to that of calcium. However, during both the sampling seasons (Ca+Mg) constitutes more than 85 % of the total cations.

(2) The Mg:Ca ratios decrease to 0.4 in peak flow compared to 0.6 in lean flow, Figure IV-10.

(3) The Na:Cl ratios do not show any systematic seasonal trends, Figure IV-11.

(4) The SO_4 : Cl equivalent ratios also tend to increase during peak flow, Figure IV-12. The ratios range between 5.9 to 10.7 during peak flow and between 3.5 to 7.7 during lean flow. However, in both the

seasons bicarbonate accounts for more than 75 % of the anions.

(5) The TDS contents of these rivers during peak flow, range between 94 to 170 mg/l and during lean flow the range is between 114 to 233 mg/l, Figure IV-13. The higher values occurring during lean flow reflect the importance of relatively higher chemical weathering in the drainage basins.

(6) The major ion ratios in Brahmaputra River (at Goalpara) do not show any significant seasonal variations. However, the TDS content decreases to 92 mg/l in moderate flow compared to 147 mg/l in lean flow.

IV.4.(c) Lowland Rivers

In this section, the major element chemistry of the Yamuna (between Saharanpur and Allahabad), Chambal, Betwa, Ken, Son and Gomti Rivers will be discussed. The dominant lithologies of their drainage basins have been decribed in Chapter II. The salient features of the major ion composition (Table IV-8) of these lowland rivers are:

(i) Sodium, calcium and magnesium are the major cations and are equally significant in the cation balance, as

Figure IV - 6.

Triangular diagrams representing the abundances of major cations (Na, K, Mg and Ca, in units of µEq/l) in the highland and lowland rivers and in the Ganga main channel.

Figure IV - 7.

Scatter diagrams of (Na+K), (Ca+Mg) and Total Cations for the highland and lowland rivers.

Figure IV - 8.

Scatter diagrams of (Ca+Mg) and HCO_3 for the highland and lowland rivers.

Symbol key used for Figures IV-1, 2 and 3:

● Lean flow
O Peak flow
▲ Moderate flow

Figure IV - 6

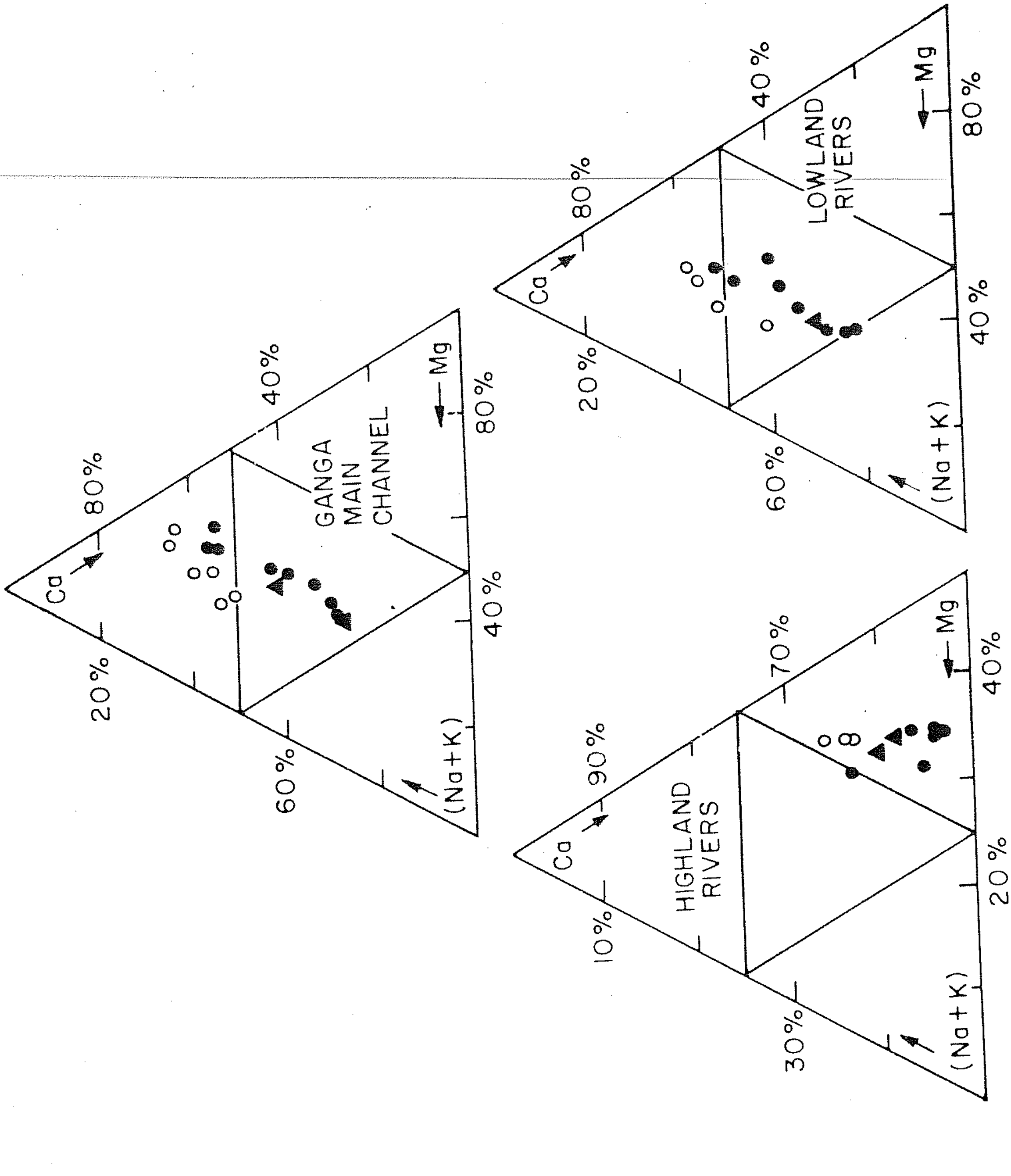

GANGA MAIN CHANNEL
LOWLAND RIVERS
HIGHLAND RIVERS
Ca
Mg
(Na+K)
20%
40%
60%
80%
10%
30%
70%
90%

Figure IV - 7

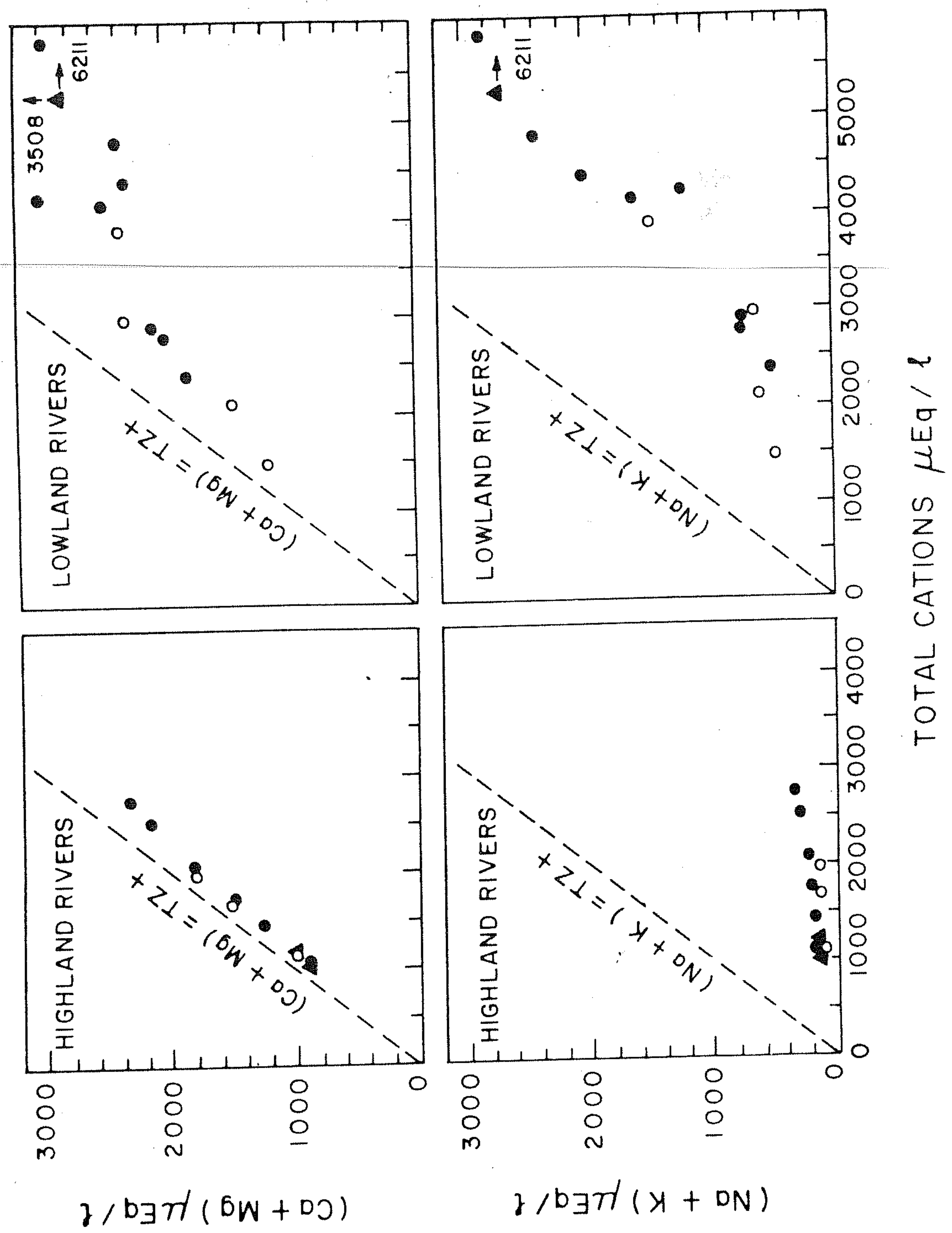
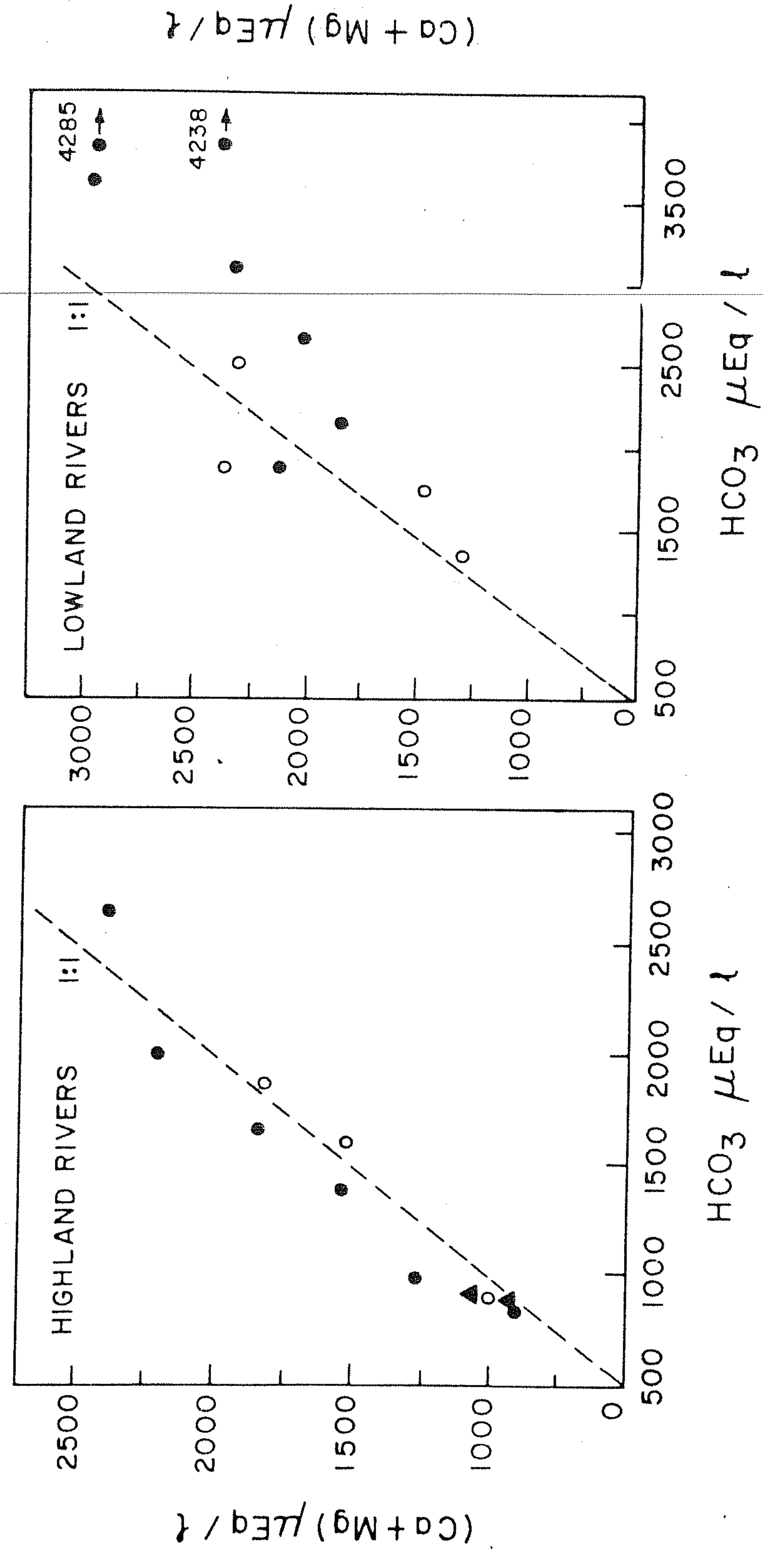

HIGHLAND RIVERS
LOWLAND RIVERS
HIGHLAND RIVERS
LOWLAND RIVERS
(Ca + Mg) = TZ+
(Na + K) = TZ+
3508
6211
6211
0
1000
2000
3000
4000
5000
TOTAL CATIONS μEq/ℓ
(Ca + Mg) μEq/ℓ
(Na + K) μEq/ℓ

Figure IV - 8


HIGHLAND RIVERS
1:1
(Ca + Mg) μEq / l
0
1000
1500
2000
2500
500
1000
1500
2000
2500
3000
HCO_3 μEq / l
LOWLAND RIVERS
1:1
4285
4238
(Ca + Mg) μEq / l
0
1000
1500
2000
2500
3000
500
1500
2500
3500
HCO_3 μEq / l

Seasonal variations in major ion ratios in highland and lowland rivers are shown in Figures IV-9 through IV-13.

Figure IV-9 : Variations in (Ca+Mg):(Na+K) equivalent ratios.

Figure IV-10 : Variations in Mg:Ca equivalent ratios.

Figure IV-11 : Variations in Na:Cl equivalent ratios.

Figure IV-12 : Variations in SO_4:Cl equivalent ratios

Figure IV-13. : Seasonal variations in Total Dissolved Solids.

Symbol key used for Figures IV-9 through IV-13.

- ● Lean flow
- ○ Peak flow
- ▲ Moderate flow

Figure IV - 9

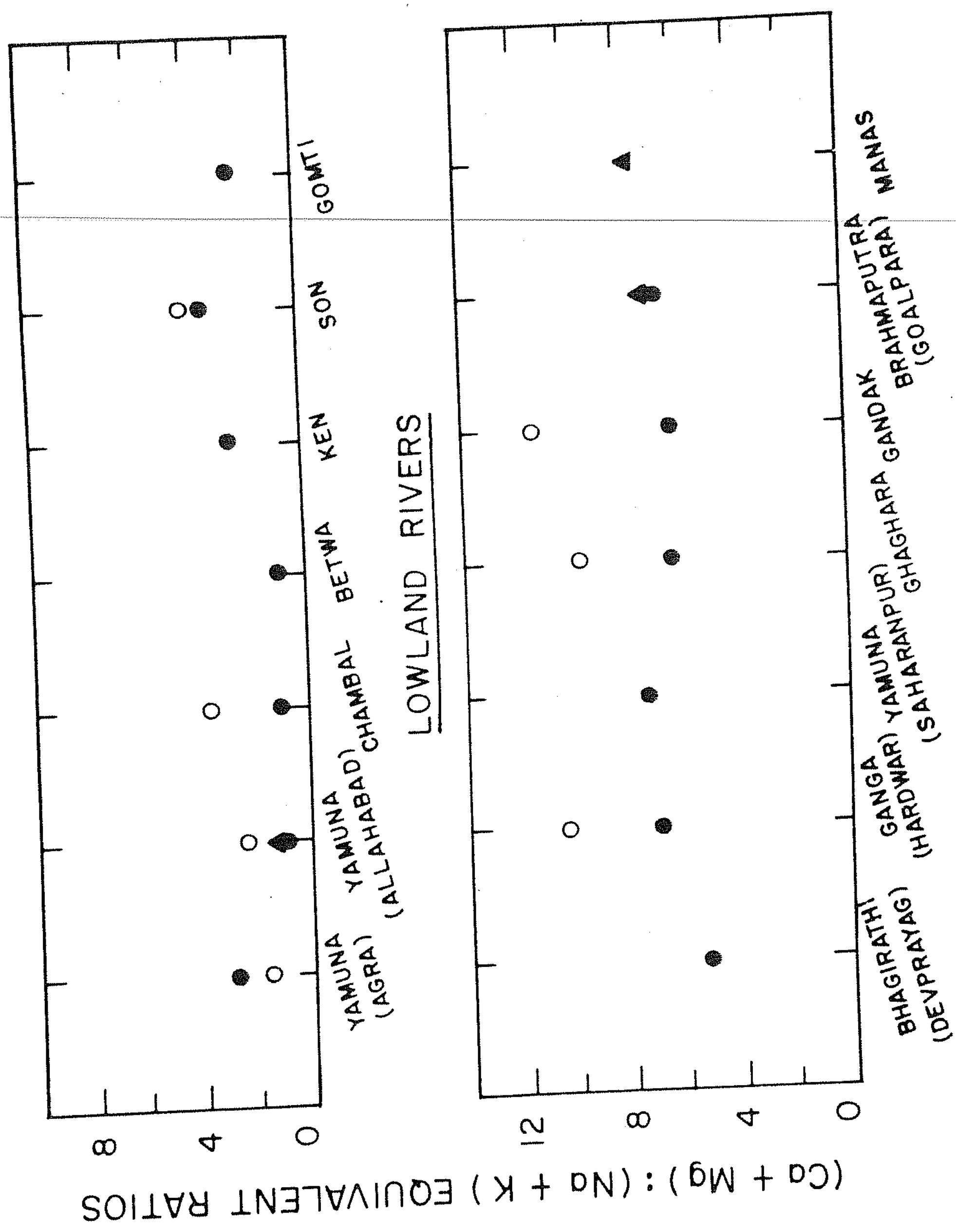

(Ca + Mg) : (Na + K) EQUIVALENT RATIOS
0
4
8
LOWLAND RIVERS
YAMUNA (AGRA)
YAMUNA (ALLAHABAD)
CHAMBAL
BETWA
KEN
SON
GOMTI
0
4
8
12
HIGHLAND RIVERS
BHAGIRATHI (DEVPRAYAG)
GANGA (HARDWAR)
YAMUNA (SAHARANPUR)
GHAGHARA
GANDAK
BRAHMAPUTRA (GOALPARA)
MANAS

Figure IV - 10

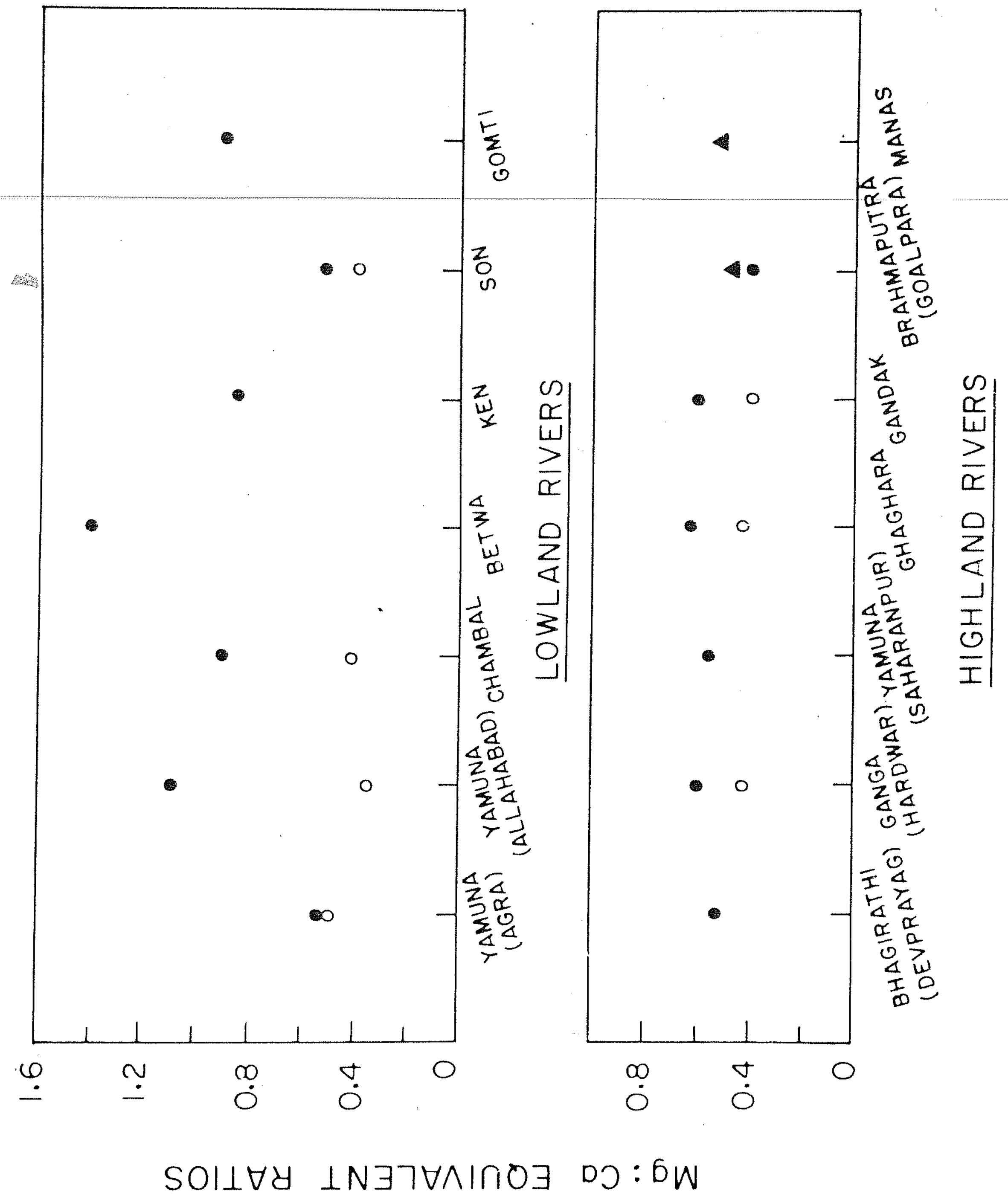

Mg:Ca EQUIVALENT RATIOS
1.6
1.2
0.8
0.4
0
YAMUNA (AGRA)
YAMUNA (ALLAHABAD)
CHAMBAL
BETWA
KEN
SON
GOMTI
LOWLAND RIVERS
0.8
0.4
0
BHAGIRATHI (DEVPRAYAG)
GANGA (HARDWAR)
YAMUNA (SAHARANPUR)
GHAGHARA
GANDAK
BRAHMAPUTRA (GOALPARA)
MANAS
HIGHLAND RIVERS

Figure IV - 11

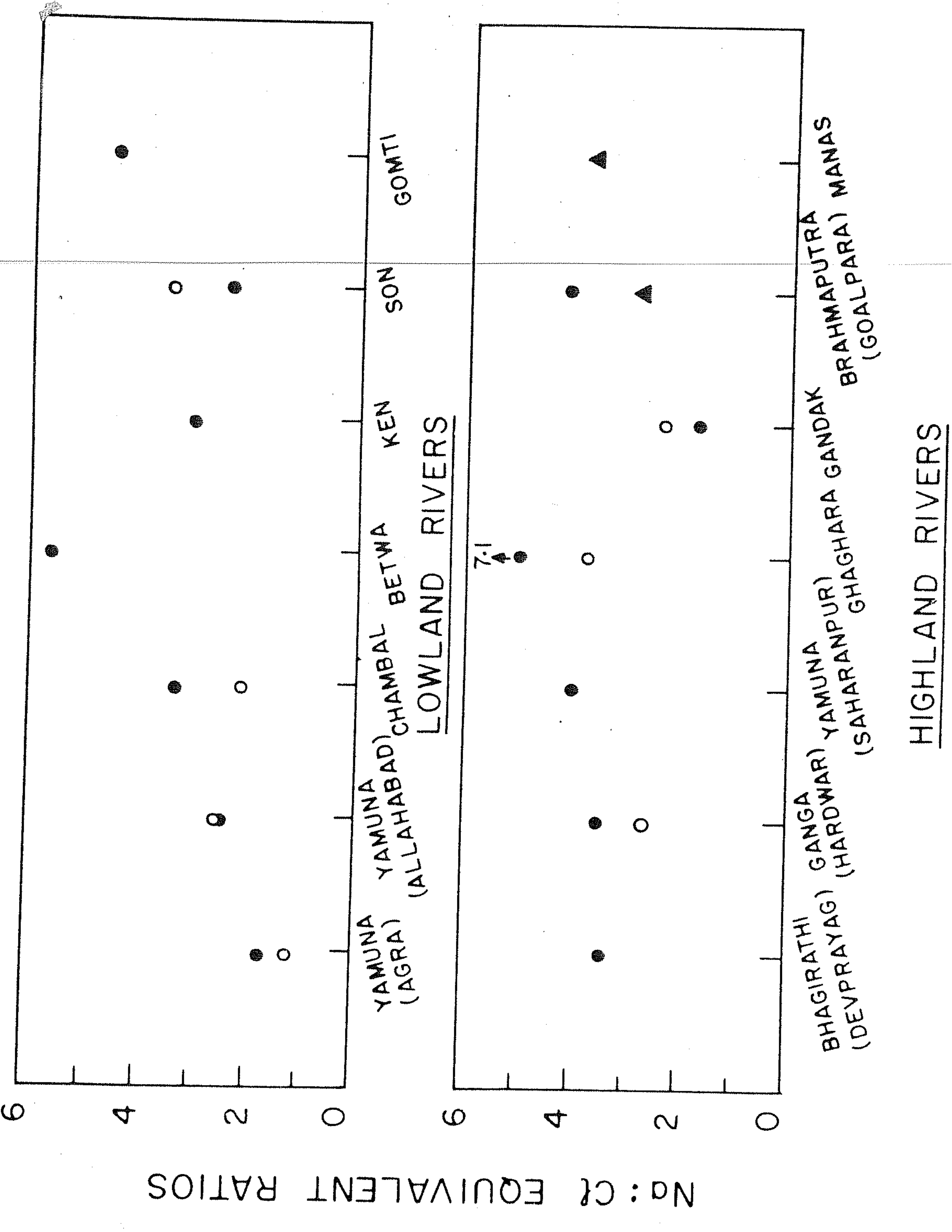

Na : Cl EQUIVALENT RATIOS
6
4
2
0
LOWLAND RIVERS
YAMUNA (AGRA)
YAMUNA (ALLAHABAD)
CHAMBAL
BETWA
KEN
SON
GOMTI
HIGHLAND RIVERS
BHAGIRATHI (DEVPRAYAG)
GANGA (HARDWAR)
YAMUNA (SAHARANPUR)
GHAGHARA
GANDAK
BRAHMAPUTRA (GOALPARA)
MANAS
7.1

Figure IV - 12

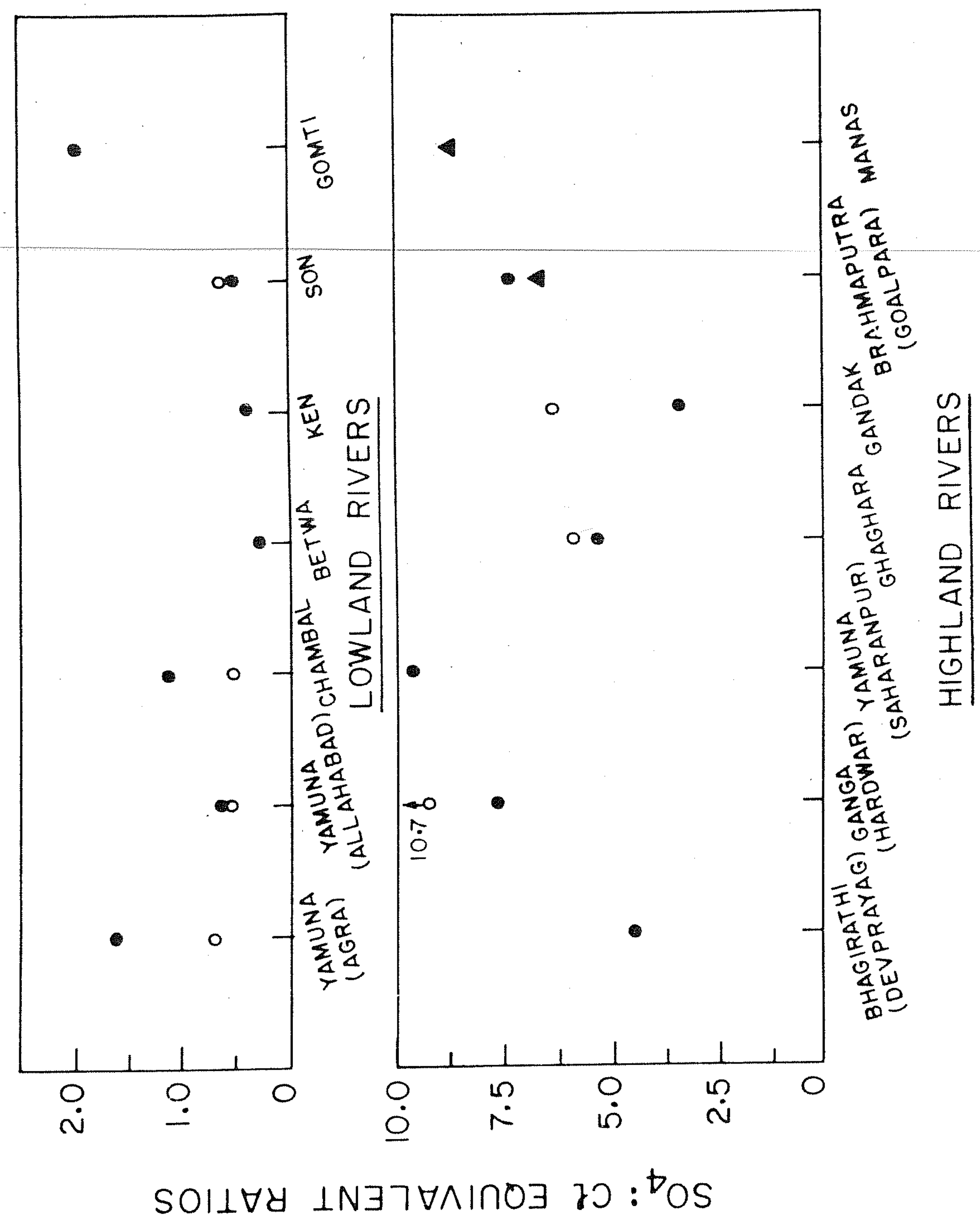

LOWLAND RIVERS
YAMUNA (AGRA)
YAMUNA (ALLAHABAD)
CHAMBAL
BETWA
KEN
SON
GOMTI
2.0
1.0
0
HIGHLAND RIVERS
BHAGIRATHI (DEVPRAYAG)
GANGA (HARDWAR)
YAMUNA (SAHARANPUR)
GHAGHARA
GANDAK
BRAHMAPUTRA (GOALPARA)
MANAS
10.7
10.0
7.5
5.0
2.5
0
SO4 : Cℓ EQUIVALENT RATIOS

Figure IV - 13

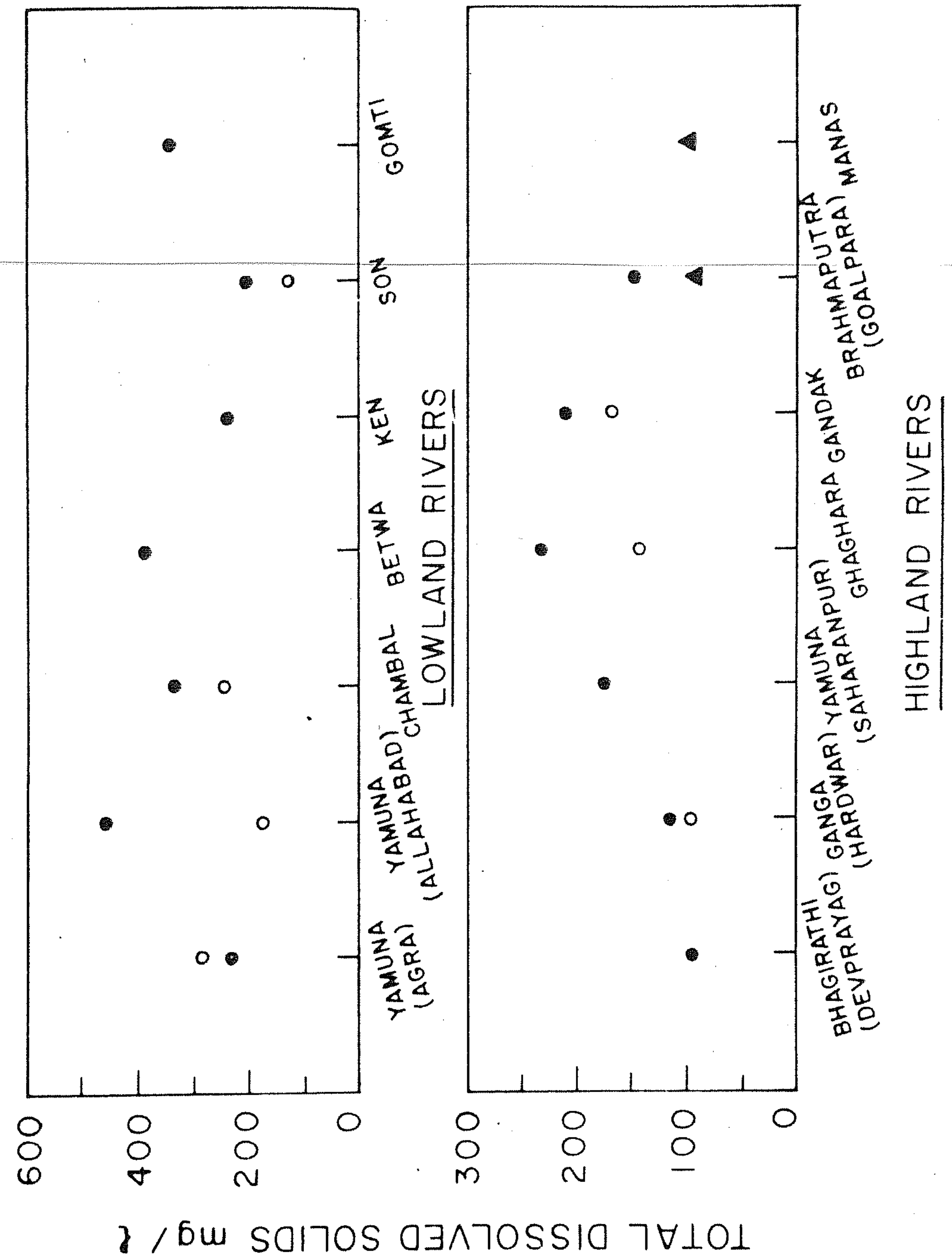

TOTAL DISSOLVED SOLIDS mg/ℓ
600
400
200
0
300
200
100
0
YAMUNA (AGRA)
YAMUNA (ALLAHABAD)
CHAMBAL
BETWA
KEN
SON
GOMTI
LOWLAND RIVERS
BHAGIRATHI (DEVPRAYAG)
GANGA (HARDWAR)
YAMUNA (SAHARANPUR)
GHAGHARA
GANDAK
BRAHMAPUTRA (GOALPARA)
MANAS
HIGHLAND RIVERS

Table IV-8 <u>Major ion composition of Lowland Rivers</u>

Sample Code*	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	TDS
	μmole/l								mg/l
				Lean Flow, March 1982					
5.Yamuna	672	89	370	698	1891	400	331	166	227
10.Yamuna	1529	107	539	710	2683	775	431	145	322
12.Yamuna	2775	87.1	778	702	4285	1163	379	123	461
6.Chambal	1971	68.2	555	610	3095	594	336	83	333
9.Betwa	2377	52.5	690	502	4238	426	71	237	388
19.Ken	701	54.3	461	550	2683	233	52	214	241
15.Son	458	58.1	313	610	2165	200	52	235	203
14.Gomti	1149	98.5	695	794	3644	258	255	210	347

Table IV-8 Contd.

Sample Code*	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	TDS
	µmole/l								mg/l
				Peak Flow, September 1982					
24.Yamuna	1401	130	395	794	1921	1172	412	170	287
30.Yamuna	556	57.3	190	547	1753	222	67	164	173
25.Chambal	593	53	337	829	2531	284	76	296	247
34.Son	240	39.7	166	434	1372	71	22.4	210	129
				Moderate Flow, December 1982					
39.Yamuna	2622	81.1	787	967	4427	1128	321	253	477

* Sample Code indicates Station No. and River, See Figure III-1

evident from the trilinear diagram (Figure IV-6). This inferrence can also be deduced from the plots of (Na+K) and (Ca+Mg) versus TZ^+ (Figure IV-7), which show that all the lowland rivers plot below the equilines of both (Na+K):TZ^+ and (Ca+Mg):TZ^+ ratios. The Mg:Ca ratios increase during lean flow whereas K/Na ratios decrease.

(ii) Analogous to that in the highland rivers, bicarbonate is the major anion in lowland river waters and it accounts for over 70 % in the anion balance. However, unlike highland rivers, sulfate and chloride are more enhanced in some of the lowland rivers, together they constitute about 30 % of the anions. The SO_4:Cl equivalent ratios vary from 0.8 to 2.0.

(iii) The plot of (Ca+Mg) versus bicarbonate (Figure IV-8) shows that most of the samples, during lean flow, fall far below the 1:1 trend. This requires that a significant fraction of bicarbonate has to be balanced by (Na+K).

(iv) Compared to highland rivers, the lowland rivers are characterised by relatively high TDS contents. The high TDS values result from increased contribution of soil salts during lean flow conditions, (Table IV-8).

These general observations reveal that the major ion composition of the lowland rivers is dictated by the weathering of carbonates, silicates and soil salts. This is very much unlike the case of highland rivers, where the major ion chemistry is dominated by weathering of carbonates. The relative contributions from weathering of carbonates, silicates and soil salts to the lowland rivers, vary depending upon the hydrological conditions in the river basin.

IV.4.(d) Seasonal variations in Lowland Rivers

IV.4.d.(i) Chambal, Yamuna and Gomti

The water chemistry of Chambal, Yamuna and Gomti Rivers shows close similarities. The Chambal River drainage basin is characterised by Vindhyan sandstones, quartzites, siliceous limestones and dolomites (Wadia, 1981). The stretch of Yamuna River between Saharanpur and Allahabad (where it joins the Ganga) flows through alluvial plains, and the alluvium is rich in 'Kankar Carbonates' (Wadia, 1981). The entire drainage basin of Gomti River also lies in the alluvial plains. The Chambal and Yamuna Rivers were sampled during lean and peak flow conditions whereas Gomti River was sampled only during lean flow.

The abundance ratios of the cations and anions (Table IV-9) in these river waters have been used to evaluate the seasonal variations in the major ion chemistry of these rivers, Figures IV-9 through IV-13.

Table IV-9 Abundance ratios of cations and anions in Chambal, Yamuna and Gomti Rivers: Seasonal Variations

River (Sampling period)	(Ca+Mg): TZ^+	(Ca+Mg): (Na+K)	HCO_3: TZ^-	(SO_4+Cl): HCO_3
Chambal				
(Lean)	0.53	1.14	0.71	0.41
(Peak)	0.78	3.6	0.85	0.17
Yamuna*				
(Lean)	0.51	1.03	0.69	0.44
(Peak)	0.71	2.4	0.83	0.20
Gomti				
(Lean)	0.70	2.4	0.83	0.21

*Yamuna sample at Allahabad, before it joins the Ganga

It is interesting to note that in both Chambal and Yamuna Rivers, the (Ca+Mg):(Na+K) ratios decrease considerably during lean flow conditions. This decrease is because of the large increase in sodium concentration of these river waters (Table IV-8). This increase in sodium content is paralleled by a corresponding increase in (SO_4+Cl) which is also reflected by the significant increase in (SO_4+Cl): HCO_3 ratio during lean flow.

The relative increase in sodium, chloride and sulfate concentrations during lean flow most likely results from the dissolution of soil salts. The wide spread occurrence of alkaline and saline soils all along the course of the Chambal and Yamuna Rivers have been well documented by Abrol and Bhumbla (1971) see Figure II-3. The saline soils are extremely rich in soluble salts such as sodium chloride and sodium sulfate. It has been reported that a shallow underground water table fluctuating between 1 to 3.5 m depth over the annual cycle prevails in these soils (Bhargava et al, 1981). Groundwater in these areas serves as the main source of soil salinization. Mithal (1972) has reported the chemical characteristics of groundwaters from these river basins. His study shows that the chemical characteristics of these groundwaters are dominated by alkalies and $(Cl+SO_4)$ exceed bicarbonate. The water table maps in these river basins indicate that the rivers are effluent in nature (Mithal, 1972). Hence during lean flow (summer months) there is a significant contribution of the sodium salts (NaCl and Na_2SO_4) from saline soils by effluent seepage of groundwater. In Gomti River the cations and anions ratios, during lean flow, differ from those of Yamuna and Chambal Rivers (Table IV-9). The contribution from saline soils seems to be less pronounced as evident from relatively high abundance of bicarbonate (HCO_3:TZ$^-$ ratio = 0.83). The high abundance of sodium most likely results either from silicate weathering or by contribution from alkali soils (see Figure II-3). The relative inputs from these two sources is difficult to estimate. The alkaline soils are characterised by the dominance of sodium bicarbonate and carbonate as the soluble salts.

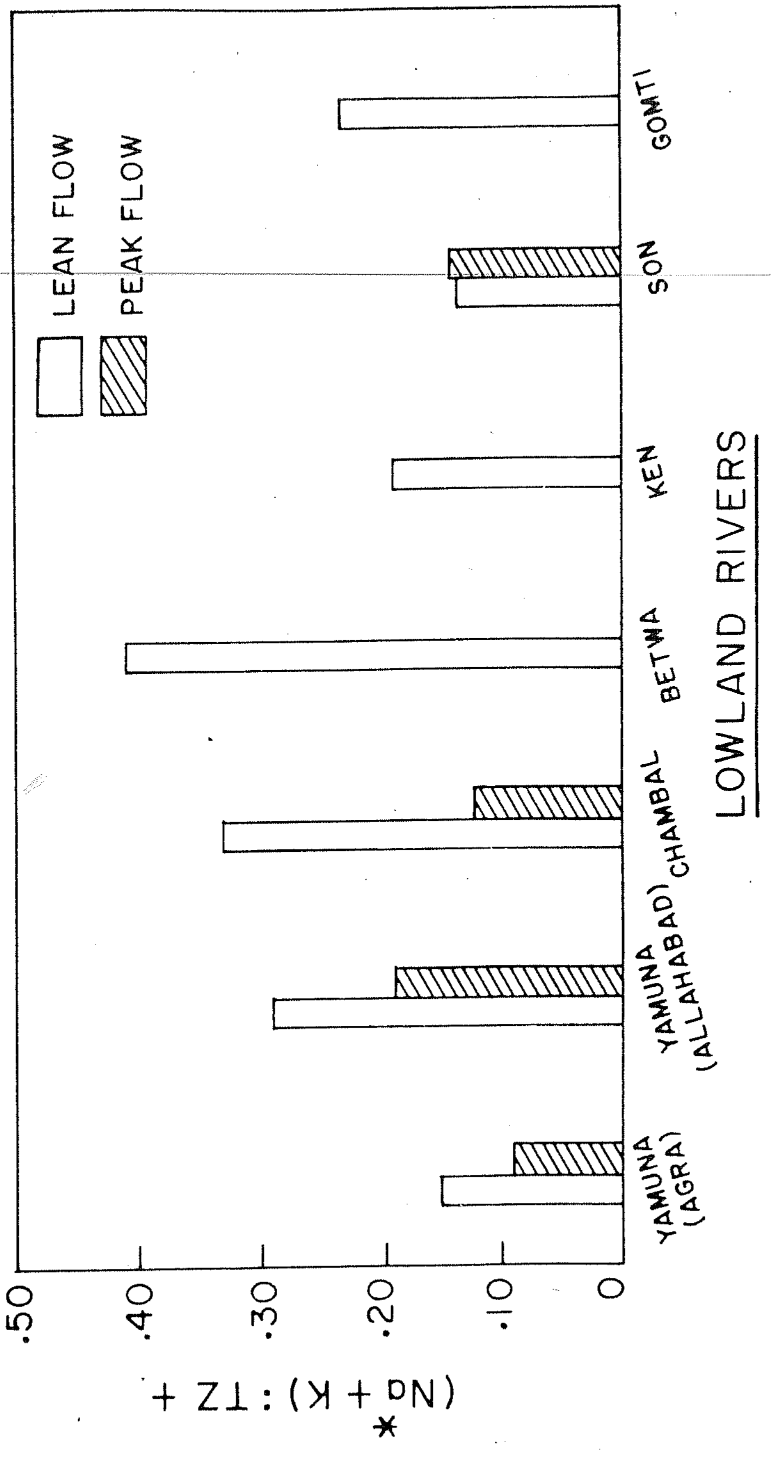
In Chambal and Yamuna Rivers the abundances of sodium, chloride and sulfate decrease considerably during peak flow conditions, Table IV-8. The (Ca+Mg) account for more than 70 % in the cation balance and HCO_3^- accounts for about 85 % of the anions, Table IV-9. This observation seems to favour the carbonate weathering as the major source of dissolved constituents and that the contribution from soil salts is relatively small during peak flow. However, the contribtuion of cations via silicate weathering is difficult to estimate. A rough estimate of the contribution from silicates, during peak flow, can be obtained using the $(Na^{*}+K):TZ^{+}$ ratios (Na^{*} signifies sodium corrected for chloride) as an index of silicate weathering Figure IV-14. In Chambal River, during peak flow, the $(Na^{*}+K):TZ^{+}$ ratio is 0.12 which indicates that sodium and potassium derived from silicate weathering can account for about 12 % (the equivalent fraction) of the abundance of total cations in the river water. A similar estimate made for Yamuna River reveals that the contribtuion of sodium and potassium via silicate weathering, if operative in the river basin, can account for 19 % of the total cations during peak flow. The low abundance of silica, 296 and 164 µmole/l and the $SiO_2:HCO_3$ molar ratio 0.12 and 0.09 respectively for Chambal and Yamuna, also indicate that the contribution from silicate weathering is relatively small.

During lean flow, the contribution of sodium from soil salts makes it difficult to discern the magnitude of silicate weathering. The upper limits of silicate weathering during lean flow are shown in Figure IV-14. If sodium is corrected for its sodium chloride and sodium sulfate components, 705 and 854 µmole/l of residual sodium (Na^{**}) remains, respectively for Chambal and Yamuna Rivers. Based on this residual sodium, the $(Na^{**}+K):TZ^{+}$ ratio is

Figure IV - 14.

$(Na^* + K) : TZ^+$ equivalent ratios in lowland rivers used as an index of silicate weathering. Na^* signifies sodium corrected for chloride.

Figure IV - 14



LOWLAND RIVERS

found to be 0.18 and 0.16 for Chambal and Yamuna respectively. Thus it can be inferred that in Chambal and Yamuna River drainage basins, during peak flow, the carbonate weathering dominates the chemistry. During lean flow there is a significant contribution from soil salts by effluent seepage of groundwaters and contribution of alkali metals via silicate weathering is less than 20 % in these drainage basins.

IV.4.d.(ii) Betwa River

Betwa River was sampled during lean flow of March 1982. It is characterised by relatively high TDS content, 388 mg/l (Table IV-7). Bicarbonate accounts for 88 % of the anions and SO_4:Cl equivalent ratio is 0.3. The abundance of cations in the Betwa River is unique, sodium is the most significant in cation balance. Calcium plus magnesium constitute about 50 % of the cations and Mg:Ca ratio is 1.4 . The high sodium concentration , the high Mg:Ca ratio and sodium excess over chloride (Na:Cl = 5.6) is indicative of significant input from silicate weathering. The extent of silicate weathering is also borne out from $(Na^* + K) : TZ^+ = 0.42$, which indicates that silicate weathering can account for as much as 42 % , Figure IV-14.

This is consistent with the geology of the river basin which is dominated by Archean granitic and gneissic rocks, shales and sandstones. However, the silica concentration of 236 μmole/l is not commensurate with the predicted contribution from silicate weathering. The low silica may be because of removal by biological processes in the reservoirs upstream of the sampling site.

IV.4.d. (iii) Ken and Son Rivers

Both Ken and Son Rivers have similar water chemistry, which differs from that of the other lowland rivers. The regional lithologies of the river drainage basins are dominated by Vindhyan sandstones, limestones and shales. These shales are carbonaceous, siliceous and calcareous. In Ken and Son Rivers, calcium and magnessium are the major cations and bicarbonate accounts for about 90% of the anions, Table IV-10. The Mg:Ca ratio varies between 0.38 to 0.84. These observations indicate that chemistry of these river waters is dominated by weathering of carbonate rocks of the drainage basins. The silica concentrations in Ken and Son Rivers, during lean flow,

Table IV-10 Abundance ratios of cations and anions in Ken and Son Rivers

River (Sampling period)	(Ca+Mg) : TZ^+	(Ca+Mg) : (Na+K)	HCO_3 : TZ^-	(SO_4+Cl) HCO_3
Ken (Lean)	0.73	2.7	0.89	0.13
Son (Lean)	0.78	3.6	0.88	0.14
(Peak)	0.81	4.3	0.92	0.08

are 214 and 235 μmole/l, respectively. The $(Na^*+K) : TZ^+$ ratio is about 0.15 (Figure IV-14) which indicates that contribution of alkali metals from silicate weathering is of minor importance in these river waters. The major ion ratios in Son River waters do not show any seasonal variations. However, the TDS content during lean flow is 213 mg/l which decreases to 136 mg/l during peak flow. The Ken River during lean flow is also characterised by relatively low TDS content, 254 mg/l.

IV.4.(e) Ganga main channel

Data on seasonal and downstream variations in the major ion composition of the Ganga main channel are given in Table IV-11 and in Figures IV-15, 16,and 17. The chemistry of the Ganga main channel is controlled by the influx of waters from the various tributaries. The effects of tributaries are clearly seen as regard to the downstream variations in the major ion composition. These effects are more pronounced during lean flow of the rivers.

During lean flow, there is a significant increase in the sodium content along the course of Ganga main stream between Rishikesh and Varanasi, Figure IV-15. Further downstream with the influx of Ghaghara, Gandak and Son Rivers, the sodium content decreases. This variation in sodium content is reflected in the (Ca+Mg):(Na+K) equivalent ratio which decreases from 6.9 to 1.25 between Rishikesh and Varansi (Figure IV-18) and again increase to 2.3 after the confluence of Ghaghara and Gandak Rivers. Bicarbonate also shows a systematic increasing trend (Figure IV-17, Table IV-11), it accounts

Table IV-11 Major ion composition of Ganga Main Stream: Downstream and Seasonal Variations

Sample* Code	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	TDS mg/l
	µmole/l								
				Lean Flow, March 1982					
2.Devprayag	141	36.6	160	300	854	42	95	157	92.7
3.Rishikesh	145	40.4	239	398	1004	42	162	152	114
4.Garhmukteshwar	322	80.8	329	612	1891	58	190	191	190
7.Kanpur	776	99.7	494	683	2943	168	214	118	274
11.Upstream Allahabad	1060	105	531	560	2637	291	245	70.6	263
13.Varanasi	2121	99.7	695	690	3903	797	331	93.4	401
16.Upstream Patna	1767	94.7	675	666	3567	607	264	160	361
17.Downstream Patna	1096	85.8	593	760	3232	400	203	147	313

Table IV-11 Contd.

Sample* Code	Na+	K+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	TDS
	µmole/1								mg/1
Peak Flow, September 1982									
26.Hardwar	59.4	38.2	153	353	894	22.6	121	109	94.2
35.Garhmuk-teshwar	105	67.9	182	471	1159	19.4	143	127	121
27.Kanpur	354	81.7	242	565	1829	77.5	103	157	173
29.Allahabad	425	78.5	201	458	1570	116	85	121	151
31.Varanasi	473	61.6	188	514	1707	162	71.7	147	164
33.Patna	280	62.6	203	547	1707	87.2	58	129	156
Moderate Flow, December 1982									
40.Varanasi	2185	87.6	724	696	4047	820	278	224	415
38.Patna	1092	75.2	543	790	3135	361	148	197	303

* Sample Code indicates Station No. and Location, see Figure III-1 and Table III-1

Seasonal and downstream variations in the major ion composition of the Ganga main channel are shown in Figures IV-15, 16 and 17. Arrows along the X-axis indicate the confluence point of the tributaries (represented by the numbers in parentheses) with the main channel.

Figure IV-15 : Shows variations in sodium and potassium concentrations.

Figure IV-16 : Shows variations in magnesium and calcium concentrations.

Figure IV-17 : Shows variations in bicarbonate, calcium and sulfate concentrations.

Symbol key used for Figures IV-15,16 and 17:

●	Lean flow
O	Peak flow
▲	Moderate flow

Figure IV - 15

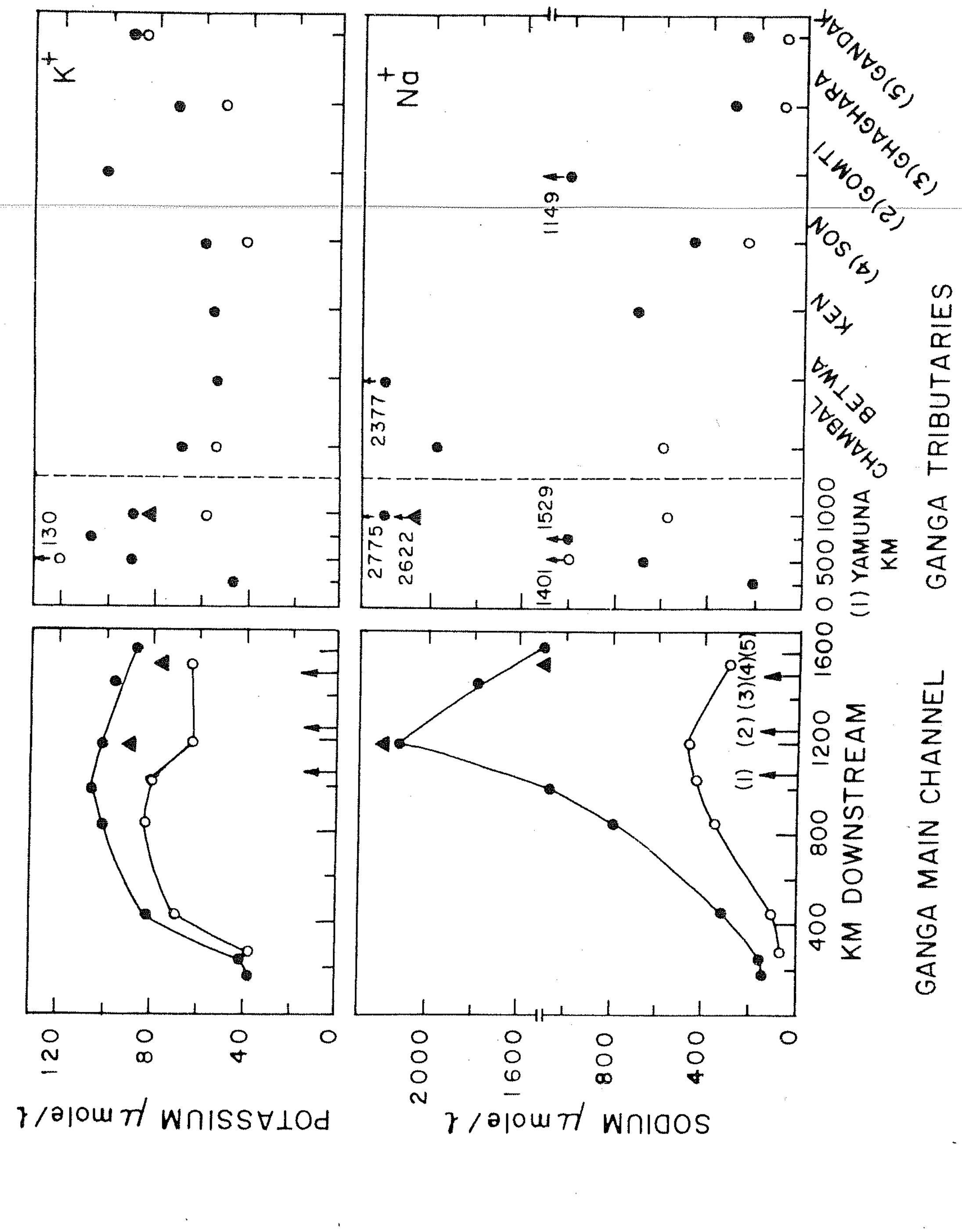

POTASSIUM μmole/ℓ
SODIUM μmole/ℓ
K+
Na+
0
40
80
120
400
800
1600
2000
130
2775
2622
1401
1529
2377
1149
400
800
1200
1600
KM DOWNSTREAM
(1)
(2)
(3)(4)(5)
GANGA MAIN CHANNEL
0 500 1000
(1) YAMUNA
KM
CHAMBAL
BETWA
KEN
(4) SON
(2) GOMTI
(3) GHAGHARA
(5) GANDAK
GANGA TRIBUTARIES

Figure IV - 16

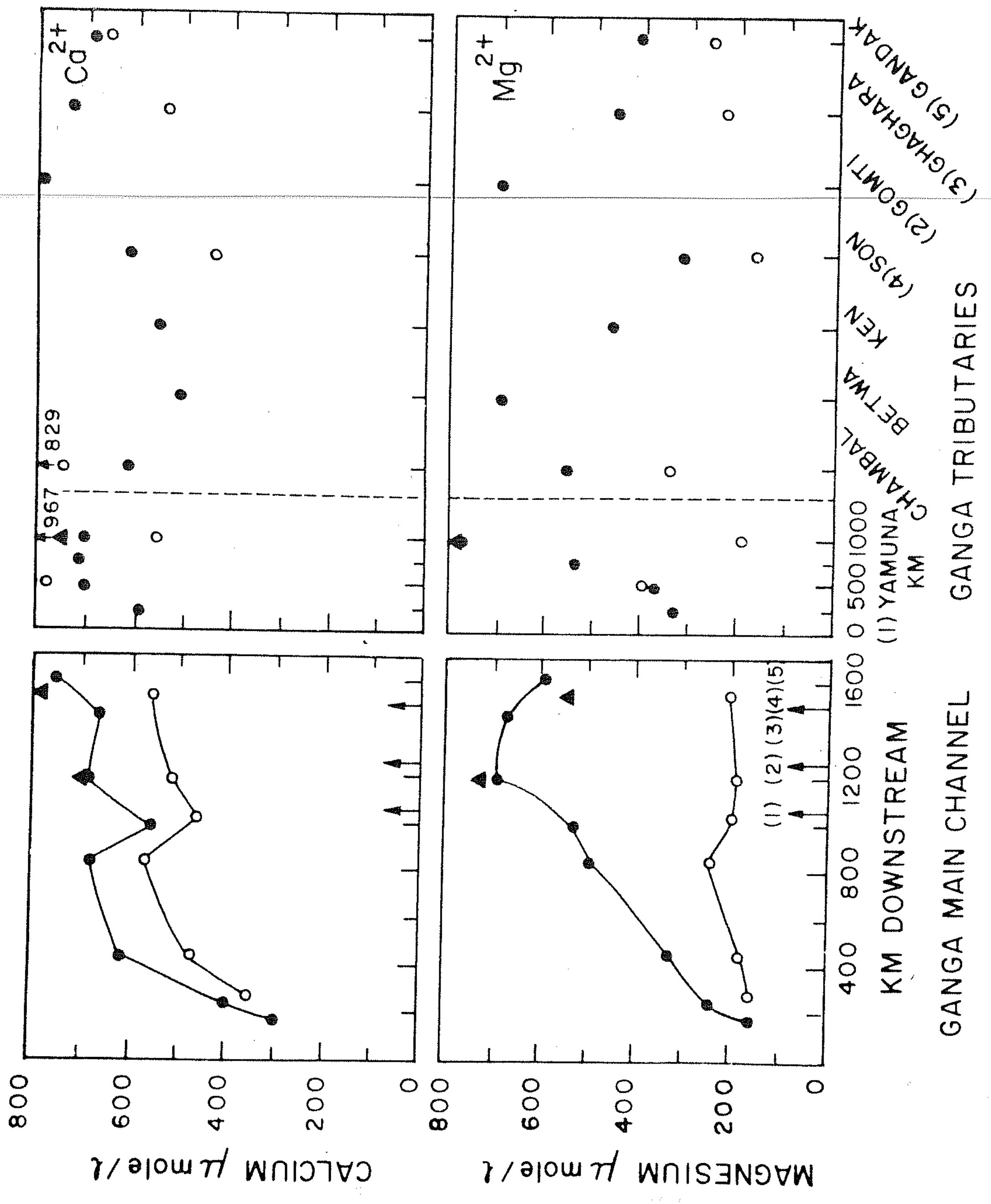
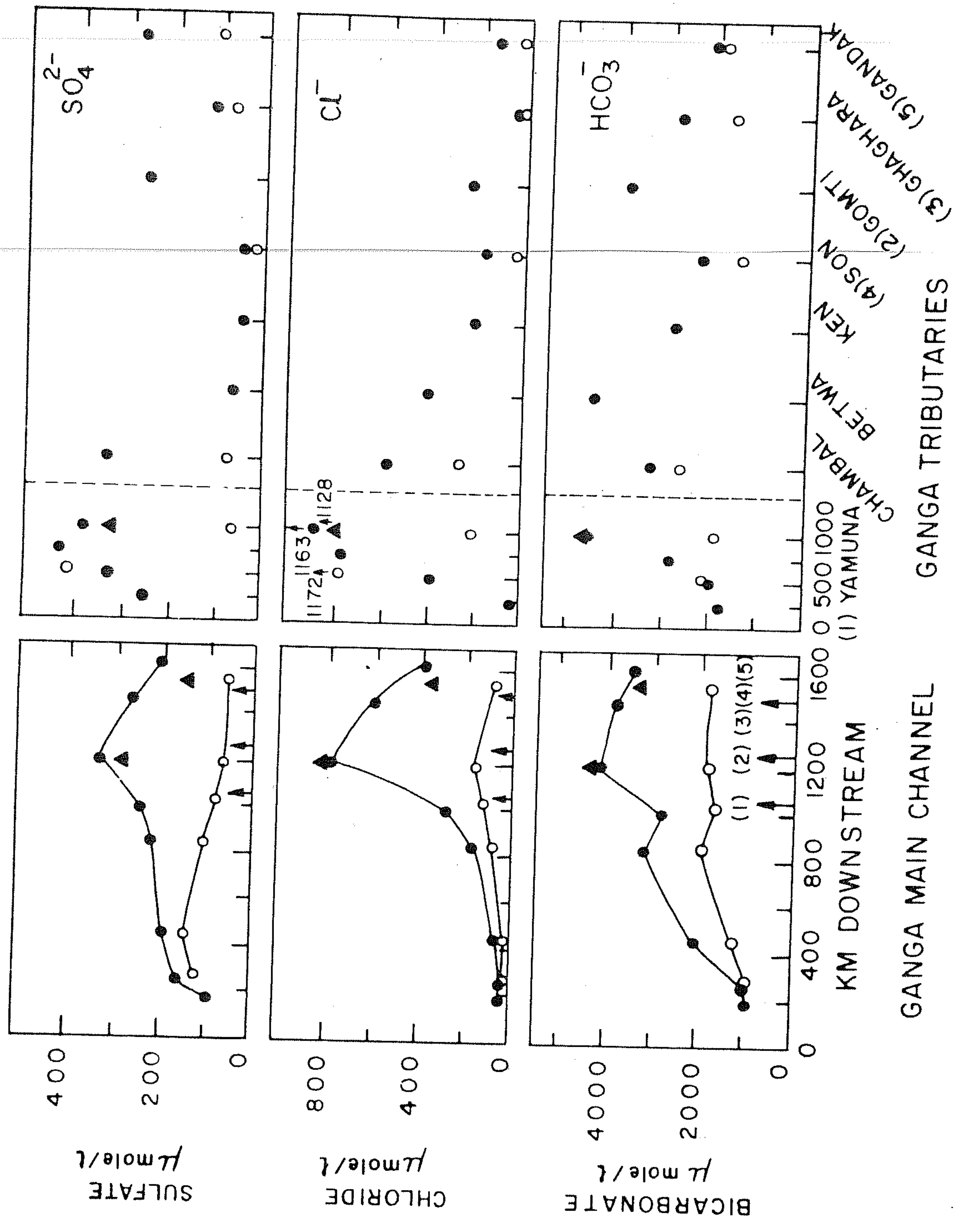

CALCIUM μ mole/l
MAGNESIUM μ mole/l
0
200
400
600
800
400
800
1200
1600
KM DOWNSTREAM
GANGA MAIN CHANNEL
(1) (2) (3)(4)(5)
Ca^{2+}
Mg^{2+}
967
829
0 500 1000
KM
(1) YAMUNA
CHAMBAL
BETWA
KEN
(4)SON
(2)GOMTI
(3)GHAGHARA
(5)GANDAK
GANGA TRIBUTARIES

Figure IV - 17



SULFATE
μmole/l
400
200
0
CHLORIDE
μmole/l
800
400
0
BICARBONATE
μmole/l
4000
2000
0
0
400
800
1200
1600
KM DOWNSTREAM
GANGA MAIN CHANNEL
(1) (2) (3)(4)(5)
SO_4^{2-}
Cl^-
HCO_3^-
1163
1172
1128
0 500 1000
(1) YAMUNA
CHAMBAL
BETWA
KEN
(4)SON
(2)GOMTI
(3)GHAGHARA
(5)GANDAK
GANGA TRIBUTARIES

Figure IV - 18.

Ganga main channel : Seasonal and downstream variations in the equivalent ratios of (Ca + Mg) : (Na + K) and SO_4 : Cl.

Figure IV - 19.

Seasonal and downstream variations in conductivity and Total Dissolved Solids in the Ganga main channel.

Symbol key used for Figures IV-18 and 19:

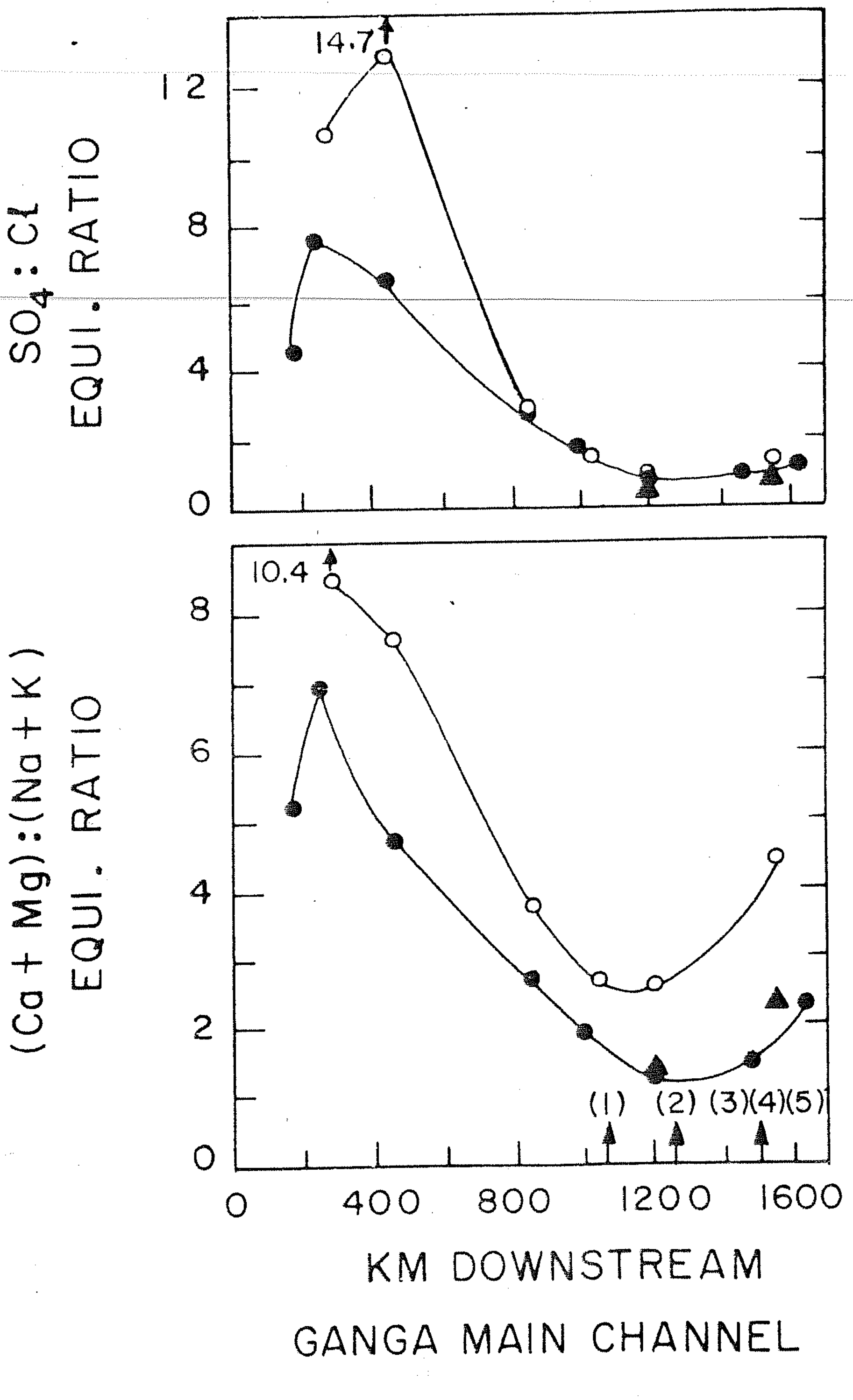
● Lean flow

○ Peak flow

▲ Moderate flow

Arrows along the X-axis indicate the confluence point of the tributaries (see Figures IV-15 through 17) .

Figure IV - 18



GANGA MAIN CHANNEL

for over 70 % of the anions. During lean period, ($Cl+SO_4$) are more significant in the anion balance, chloride being particularly more enhanced with the result that the SO_4:Cl ratio decreases with the downstream flow (Figure IV-18). This systematic increase in sodium, chloride and sulfate concentrations along the main channel, indicate that during lean flow there is a significant contribution from soil salts. Figure II-3 shows wide spread occurrence of alkaline soils along the course of Ganga River between Kanpur and Patna. During lean flow, the TDS content varies from 114 to 313 mg/l between Rishikesh and Patna, a maximum value of 401 mg/l occurs after the confluence of Yamuna with the main channel (Figure IV-19 and Table IV-11). It can be seen from the ternary diagram (Figure IV-6) that during lean flow, sodium and calcium are the major cations. This observation seems to suggest that the major ion composition of the Ganga main channel along its course is dominated by carbonate weathering and soil salts in varying proportions.

During peak flow conditions, the major ion composition in Ganga main stream do not show any significant downstream variations, Figures IV-15, 16 and 17 and

Table IV-11. The TDS content varies from 94 to 156 mg/l between Hardwar and Patna, Figure IV-19. The low abundances of sodium, chloride and sulfate indicate that contribution from soil salts is less significant. It is interesting to note that during peak flow all the data points when plotted on a ternary diagram (Figure IV-6) fall in the calcium dominated region. Calcium and magnesium account for about 80 % of the cations whereas bicarbonate accounts for 80-90 % of the anions. This indicates that, during peak flow, chemistry of the Ganga main channel (between Hardwar and Patna) is dictated by carbonate weathering. Handa (1972) reported a similar observation that during the peak flow season not only the dissolved salts content of the Ganga River water decreases, but the proportion of the calcium and magnesium ions relative to sodium ion and that of bicarbonate ion relative to chloride and sulfate ions also go up. However, no explanation was given for such an observation.

IV.4.(f) Brahmaputra River

During both the sampling seasons (i.e. moderate and lean flows) the Brahmaputra River does not exhibit any significant downstream variations in the major ion composition, Table IV-12. For example during moderate

Table IV-12 Major ion composition of Brahmaputra River: Downstream and seasonal variations

Sample Code*	Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	Cl^-	SO_4^{2-}	SiO_2	TDS
	µmole/l								mg/l
				Moderate Flow, April 1982					
20.Dibrugarh	73	56.4	163	370	1021	19.4	113	172	107
21.Gauhati	78	46.2	145	313	884	25.8	99	122	91.3
22.Goalpara	80	46.2	148	318	884	29	99	118	91.5
23.Goalpara+	94	42	181	348	930	25.8	113	131	98.5
				Lean Flow, December 1982					
37.Gauhati	163	57.2	208	541	1368	40	148	202	144
36.Goalpara	164	58	214	553	1406	40	148	204	147

* Sample code indicates station No. and location, see Figure III-1 and Table III-3

\+ Manas River at Goalpara, before confluence with Brahmaputra flow, the TDS content varies from 92 to 107 mg/l along the traverse between Dibrugarh and Goalpara. However, the seasonal variations in the major ion composition are clearly evident. The TDS content at Goalpara increases from 92 mg/l (during moderate flow) to 147 mg/l (during lean flow). Calcium and magnesium are the major cations, and bicarbonate accounts for 80 % of the anions. Sulfate is the next abundance anion and SO_4:Cl ratio varies between 6.8 to 7.4 . These observations seem to suggest that the major ion composition is dominated by the weathering of carbonates. The high abundance of sulfate is consistent with the occurrence of pyrite sediments in the Brahmaputra River drainage basin.

IV.4.(g) Fluxes of dissolved major ions via Ganga and Brahmaputra Rivers

One of the goals in measuring the abundances of major ions in river waters is to calculate their fluxes to the oceans via rivers. The knowledge about the elemental fluxes via rivers is essential for a proper understanding of the geochemical cycle involving the transfer of material between various reservoirs of the earth.

In this section, an attempt has been made to calculate the average annual fluxes of dissolved major ions transported by the Ganga and its tributaries and also by the Brahmaputra River. For calculation of elemental fluxes via rivers, data on the chemical composition and the average annual water discharge are required. The abundances of major ions are measured during this work, however data on the water discharge of the rivers within the Ganga Basin could not be obtained because of logistic and other regulatory problems. Therefore for calculation of elemental fluxes I have used the discharge data compiled by UNESCO (1964) and by Rao (1975). The mean annual discharge of the Ganga River, based on the 11 years record of the UNESCO (1964), at Farakka is 415×10^{12} L/yr. Of this, 83 % of the discharge occur during July - October and the remaining 17 % occur during November - June. In the present study, samples for chemical analysis from the Ganga main stream were collected only upto Patna. The average annual flow in Ganga at Patna is 364×10^{12} L/yr (Rao, 1975). For flux calculations it is assumed that 83 % of the annual discharge occur during July-October and the remaining 17 % during Nov. - June, as observed at Farakka.

The discharge-weighted average chemical composition of all the rivers within the Ganga Basin have been calculated as : $\bar{C} = 0.83\ C_P + 0.17\ C_L$, where $\bar{C}$ is discharge weighted average composition and C_P and C_L are the observed abundances of major ions during peak flow (September 1982) and lean flow (March 1982), respectively. It is assumed that the abundances of major ions measured during lean flow (March 1982) represent the average chemical composition of the river water flowing during the months of November through June, which accounts for 17 % of the annual discharge. This assumption appears to be valid as can be seen from the data in Table IV-11. The chemical composition of the Ganga main stream, as derived from the samples collected at Varanasi and Patna, during lean flow (March 1982) and moderate flow (December 1982) is very similar. Similarly, it is assumed that the abundances of major ions measured during peak flow (September 1982) represent the average chemical composition of the peak discharge during July through October months, which accounts for 83 % of the annual discharge. The discharge weighted average major ion composition of the Ganga and its tributaries is presented in Table IV-13.

A comparison of the data in Table IV-13 reveals that Chambal and Yamuna Rivers are the most saline rivers while Son is the least saline river. The high concentrations of Na, Cl and SO_4 in the Yamuna and Chambal Rivers are due to the contribution from alkaline and saline salt-

Table IV-13. Average major ion composition of Ganga and its tributaries

River	Na	K	Mg	Ca	HCO_3	Cl	SO_4	SiO_2	TDS
	µmole/l								mg/l
Ganga*	533	83	257	475	1751	146	112	112	170
Yamuna	933	62	290	573	2183	382	120	157	222
Chambal	827	55.6	374	792	2627	337	120	250	262
Ghaghara	131	61	270	562	1777	29	82	124	159
Son	277	43	191	464	1507	93	27	214	142
Gandak	104	85	285	655	1886	52	130	147	177
Ganga**	419	67	269	583	1966	140	83	132	183
World Average+	191	38.2	166	398	1019	105	95.5	207	115

*Ganga at Allahabad before confluence with Yamuna

**Ganga at Patna after confluence of Ghaghara, Son and Gandak

+From Hu Ming-hui et al (1982)

affected soils in their drainage basins. Also, all the tributaries of Ganga are relatively more concentrated in TDS compared to the world average river water. The average chemical composition of the Ganga River (at Patna, Table IV-13) is significantly different from that reported by Subramanian (1979) for a single sample collected from the same site during monsoon, 1977. His data shows that the concentration of SO_4 is higher by a factor of about 10 whereas K, Mg and Cl are high by a factor about 3 to 5. The cause for this large disparity between the two sets of data is unclear. However, as mentioned earlier, the data of Subramanian (1979) suffer from a lack of charge balance between cations and anions. In his sample collected from Patna, the ratio of cations to anions is about 1.4 .

The annual fluxes of dissolved major ions carried by the Ganga and its Tributaries are given in Table IV-14. These fluxes are derived from the average chemical composition (Table IV-13) and multiplying these concentrations by the average annual discharge. As evident from the Table IV-14, the Yamuna carries 40 % of the total dissolved salts that are transported by the tributaries to the Ganga main stream.

The seasonal and average annual fluxes of major ions for the Ganga main stream (at Patna) and Brahmaputra River (at Goalpara) are given in Table IV-15. The discharge data for the Brahmaputra River at Gauhati (Hydrology Review, 1975) show that the moderate/peak discharge occur during April through October months and it account for 86 % of the total annual discharge. The remaining 14 % account for the lean flow during November through March months .

Table IV-14. Average annual fluxes of dissolved major ions: Ganga Tributaries

River	Discharge 10^{12} L/yr	Na	K	Mg	Ca	HCO_3	Cl	SO_4	SiO_2	TDS
		10^9 mole/yr								10^6 tons/yr
Ganga*	59	31.4	4.9	15.2	28	103	8.6	6.6	6.6	10
Yamuna	93	86.7	5.8	27	53.3	203	35.5	11.2	14.6	20.6
Chambal	30	24.8	1.7	11.2	23.8	78.8	10.1	3.6	7.8	7.8
Ghaghara	94	12.3	5.8	25.4	53	168	2.7	7.8	11.7	15
Son	32	8.9	1.4	6.1	14.8	48.2	3.0	0.9	6.9	4.5
Gandak	52	5.4	4.4	15	34.2	98.4	2.7	6.8	7.7	9.2

*Ganga at Allahabad before confluence with Yamuna

Table IV-15. Seasonal and annual fluxes of dissolved major ions via Ganga and Brahmaputra Rivers

River (Location)	Season	Discharge	Na	K	Mg	Ca	Cl	SO_4	SiO_2	TDS
		10^{12}L	10^9 mole							10^6 tons
Ganga (Patna)	July-Oct. (Peak flow)	302	84.6	18.9	61.3	165	26.3	17.5	39	47.1
	Nov - June (Moderate/ Lean flow)	62	68	5.3	36.8	47	24.8	12.6	9	19.4
	Annual	364	153	24.2	98	212	51	30	48	66.5
Brahmaputra (Goalpara)	April-Oct (Moderate/ Peak flow)	439	35	20.3	65	140	12.7	43.5	52	40
	Nov - Mar (Lean flow)	71	12	4.1	15	39	2.8	10.5	14.5	10.4
	Annual	510	47	24.4	80	179	15.5	54	66.5	50.4
World+ Rivers	Annual	31,400	6000	1200	5200	12500	3300	3000	6500	3600

+From Hu Ming-hui et al (1982)

This information together with the observed abundances of major ions (Table IV-12) have been used to compute the seasonal and annual fluxes of major ions carried by the Brahmaputra River (at Goalpara). Comparison of the fluxes between Ganga and Brahmaputra shows that, though the water discharge of the Ganga is about 70 % of that of the Brahmaputra it carries about 25 % more salts to the sea. The Ganga carries substantially more sodium, calcium and chloride. Furthermore, in the Ganga main stream although the lean flow is only one-fifth of the peak discharge, the fluxes of sodium, chloride and sulfate during lean and peak flows are nearly the same. This indicates the importance of soils salts contributing during lean flow conditions. The Brahmaputra transports relatively large amount of sulfate and silica and the flux of potassium is similar to that of the Ganga. An observation consistent with the occurrence of pyritic sediments in the river drainage basin.

On a global scale, the Ganga and Brahmaputra Rivers account for about 3 % of the total flux of dissolved major ions to the oceans via rivers. From the data in Table IV-15, the chemical weathering rates in the Ganga and Brahmaputra River basins have been computed, Table IV-16. The total denudation rate is taken to be sum of the chemical weathering and erosion rates.

Table IV-16. Chemical Weathering, Erosion and Total Denudation Rates in the Ganga and Brahmaputra River basins

Basin	Chemical	Erosion*	Total	Total**
	10^4 kg/km^2/yr			cm/10^3yr
Ganga+	7.7	55.7	63.4	32
Brahmaputra+	8.7	126	134.7	67

* From the data of Raymahashay (1970)

** Assuming a density of 2 gm/cm^3.

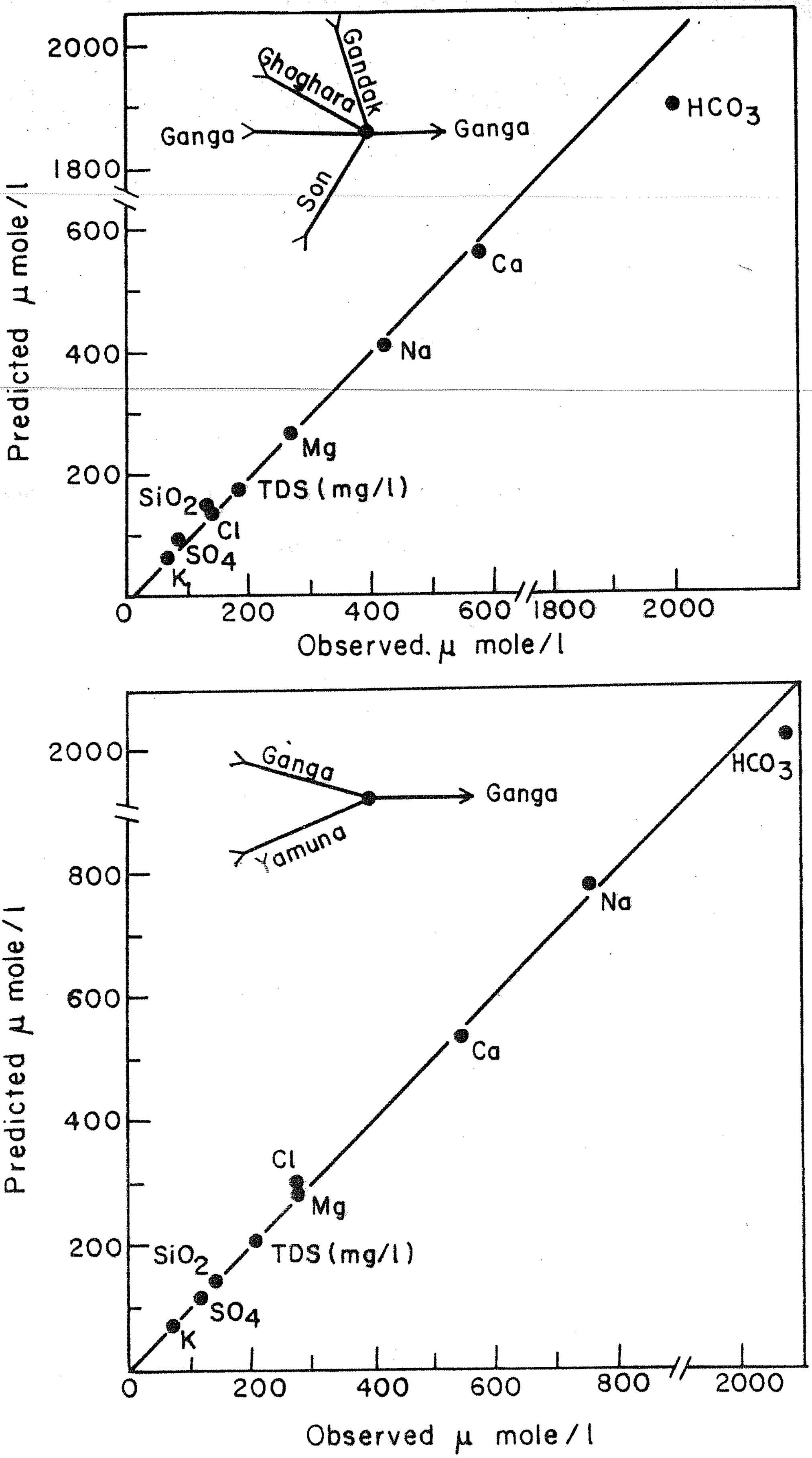
\+ Drainage areas of Ganga and Brahmaputra, used for calculations, are 861×10^3 and 580×10^3 km^2, respectively.

A material balance calculations have been made to evaluate the behaviour of various elements during mixing of the tributaries with the Ganga main channel. Two particular confluence of the tributaries and the main channel are examined: (1) The confluence of Ganga and Yamuna at Allahabad and (2) The confluence of Ghaghara, Son and

Figure IV - 20.

The observed and predicted concentrations of the major ions in the Ganga main channel after the confluence of the tributaries.

Figure IV - 20



2000
1800
600
400
200
Predicted µ mole/l
0
200
400
600
1800
2000
Observed. µ mole/l
Gandak
Ghaghara
Ganga
Ganga
Son
HCO3
Ca
Na
Mg
TDS (mg/l)
SiO2
Cl
SO4
K
2000
800
600
400
200
Predicted µ mole/l
0
200
400
600
800
2000
Observed µ mole/l
Ganga
Ganga
Yamuna
HCO3
Na
Ca
Cl
Mg
TDS (mg/l)
SiO2
SO4
K

Gandak with the Ganga at Patna. The main channel concentrations after the confluence, predicted from the concentrations and fluxes of the major ions up river of the main channel and the tributaries, agree with the observed concentrations, Figure IV-20. This demonstrates the conservative transport of dissolved major ions in the Ganga River system.

CHAPTER V. ISOTOPE GEOCHEMISTRY

V.1. D/H and $^{18}O/^{16}O$ isotopic composition of river waters

V.1.(a) Introduction

Water flow in a river system has two principal components: the direct run-off of local precipitation and the effluent discharge from the groundwater reservoirs. The relative contribution from each of these sources varies depending upon the hydrogeological characteristics of a river drainage basin. Thus, each of these sources with their characteristic D/H and $^{18}O/^{16}O$ isotopic ratios will determine the isotopic composition of the river waters.

The isotopic composition of hydrogen and oxygen in atmospheric water vapour and precipitation exhibit large variations. Several environmental factors such as latitude, altitude, climate and distance from the coast have been recognised which contribute to the D/H and $^{18}O/^{16}O$ isotopic variations in atmospheric water vapour and local precipitation (Craig, 1961; Ehhalt, 1963; Dansgaard,1964; Stewart, 1975 and Gat, 1980). The imprints of these variations have been observed in large and small river systems in which the surface run-off dominates the discharge

For example, the importance of both altitude and climate effects have been documented by Brown et al (1971) in a survey of Canadian surface waters. Matsui et al (1976) proposed that altitude effect may account for the significant difference in the Deuterium and Oxygen-18 contents ~~of the surface waters within the Amazon River system.~~ The most comprehensive study of Mackenzie River basin has been carried out by Hitchon and Krouse (1972). They document the strong dependence of the isotopic composition of surface waters on climatic parameters which control the isotopic composition of precipitation.

The D/H and $^{18}O/^{16}O$ isotopic composition of groundwaters by and large mimic the average annual isotopic composition of local precipitation. However, in many cases the isotopic composition of precipitation and that of the groundwaters derived from it are mismatched. Cases are known where groundwaters are either enriched or depleted in heavy isotopes relative to average precipitation. The causes for such an enrichment or depletion have been studied by Gat and Tzur (1967), Zimmermann et al (1967) and Dincer et al (1974).

Since the Deuterium and Oxygen-18 contents of the precipitation and groundwaters, within the river drainage basin, vary both geographically and in time, the isotopic composition of hydrogen and oxygen in river water can by no means be constant throughout the year. Furthermore, the isotopic labelling imparted to a river by the relative contributions from surface and sub-surface systems can be greatly modified if evaporation occurs. Lakes or large dam systems can affect the flow in the rivers considerably. Thus by evaluating the D/H and $^{18}O/^{16}O$ isotopic ratios in a river system and its source waters it is possible to make material balance calculations and estimates of evaporation losses which are of practical importance in water resources management studies.

V.1.(b) Geographical and seasonal variations in isotopic composition of the Ganga and Brahmaputra Rivers and their tributaries

In this study the isotopic ratios of D/H (expressed as δD) and $^{18}O/^{16}O$ (expressed as $\delta^{18}O$) have been measured in the same suite of samples for which the major element chemistry has been discussed in Chapter IV. Prior to this study no work has been done on the stable hydrogen and oxygen isotopic composition of the Ganga and Brahmaputra Rivers and their tributaries. Although limited in time series and in number these samples are unique and results from these samples are found to be useful in understanding the dominating factors controlling the seasonal and spatial variations in isotopic composition of these river waters. A detailed sampling of the precipitation and of groundwater sources is required to delineate the relative contributions from these hydrologic regimes which control the river supplies. The hydrologic and geologic characteristics of the Ganga and Brahmaputra River drainage basins have been described in Chapter II. The highland rivers are fed all through the year by precipitation and/or snow/glacier-melt waters. In lowland rivers, the surface run-off of local precipitation during the south-west monsoon (July-September) dominates the river flow. During rest of the year these rivers receive considerable supply from groundwater regimes.

The data on regional and seasonal variations in D/H and $^{18}O/^{16}O$ isotopic composition of the highland and lowland rivers are presented in Tables V-1 and 2 and in Figure V-1. The highland rivers, viz, Ganga (upto Hardwar), Ghaghara and Gandak when sampled during their peak flow (September 1982) show remarkable similarities in δD values, the extreme values being -66 ‰ and -70 ‰ (Table V-1) However, the $\delta^{18}O$ values of these river waters exhibit unambiguously measurable variations, the extreme values

Table V-1. δD and $\delta^{18}O$ variations in Highland Rivers

Sample Code*	Lean Flow, March 82		Peak Flow, Sept 82	
	δD (°/oo)	$\delta^{18}O$ (°/oo)	δD (°/oo)	$\delta^{18}O$ (°/oo)
2,-.Bhagirathi	-61	-9.6		
3,26.Ganga	-61	-9.2	-70	-11.5
1,-.Yamuna	-51			
8,28.Ghaghara	-54	-8.4	-70	- 9.4
18,32.Gandak	-63	-8.9	-66	-10.2
22,36.Brahmaputra	-65+		-37++	
23,-.Manas			-41++	- 6.6

δD and $\delta^{18}O$ values are expressed w.r. to SMOW standard.

* Sample Code indicates Station Nos. and River, to be used in conjunction with Figure III-1 and Tables III-1, 2 and 3.

\+ Sample collected during Lean Flow, December 82 (Table III-3)

++Samples collected during Moderate Flow, April 82 (Table III-3)

Table V-2. δD and $\delta^{18}O$ variations in Lowland Rivers

Sample Code*	Lean Flow, March 82		Peak Flow, Sept. 82	
	δD (‰)	$\delta^{18}O$ (‰)	δD (‰)	$\delta^{18}O$ (‰)
5,24.Yamuna	-50	-7.8	-60	
10.-.Yamuna	-40	-6.3		
12,30.Yamuna	-27 (-28)+	-3.3	-54	-8.2
6,25.Chambal	-19	-2.4	-19	-3.5
9,-. Betwa	-29	-3.6		
15,34.Son	-27	-2.9	-49	-7.8
14,-. Gomti	-48	-7.1		

δD and $\delta^{18}O$ values are expressed w.r. to SMOW standard

*Sample Code indicates Station Nos. and River, to be used in conjunction with Figure III-1 and Table III-2

+ Number in parenthesis indicates δD value during Moderate Flow, December 1982

Figure V - 1.

Seasonal variation in D/H isotopic composition (expressed as δD) of the highland and lowland rivers.

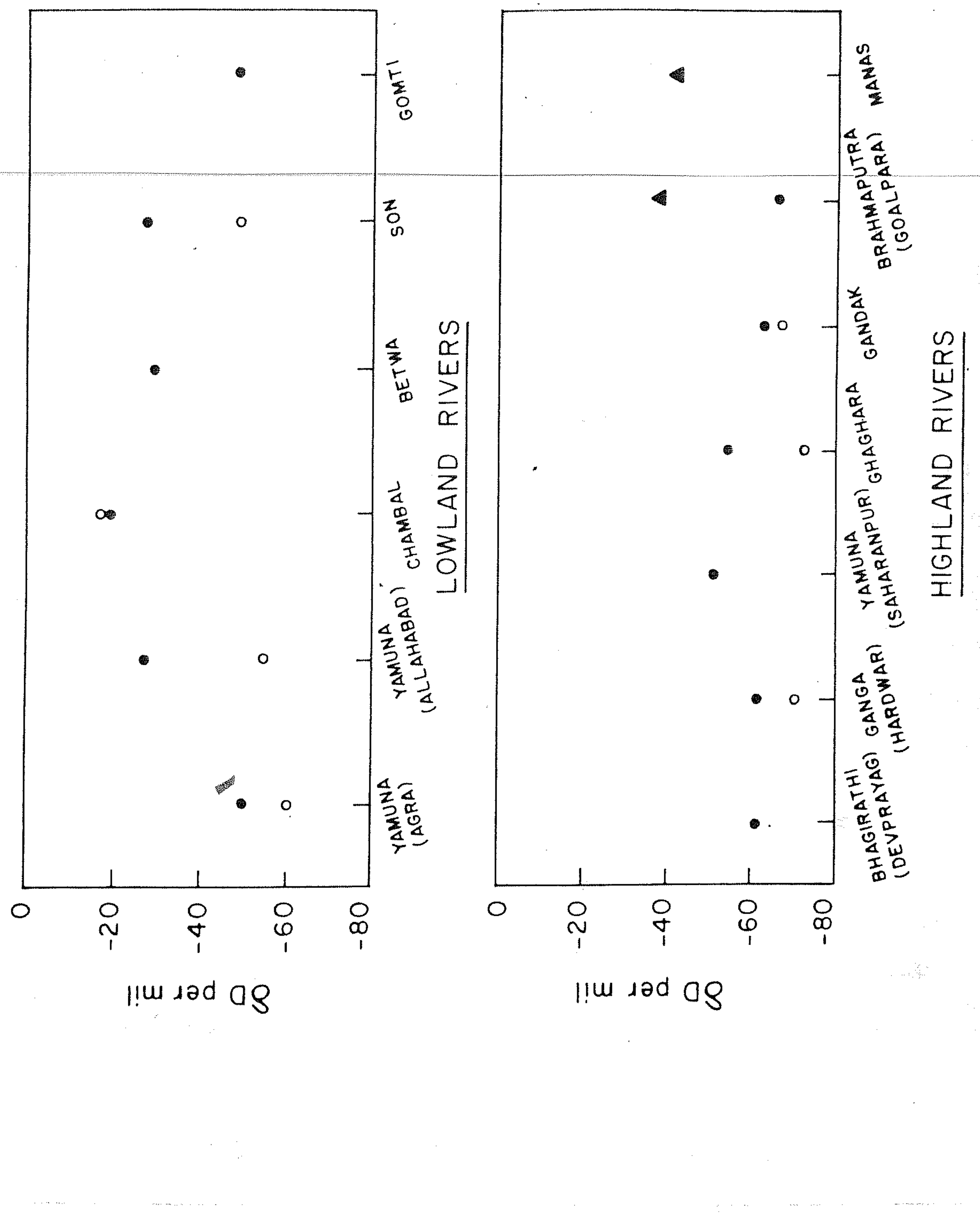
Symbol key

● Lean flow, March 1982

○ Peak flow, September 1982

▲ Moderate flow, December 1982

Figure V - 1


LOWLAND RIVERS
δD per mil
0
-20
-40
-60
-80
YAMUNA (AGRA)
YAMUNA (ALLAHABAD)
CHAMBAL
BETWA
SON
GOMTI
HIGHLAND RIVERS
δD per mil
0
-20
-40
-60
-80
BHAGIRATHI (DEVPRAYAYAG)
GANGA (HARDWAR)
YAMUNA (SAHARANPUR)
GHAGHARA
GANDAK
BRAHMAPUTRA (GOALPARA)
MANAS

being -9.4 $^{o}/oo$ and -11.5 $^{o}/oo$, the isotopically lighter sample collected from the Ganga (at Hardwar). The isotopic composition of these river waters is very similar to that of the precipitation samples during south-west monsoon (July to September), collected at New Delhi (IAEA, 1975). This suggests that the isotopic imprint of these surface waters during peak discharge represent the direct run-off of seasonal precipitation.

During lean flow in summer months, Ganga (up to Hardwar), Ghaghara and Gandak show a slight enrichment in both Deuterium and Oxygen-18 contents. The δD values range between -54 $^{o}/_{oo}$ to -63 $^{o}/_{oo}$ and $\delta^{18}O$ ranges between -8.4 $^{o}/_{oo}$ to -9.2 $^{o}/_{oo}$, Table V-1. This seasonal variation most probably results due to the variations in the isotopic composition of head waters (precipitation and/or snow-melt water) or that caused by evaporation effects from the rivers in the downstream areas. More detailed sampling along the course of the rivers and that of the head waters is required to supplement these observations. The amplitude of seasonal variation is more pronounced in the Ghaghara River, the δD value increases from -70 $^{o}/_{oo}$ during peak flow to -54 $^{o}/_{oo}$ during lean flow in summer months. This enrichment of deuterium in the Ghaghara

River during summer months most likely results from evaporation effects during its flow through a large dam upstream of the sample site. It is interesting to note that in Brahmaputra River which is mainly fed by precipitation all through the year, the δD value increases from -65 ‰ during winter (December 1982) to -37 ‰ during summer (April 1982), Table V-1. One likely explanation for the observed seasonal trend in the δD value, is due to the variation in Deuterium content of precipitation i.e. higher heavy isotope content occurring during summer months and lower one during the winter (Dansgaard, 1953).

The lowland rivers show large seasonal and regional variations in δD and $\delta^{18}O$ values, Table V-2. During peak discharge conditions (occurring during south-west monsoon), δD varies from -19 ‰ to -60 ‰ , the values being significantly higher than those of the highland rivers. The sources which can contribute to the enrichment of Deuterium in the lowland rivers: (i) isotopically heavier precipitation in the lowland river drainage basins, (ii) effluent seepage of ground waters and (iii) the evaporation effects. If one assumes that the isotopic composition of precipitation at Delhi (IAEA, 1975) represents the average isotopic composition of the local precipitation in these drainage basins, then only (ii) and (iii) can contribute to the observed enrichment. However, more data is required to quantify the relative contributions from different hydrologic regions. During lean flow in summer months, δD and $\delta^{18}O$ values are considerably high compared to that during peak flow. A plot of δD versus $\delta^{18}O$ for seven data points (Table V-2) during lean flow, yield the relation :

$$\delta D(‰) = (5.2 \pm 0.4)\, \delta^{18}O - 9.3 \text{ ; corr.coeff.} = 0.98.$$

The slope (5.2±0.4) of the best fit line when compared with the meteoric water line, $\delta D = 8\delta^{18}O + 10$, suggests that the isotopic enrichment in the lowland rivers during summer months (lean flow) is mainly caused by the evaporation effects. All the lowland rivers have large reservoir and dam systems constructed for irrigation purposes upstream of the sample sites. These dams serve as the sites for evaporation.

The Ganga River along its course receives large number of tributaries and hence the D/H and $^{18}O/^{16}O$ isotopic composition along the course is dictated by the mixing volumes of the various tributaries (with their characteristic isotopic composition), and by evaporation effects. The downstream and seasonal variations in δD and $\delta^{18}O$ values in the Ganga main channel are shown in Table V-3 and Figure V-2. During lean flow in summer months the downstream variation in the Ganga main channel are conspicuously evident. At Devprayag (sample representing the head waters) the δD value is -61 ‰and about 1200 km downstream after the confluence of the Yamuna δD value increases to -28 ‰ . Further downstream the δD value tends to decrease after the confluence of the Ghaghara and Gandak Rivers which are isotopically lighter at the confluence point compared to the main channel. Based on a simple mixing model it can be inferred that these downstream variation in δD values, during lean flow, is due to the mixing of the various tributaries with the Ganga main channel. However, during peak discharge conditions the downstream variation in D/H isotopic composition of the Ganga main channel are smoothed out and the isotopic composition along the course closely approaches that of the seasonal precipitation. The data on the δD values in the Brahmaputra River are few to analyse for its downstream variation, Table V-4. However, the seasonal variation is conspicuously evident, δD values are significantly higher during summer months compared to those of winter months.

Table V-3 δD and $\delta^{18}O$ variations in Ganga main stream

Sample Code*	Lean Flow, March 82		Peak Flow, Sept 82	
	$\delta D(^{o}/_{oo})$	$\delta^{18}D(^{o}/_{oo})$	$\delta D(^{o}/_{oo})$	$\delta^{18}O(^{o}/_{oo})$
2,- .Devprayag	-61	-9.6		
3,26.Hardwar	-61	-9.2	-70	-11.5
4,35.Garhmukteswar	-51		-73	
7,27.Kanpur	-37		-69	
11,29.Allahabad	-39		-69	
13,31.Varanasi	-28 (-39)+		-55	
16,- .Upstream Patna	-35			
17,33.Downstream Patna	-39 (-41)	-3.8	-73	-10.6

δD and $\delta^{18}O$ values are expressed w.r. to SMOW standard.

*Sample Code indicates Station Nos. and Location, to be used in conjunction with Figure III-1 and Table III-1

+Numbers in parentheses indicate δD values during Moderate Flow, December 1982

Figure V - 2

Downstream and seasonal variations in D/H isotopic composition (expressed as δD) of the Ganga main channel.

Figure V - 2

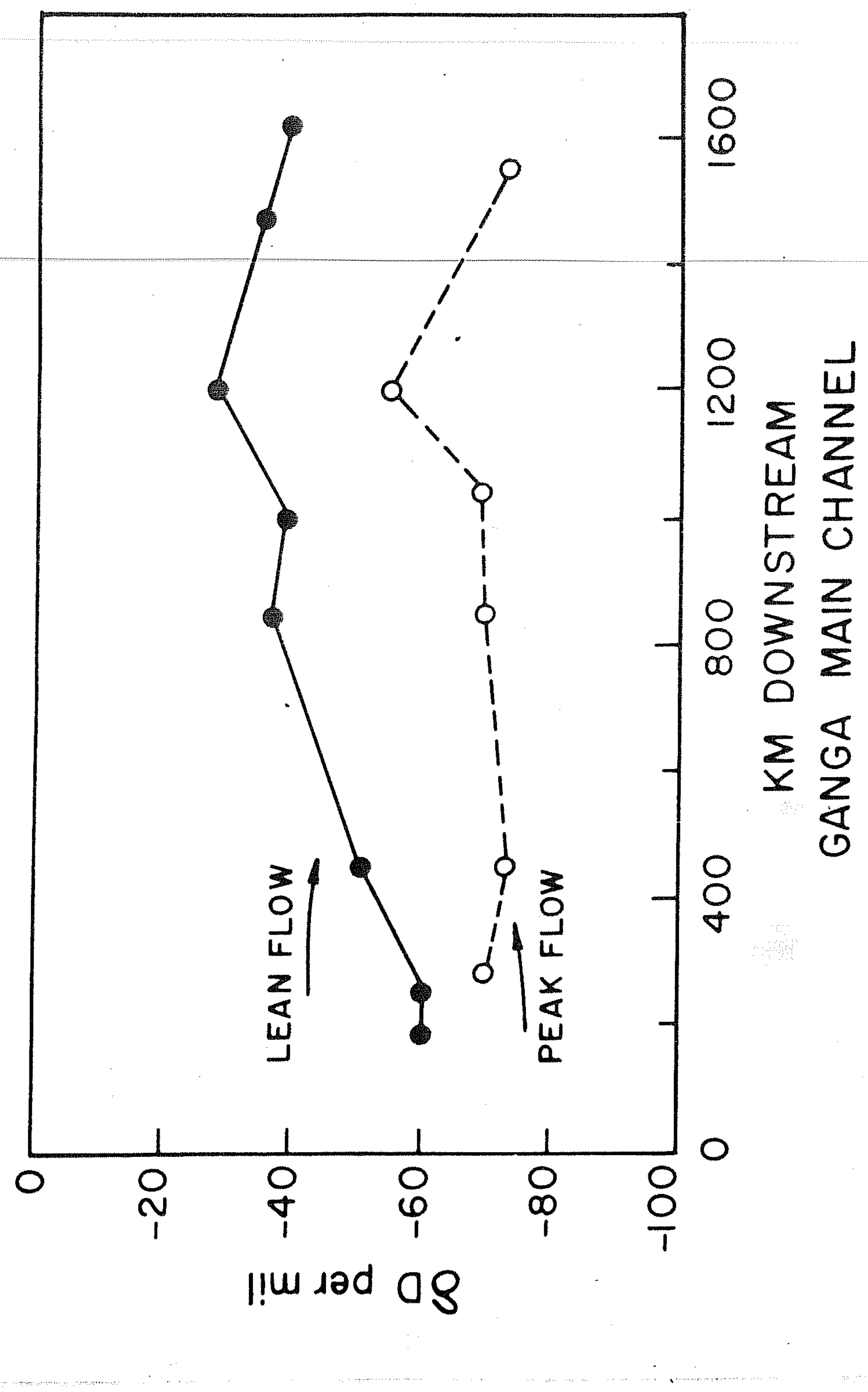

δD per mil
0
-20
-40
-60
-80
-100
0
400
800
1200
1600
KM DOWNSTREAM
GANGA MAIN CHANNEL
LEAN FLOW
PEAK FLOW

Table V-4. δD variations in Brahmaputra River

Sample Code*	Moderate Flow, April 82 $\delta D (^{o}/_{oo})$	Lean Flow, Dec 82 $\delta D (^{o}/_{oo})$
20.-.Dibrugarh	-46	
21.37.Gauhati	-39	-66
22.36.Goalpara	-37	-65

* Sample Code indicates Station Nos. and Location, to be used in conjunction with Figure III-1 and Table III-3

The isotopic composition of the river waters analysed in this study yield the following relation between δD and $\delta^{18}O$, Figure V-3:

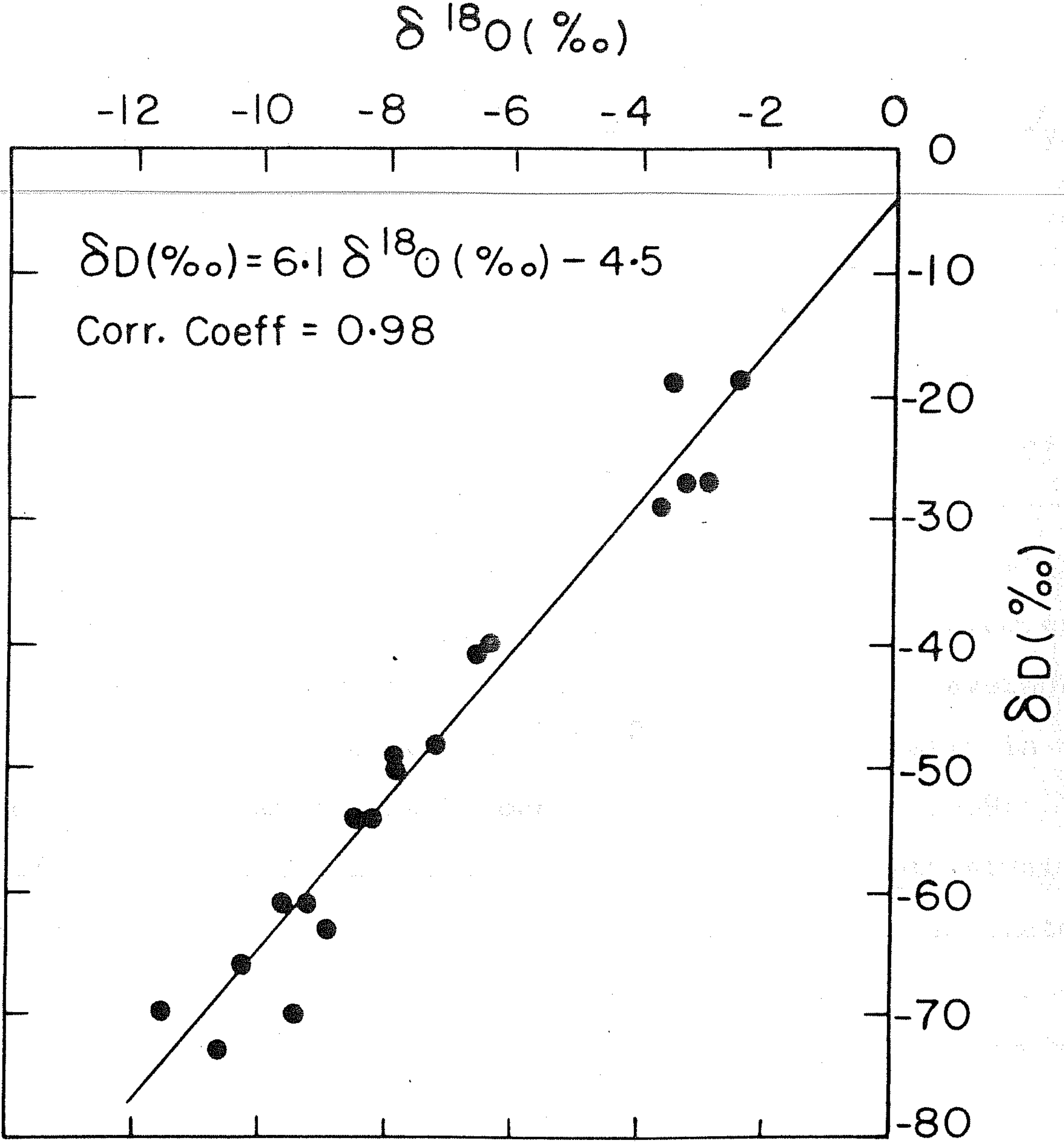
$\delta D(‰) = 6.1\ \delta^{18}O - 4.5$; (corr.coeff. = 0.98, n=19) .

Both the slope and the intercept differ from that of the meteoric water line (Craig, 1961). The lower slope (Figure V-3) for the linear relation between δD and $\delta^{18}O$ is an indication of evaporation losses. The world-wide isotope data of precipitation (IAEA, 1981) show that the regional precipitation lines from semi-arid and arid regions have a slope of less than 8 on the δD versus $\delta^{18}D$ diagram. More data on isotopic composition of these rivers and that of local precipitation in these river drainage basins are required to examine the factors controlling the δD - $\delta^{18}O$ relation.

Figure V - 3.

Relationship between δD and $\delta^{18}O$ values in the seasonal river water samples within the Ganga and Brahmaputra River basins.

Figure V - 3



δ 18O (‰)
-12
-10
-8
-6
-4
-2
0
δD(‰) = 6.1 δ18O (‰) - 4.5
Corr. Coeff = 0.98
0
-10
-20
-30
-40
-50
-60
-70
-80
δD (‰)

V.2. Isotopes of Uranium and Thorium in river waters and suspended sediments

V.2.(a) Introduction

The concentration of uranium and $^{234}U/^{238}U$ activity ratio in river waters and fluvial sediments are important parameters needed to construct the marine geochemical balance of this natural radionuclide. Furthermore, because uranium isotopes are the progenitors of a series of radioactive nuclides which are used commonly as chronometers to study earth surface processes, the study of uranium isotopes in natural waters continues to be of considerable interest to geochemists. A number of studies have been made which attempt to estimate the 'best average' concentration of uranium and $^{234}U/^{238}U$ activity ratio in world rivers (Moore, 1967; **Bhat** and Krishnaswami, 1969; Turekian and Chan, 1971; Cherdyntsev, 1971; Sackett et al, 1973; Ku et al, 1977; Borole et al, 1982). These estimates show a general agreement in the average uranium concentration in river waters, 0.3 to 0.6 µg/l.

The geographical variability of uranium content in river waters and its interrelationship with known geochemical parameters such as HCO_3^- and total dissolved solids has been well documented. Broecker (1974) and Mangini et al (1979) suggested that the uranium concentration in surface waters depends on the concentration of HCO_3^- in river water because of the importance of the uranyl - carbonate ion in the solution. Turekian and Cochran (1978) have suggested that the correlation of uranium with total dissolved solids in river water represents a general control on uranium during weathering processes. Bhat and Krishnaswami (1969) also report a correlation between uranium and total dissolved solids. Similarly, on the basis of the relationship between uranium and total dissolved solids, Borole et al (1982) derive a mean uranium content of 0.25 µg/l and the ^{238}U flux of $0.9X10^{10}$ g/yr to the oceans via rivers.

The fractionation of ^{234}U from its parent ^{238}U that occurs during weathering processes is conspicuously reflected in the $^{234}U/^{238}U$ activity ratio of river waters, the average ratio is about 1.2 to 1.3 (Cherdyntsev, 1971; Osmond and Cowart, 1976 and Borole et al 1982).

Studies on the geochemistry of uranium isotopes in the Ganga and Brahmaputra Rivers are limited to the work of Bhat and Krishnaswami (1969) and Bhat (1970). Their work covers only the Ganga River and that too its main channel, where they have reported the downstream and seasonal variations in the concentration of uranium and $^{234}U/^{238}U$ activity ratios. These consideration led me to undertake a detailed study of the uranium isotope systematics in the Ganga and Brahmaputra Rivers and their tributaries. This work was undertaken with a view to provide more information on the behaviour of uranium isotopes in different weathering environments. Prior to this work, no data was available on the concentration of uranium and $^{234}U/^{238}U$ activity ratios in any of the tributaries of the Ganga. Also, for the first time samples from the Brahmaputra River have been analysed for uranium isotopes.

V.2.(b) Dissolved ^{238}U and $^{234}U/^{238}U$ activity ratios in the Ganga and Brahmaputra Rivers

Samples from the Ganga main channel, its tributaties and from the Brahmaputra River were collected during March 1982, September 1982 and December 1982, the relevant details are given in Chapter III. The concentration of ^{238}U and $^{234}U/^{238}U$ activity ratio have been measured in water and suspended sediments to evaluate the interrelationship between them and to obtain the fluxes of these nuclides to the estuaries. Another aspect of this study has been to evaluate the seasonal variation in uranium content of the individual rivers.

The data for the dissolved ^{238}U concentration and the $^{234}U/^{238}U$ activity ratios in the lowland and highland tributaries of the Ganga main channel are given in Table V-5. The ^{238}U concentration in the tributaries during peak flow (September 1982) range between 0.44-2.8 µg/l and that during lean flow (March 1982) range between 0.73 - 4.4 µg/l. The ^{238}U concentration in peak flow is lower by a factor of two than that in the lean flow

The seasonal variation in ^{238}U concentration is more pronounced in the lowland tributaries , an observation similar to the seasonal variation in their major ion composition. Of the lowland tributaries, only Chambal has been analysed previously for uranium concentration (Pillai et al, 1966). Their data on the concentration of uranium in Chambal River, 0.9 to 1.7 µg/l, show a remarkable agreement with the results obtained in the present study, Table V-5.

The distinct difference between the lowland and highland tributaries is in the $^{234}U/^{238}U$ activity ratios. In the lowland tributaries, activity ratios vary from 1.16 ± 0.03 to 1.84 ± 0.03 which are significantly higher than that of the highland rivers, 1.02 ± 0.02. A probable cause for these high activity ratios in the lowland tributaries is the differences in the geology of their drainage basins. The

Table V-5. Ganga Tributaries: Seasonal variation in dissolved ^{238}U concentration, $^{234}U/^{238}U$ activity ratio and Σ Cations

Sample Code*	Lean Flow, March 1982			Peak Flow, September 1982		
	$^{234}U/^{238}U$ (A.R.)	^{238}U (μg/l)	ΣCations (mg/l)	$^{234}U/^{238}U$ (A.R.)	^{238}U (μg/l)	ΣCations (mg/l)
			Lowland Tributaries			
5,24.Yamuna	1.08±0.02	2.41±0.07	55.8	1.03±0.01	2.73±0.07	78.7
10,- .Yamuna	1.09±0.02	3.80±0.16	80.9			
12,30.Yamuna	1.30±0.02 (1.39±0.02)	4.37±0.17 (3.60±0.09)	114.2 (121.3)+	1.24±0.02	1.36±0.03	41.6
6,25,Chambal	1.52±0.04	1.87±0.09	85.9	1.41±0.02	0.88±0.01	57.1
9,-.Betwa	1.84±0.03	2.99±0.12	93.6			
15,34.Son	1.21±0.02	0.73±0.01	44.8	1.16±0.03	0.44±0.01	28.5
			Highland Tributaries			
8,28.Ghaghara	0.99±0.03	1.84±0.09	49.8	1.02±0.02	1.60±0.03	31.3
18,32.Gandak	1.04±0.01	3.29±0.12	46.5	1.03±0.01	2.20±0.04	37.3

*Sample Code indicates Station Nos. and tributary, to be used in conjunction with Figure III-1 and Table III-2.

+ Numbers in parentheses represent the values during Moderate Flow, December 1982.

lowland tributaries predominantly drain through gneissic rocks where as the highland tributaries drain through sedimentary rocks.

The data on the seasonal and downstream variations in the concentration of ^{238}U and $^{234}U/^{238}U$ activity ratio in the Ganga main channel are presented in Table V-6. The observed trends (Table V-6) are very similar to the data reported by Bhat and Krishnaswami (1969). During lean flow, the downstream variations in the ^{238}U concentration and activity ratio are clearly evident. For example, the activity ratio increases downstream after the confluence of the Yamuna (at Allahabad) and further downstream the activity ratio decreases with the influx of the Ghaghara, Son and Gandak Rivers. Similarly, the ^{238}U concentration in the Ganga main channel increases or decreases after the confluence of the tributaries with the main channel. It is interesting to note that the activity ratios do not show any significant seasonal variation whereas ^{238}U concentration in the main channel decreases by a factor of about 2 to 3 during peak flow conditions. Based on the simple mixing model it has been evaluated that the transport of uranium in the Ganga River system is conservative. The observed and predicted ^{238}U concentrations in the

Table V-6 Ganga main channel: Downstream and seasonal variations in dissolved ^{238}U concentration, $^{234}U/^{238}U$ activity ratio and Σ Cations

Sample Code*	Lean Flow, March 1982			Peak Flow, September 1982		
	$^{234}U/^{238}U$ (A.R.)	^{238}U (μg/l)	ΣCations (mg/l)	$^{234}U/^{238}U$ (A.R.)	^{238}U (μg/l)	ΣCations (mg/l)
2, –.Devprayag	1.08±0.02	0.92±0.03	20.6			
3,26.Hardwar	1.05±0.02	1.21±0.04	26.7	1.05±0.02	1.33±0.03	20.7
4,35.Garhmuk-teshwar	0.98±0.02	2.69±0.09	43.0	1.02±0.01	1.88±0.03	28.3
7,27.Kanpur	1.01±0.02	3.72±0.13	61.1	1.05±0.01	3.01±0.05	39.8
11,29.Allahabad	1.07±0.01	5.63±0.23	63.8	1.04±0.02	2.31±0.05	36.1
13,31.Varanasi	1.17±0.02 (1.25±0.02)+	4.59±0.24 (4.20±0.11)	96.5 (99.0)	1.12±0.02	1.63±0.03	38.4
16, –.Upstream Patna	1.17±0.02	5.29±0.21	87.4			
17,33.Downstream Patna	1.10±0.02 (1.10±0.01)	3.65±0.16 (3.53±0.07)	77.4 (72.8)	1.08±0.02	1.29±0.03	35.7

*Sample Code indicates Station Nos. and Location, to be used in conjunction with Figure III-1 and Table III-1.

+Numbers in parentheses represent the values during Moderate Flow, December 1982

Table V-7 The observed and predicted ^{238}U concentration in the Ganga main channel after the confluence of the tributaries

Confluence Site	River	Relative discharge	Average ^{238}U Concentration* (µg/l) Observed	Predicted
Allahabad	Ganga	0.39	2.87±0.06	
	Yamuna	0.61	1.87±0.04	
	Ganga+	1.0	2.13±0.05	2.26±0.03
Patna	Ganga	0.48	2.25±0.04	
	Ghaghara	0.28	1.64±0.03	
	Son	0.09	0.49±0.01	
	Gandak	0.15	2.40±0.04	
	Ganga+	1.0	1.69±0.04	1.94±0.02

* Discharge-weighted average concentrations are calculated using the relation $\bar{C} = 0.83C_p + 0.17\ C_L$, refer to section IV-4.(g).

\+ Ganga after the confluence of the tributaries.

Table V-7 The observed and predicted ^{238}U concentration in the Ganga main channel after the confluence of the tributaries

Confluence Site	River	Relative discharge	Average ^{238}U Concentration* (μg/l)	
			Observed	Predicted
Allahabad	Ganga	0.39	2.87±0.06	
	Yamuna	0.61	1.87±0.04	
	Ganga^{+}	1.0	2.13±0.05	2.26±0.03
Patna	Ganga	0.48	2.25±0.04	
	Ghaghara	0.28	1.64±0.03	
	Son	0.09	0.49±0.01	
	Gandak	0.15	2.40±0.04	
	Ganga^{+}	1.0	1.69±0.04	1.94±0.02

* Discharge-weighted average concentrations are calculated using the relation $\bar{C} = 0.83C_p + 0.17\ C_L$, refer to section IV-4.(g).

\+ Ganga after the confluence of the tributaries.

Table V-8 Brahmaputra River: Downstream and seasonal variations in dissolved ^{238}U concentration, $^{234}U/^{238}U$ activity ratio and Σ Cations.

Sample Code*	Moderate Flow, April 1982			Lean Flow, December 1982		
	$^{234}U/^{238}U$ (A.R.)	^{238}U (μg/l)	ΣCations (mg/l)	$^{234}U/^{238}U$ (A.R.)	^{238}U (μg/l)	ΣCations (mg/l)
20, –.Dibrugarh	1.02±0.02	0.51±0.01	22.7			
21,37.Gauhati	1.01±0.02	0.45±0.01	19.7	1.03±0.02	1.36±0.03	32.7
22,36.Goalpara	1.04±0.02	0.49±0.01	20.0	1.04±0.02	1.52±0.03	33.4

*Sample Code indicates Station Nos. and Location, to be used in conjunction with Figure III-1 and Table III-3.

Ganga main channel, after the confluence of the tributaries, are shown in Table-7.

The concentration of ^{238}U and $^{234}U/^{238}U$ activity ratio have been measured for the first time in the Brahmaputra River (Table V-8). Unlike in the Ganga main channel, the $^{234}U/^{238}U$ activity ratio does not exhibit any downstream or seasonal variations. However, the ^{238}U concentration shows significant seasonal variation, high values being typical of the lean flow. Based on the relation: $\bar{c} = 0.86\ C_P + 0.14\ C_L$ (where $\bar{c}$ is the discharge-weighted average concentration, C_P and C_L are concentrations during peak and lean flows, respectively), the average ^{238}U concentration in the Brahmaputra River (at Goalpara) is computed to be 0.63 μg/l, which is low by a factor of about three compared to that in the Ganga (at Patna).

The average annual flux of uranium transported by the Ganga, its tributaries and the Brahmaputra River is given in Table V-9. A comparison of the data shows that the Ganga River transports annually twice the amount of uranium to the ocean than that transported by the Brahmaputra River. Together, these two rivers transport annually about

Table V-9 Dissolved flux of uranium transported by the Ganga, its tributaries and the Brahmaputra River

River	Discharge (10^{12}L/yr)	^{238}U Concentration*	Dissolved flux (10^{8}g/yr)	Reference
Ganga[1]	59	2.87	1.7	Present study
Yamuna	93	1.87	1.7	
Chambal	30	1.05	0.3	
Ghaghara	94	1.64	1.5	
Son	32	0.49	0.2	
Gandak	52	2.40	1.3	
Ganga[2]	364	1.69	6.2	
Brahmaputra[3]	510	0.63	3.2	
Amazon	6400	0.03	1.9	Moore(1967)
World Rivers	31400	0.3	94	Borole et al.(1982)

*Discharge-weighted average concentrations

1.Ganga at Allahabad, before confluence of Yamuna

2.Ganga at Patna, after confluence of Ghaghara, Son and Gandak

3.Brahmaputra at Goalpara

10 % of the total dissolved flux of uranium carried by the world rivers. Furthermore, of the major rivers for which data are available, the Ganga-Brahmaputra ranks first for the annual input of uranium to the oceans.

The ^{238}U content of the rivers within the Ganga and Brahmaputra Basins show a linear relationship with ΣCations (Na+K+Mg+Ca), Figure V-4. The statistical parameters of the regression line for the relation:

$$^{238}U(\mu g/\ell) = m \times \Sigma\text{Cations (mg/l)} + C$$

are given in Table V-10. The average $^{238}U/\Sigma$ Cations ratio

Table V-10. Regression parameters for the linear relationship between ^{238}U and Σ Cations

River	Corr. Coeff.	Slope (m)	Y-intercept (c)
Ganga main channel	0.86 (N=16)+	$(4.8 \pm 0.7)\times10^{-2}$	0.37
Highland Rivers	0.81 (N=9)	$(5.9 \pm 1.6)\times10^{-2}$	-0.27
Lowland Rivers	0.87 (N=11)	$(3.9 \pm 0.7)\times10^{-2}$	-0.53
Brahmaputra River	0.99 (N=5)	$(7.6 \pm 0.7)\times10^{-2}$	-1.1
All Samples	0.78	$(4.0 \pm 0.8)\times10^{-2}$	0.28

+ N = number of samples

Figure V - 4

The linear relationship between ^{238}U (µg/l) and ΣCations (Na+K+Mg+Ca, mg/l) in samples from the Ganga main channel, highland rivers, lowland rivers and Brahmaputra River. Regression statistics for the linear relation are given in Table V-10

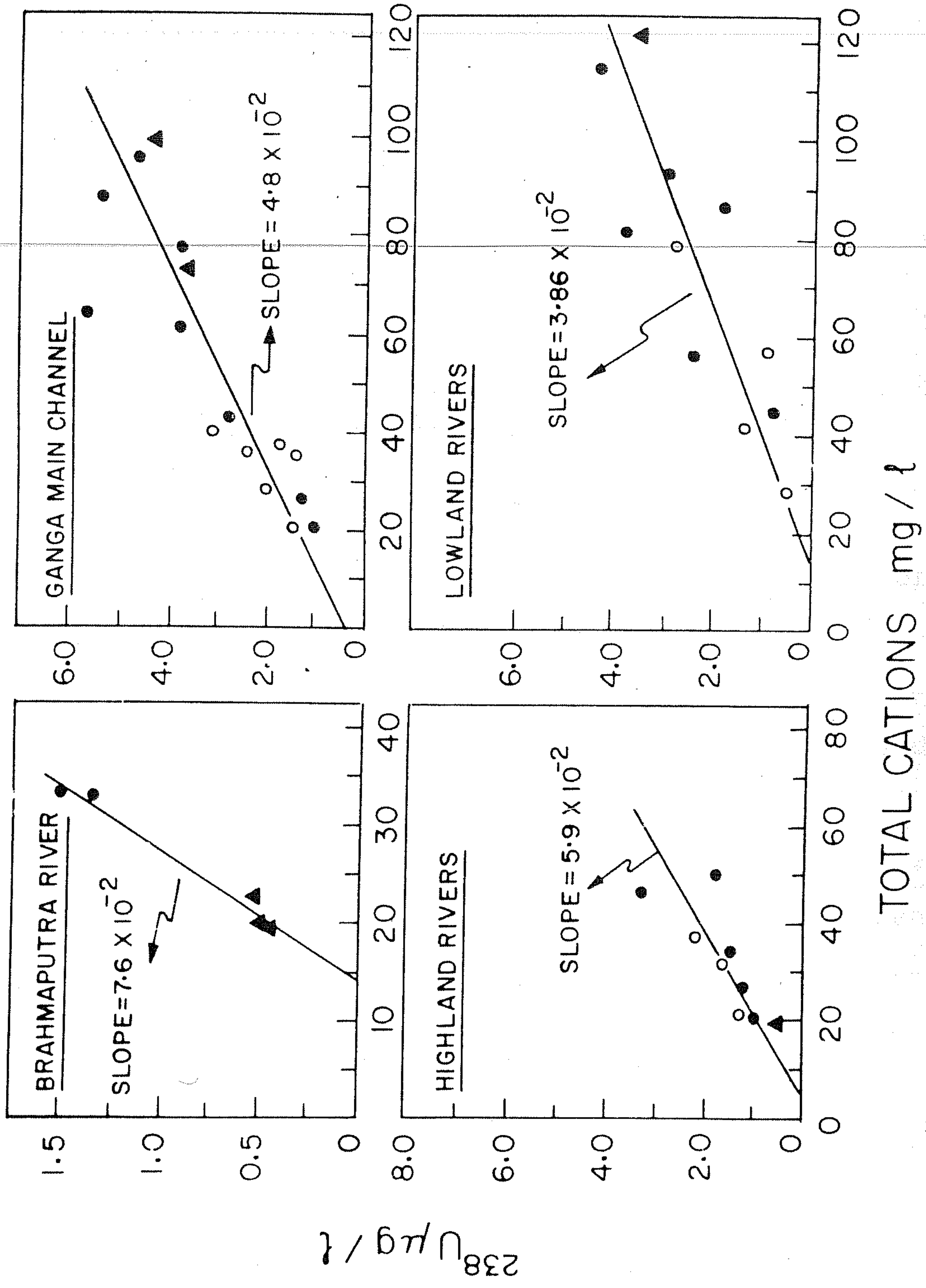
Symbol key

● Lean flow

○ Peak flow

▲ Moderate flow

Figure V - 4


BRAHMAPUTRA RIVER
SLOPE = 7·6 X 10^{-2}
GANGA MAIN CHANNEL
SLOPE = 4·8 X 10^{-2}
HIGHLAND RIVERS
SLOPE = 5·9 X 10^{-2}
LOWLAND RIVERS
SLOPE = 3·86 X 10^{-2}
^{238}U µg / ℓ
TOTAL CATIONS mg / ℓ
1.5
1.0
0.5
0
8.0
6.0
4.0
2.0
0
10
20
30
40
20
40
60
80
120
100

(deduced from the slope of the best fit lines, Table V-10) is 4.0 X10^{-2} mg U/g ΣCations, very similar to that observed in suspended sediments of these rivers (5.4X10^{-2}, ΣCations in suspended sediments is deduced from the data given in Appendix) suggesting congruent dissolution for major cations and uranium.

V.2.(c) Concentrations of U and Th isotopes in suspended sediments of the Ganga and Brahmaputra Rivers

In order to characterise the high intensity of weathering of uranium in the Ganga and Brahmaputra River drainage basins, the concentrations of ^{238}U, ^{234}U, ^{232}Th, ^{228}Th nuclides have been measured in the suspended sediments. An inspection of the data in Tables V-11, 12 and 13 show that in all the suspended sediments for which U isotopes have been analysed have ^{234}U/^{238}U activity ratios very close to equilibrium values, the activity ratio range between 0.95$\pm$0.04 to 1.04$\pm$0.03. The average concentrations of ^{238}U and ^{232}Th in suspended sediments are 4 ppm, 17.6 ppm, respectively and Th/U weight ratio is 4.4. Using their average concentration in suspended sediments, the suspended fluxes of ^{238}U and ^{232}Th via Ganga and Brahmaputra Rivers have been computed, Table V-14.

Table V-11. Ganga main stream: Concentrations of U and Th isotopes in suspended sediments

Sample Code**	$\frac{^{234}U}{^{238}U}$*	U ppm	Th ppm	^{230}Th dpm/g	^{228}Th dpm/g	$\frac{^{228}Th}{^{232}Th}$*	$\frac{^{230}Th}{^{232}Th}$*	$\frac{^{230}Th}{^{238}U}$*	Th/U wt.ratio
26.Hardwar	1.03 ±.02	3.73 ±.07	11.0 ± .1	2.69 ±.03	2.81 ±.04	1.02 ±.02	0.98 ±.02	0.96 ±.02	2.95 ±.06
35.Garhmuk-teshwar	1.00 ±.02	4.70 ±.09	18.2 ± .2	3.82 ±.04	4.67 ±.04	1.03 ±.01	0.84 ±.01	1.09 ±.02	3.87 ±.08
27,Kanpur	0.99 ±.01	4.48 ±.07	20.3 ± .2	4.40 ±.06	5.02 ±.06	0.99 ±.02	0.87 ±.02	1.31 ±.03	4.53 ±.09
29.Allahabad	0.98 ±.01	5.05 ±.08	20.4 ± .2	4.73 ±.06	5.44 ±.06	1.07 ±.02	0.93 ±.02	1.25 ±.03	4.04 ±.08
31.Varanasi	1.02 ±.02	3.55 ±.07	16.8 ± .2	3.24 ±.04	4.37 ±.05	1.04 ±.02	0.77 ±.01	1.22 ±.03	4.73 ±.11
33.Patna	1.01 ±.02	3.71 ±.07	18.0 ± .2	3.45 ±.05	4.47 ±.05	1.00 ±.02	0.77 ±.01	1.24 ±.03	4.85 ±.11

**Sample Code to be used in conjunction with Figure III-1 and Table III-1

* Activity ratio

Table V-12. Ganga Tributaries: Concentrations of U and Th isotopes in suspended sediments

Sample Code**	$\frac{^{234}U}{^{238}U}$*	U ppm	Th ppm	^{230}Th dpm/g	^{228}Th dpm/g	$\frac{^{228}Th}{^{232}Th}$*	$\frac{^{230}Th}{^{232}Th}$*	$\frac{^{230}Th}{^{238}U}$*	Th/U wt.ratio
24.Yamuna	1.00 ±.02	4.72 ±.08	18.9 ± .2	3.54 ±.05	5.32 ±.06	1.13 ±.02	0.75 ±.01	1.00 ±.02	4.00 ±.08
30.Yamuna	1.00 ±.02	3.27 ±.07	16.0 ± .2	2.86 ±.04	4.68 ±.05	1.17 ±.02	0.72 ±.01	1.17 ±.03	4.89 ±.12
25.Chambal	1.09 ±.03	2.09 ±.04	12.2 ± .2	2.14 ±.03	2.91 ±.04	0.95 ±.02	0.70 ±.01	1.36 ±.03	5.84 ±.14
34.Son	1.00 ±.02	6.81 ±.12	21.5 ± .2	5.20 ±.06	5.65 ±.07	1.05 ±.02	0.97 ±.02	1.02 ±.02	3.16 ±.07
14.Gomti	1.02 ±.03	3.21 ±.09	20.8 ± .4	3.32 ±.08	5.16 ±.10	0.99 ±.02	0.64 ±.02	1.38 ±.05	6.48 ±.22
28.Ghaghara	0.97 ±.02	4.29 ±.08	20.0 ± .2	3.82 ±.04	4.95 ±.05	0.99 ±.01	0.76 ±.01	1.19 ±.03	4.66 ±.10
32.Gandak	0.99 ±.01	4.37 ±.07	14.4 ± .1	2.85 ±.03	3.45 ±.03	0.96 ±.01	0.79 ±.01	0.87 ±.02	3.30 ±.06

**Sample Code to be used in conjunction with Figure III-1 and III-2 Table

* Activity Ratio

Table V-13. Brahmaputra River: Concentrations of U and Th isotopes in suspended sediments

Sample Code**	$\frac{^{234}U}{^{238}U}$*	U ppm	Th ppm	^{230}Th dpm/g	^{228}Th dpm/g	$\frac{^{228}Th}{^{232}Th}$*	$\frac{^{230}Th}{^{232}Th}$*	$\frac{^{230}Th}{^{238}U}$*	Th/U Wt. ratio
20.Dibrugarh	0.95 ±.04	2.61 ±.09	14.0 ± .2	2.13 ±.04	3.64 ±.06	1.04 ±.02	0.61 ±.02	1.09 ±.04	5.35 ±.20
22.Goalpara	1.04 ±.03	2.98 ±.07	21.4 ± .3	3.08 ±.06	5.22 ±.09	0.97 ±.02	0.57 ±.02	1.38 ±.04	7.18 ±.20

**Sample Code to be used in conjunction with Figure III-1 and Table III-3

*Activity Ratio

Table V-14. Suspended fluxes of ^{238}U and ^{232}Th transported by the Ganga and Brahmaputra Rivers

	^{238}U	^{232}Th
Average concentration in suspended sediments (µg/g)	4	17.6
Suspended flux* (10^8g/yr)	67	294

*The combined sediment discharge of Ganga and Brahmaputra is 1670 X 10^{12} g/yr (Milliman and Meade, 1983).

The high intensity of weathering of uranium in the Ganga and Brahmaputra River drainage basins can be deduced from the $^{238}U/^{232}Th$ and $^{230}Th/^{232}Th$ activity ratios in the suspended sediments. The plot of ^{230}Th and ^{238}U data (Tables V-11, 12 and 13) show that the ^{230}Th is enriched in suspended sediments by 30 to 40 % compared to ^{238}U, Figure V-5. This disequilibrium is caused by the preferential leaching of U from soils (suspended sediments) and redistribution of ^{230}Th in the suspended sediments during

Figure V - 5

Plot of ^{230}Th (dpm/g) versus ^{238}U (dpm/g) in suspended sediment samples from the Ganga main channel, its tributaries and the Brahmaputra River.

Symbol key:

Ganga main channel:

● Lean flow

○ Peak flow

Ganga Tributaries:

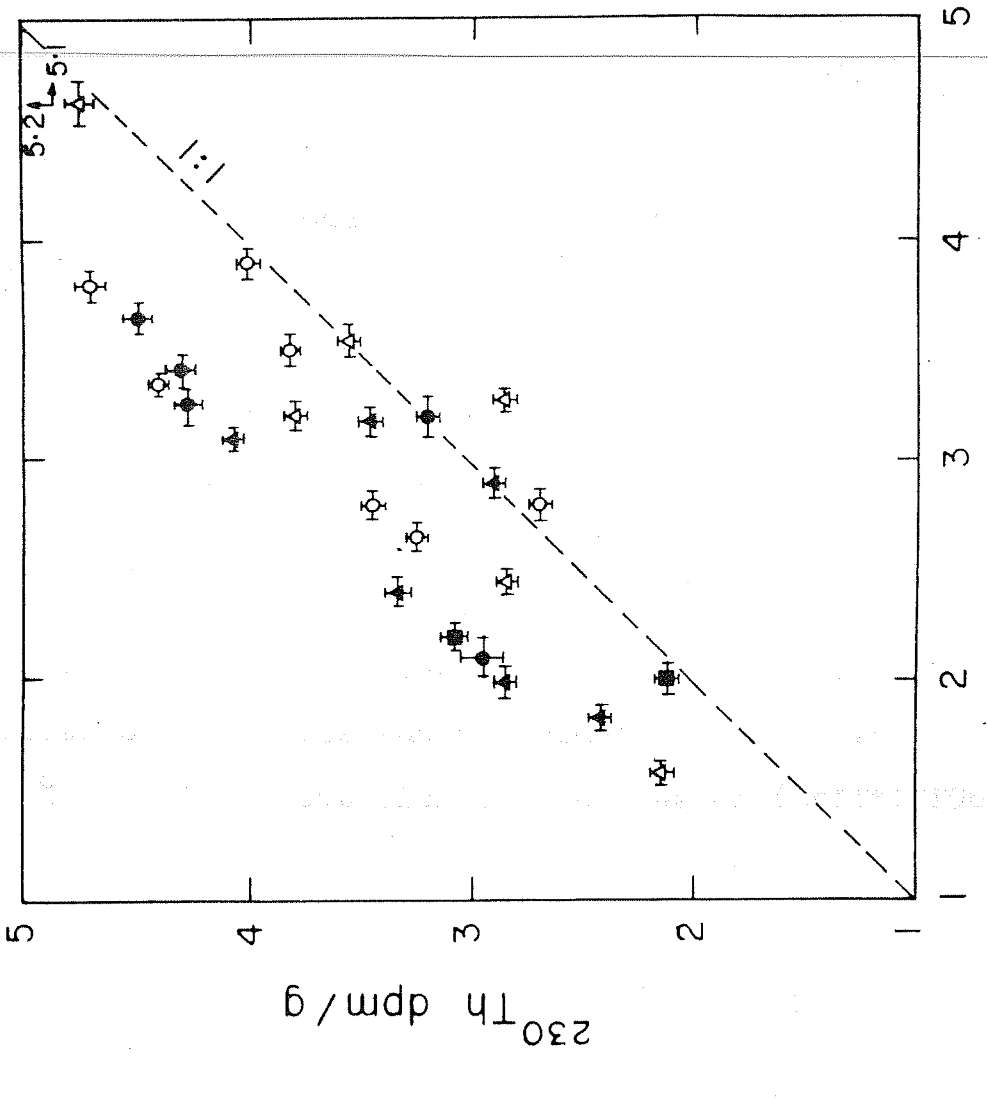
▲ Lean flow

△ Peak flow

Brahmaputra River:

■ Moderate flow

Figure V - 5



weathering processes. Using the average $^{230}Th/^{238}U$ activity ratio as 1.17 and the average concentration of ^{238}U as 3 dpm/g (Tables V-11, 12 and 13), the flux of excess ^{230}Th added to the Bay of Bengal via suspended sediments is computed to be 8.5 X 10^{14} dpm/yr (assuming conservative behaviour of ^{230}Th from Patna to Bay of Bengal). The production rate of ^{230}Th in the entire Bay of Bengal (using 2.2 X 10^{6} km^{2} area and average depth of 3000 m) is 1.5 X 10^{14} dpm/yr, which is lower by a factor of about six than the ^{230}Th excess supplied via Ganga and Brahmaputra fluvial sediments. This comparison suggest that the supply of ^{230}Th excess via fluvial sediments could be very significant on a regional basis. However, on a world ocean scale the contribution of ^{230}Th excess by river suspended sediments is only less than 10 % of its production in ocean water (Scott, 1968).

CHAPTER VI. SUMMARY AND CONCLUSIONS

A detailed geochemical study of the Ganga River, its tributaries and the Brahmaputra River has been carried out with a view to evaluate the major ion chemistry of these rivers in terms of chemical weathering of the rocks and soils of their drainage basins. In addition, the D/H and $^{18}O/^{16}O$ isotopic variations and the abundances of U-Th isotopes (^{238}U, ^{234}U, ^{232}Th, ^{230}Th, ^{228}Th)in these river waters have also been studied. Surface water samples for this geochemical study were collected during March, September and December 1982, representing the lean, peak and moderate flows occurring in these rivers.

The relief and the regional geology and lithology within the Ganga and Brahmaputra River basins are in marked contrast. The regional lithologies of the highland rivers is dominated by lower Paleozoic carbonate series of limestones and dolomites, calcareous shales and quartzites. The published stratigraphy shows occurrence of gypsum and pyritic sediments in their drainage basins. In contrast, the dominant lithologies of the lowland rivers are characterised by Archaean granites, gneissic rocks, Vindhyan sandstones and recent alluvial deposits.

The abundances of major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO_3^-, Cl^-, SO_4^{2-} and SiO_2^o) have been used to evaluate the major ion chemistry of the highland and lowland rivers and the Ganga main channel. In these river basins, the marine contribution of cyclic salts is insignificant relative to chemical weathering. In the highland rivers, Ca^{2+} and Mg^{2+} are the major cations, and together they account for about 90 % of the cations, Mg:Ca ratio is 1:2. Bicarbonate accounts for about 70-90 % of the anions and sulfate is next in abundance. The SO_4:Cl equivalent ratio ranges between 3.5 to 10.7. These observations lead to the conclusion that the chemistry of the highland rivers is dominated by weathering of carbonate rocks. The abundance of SO_4^{2-} in these river waters mainly originate through dissolution of gypsum or via pyrite reduction, an observation consistent with the regional lithologies. The effects of silicate weathering are nowhere pronounced. The TDS content of these rivers varies between 93 to 233 mg/l, low values are typical of the peak flow conditions.

Among the lowland rivers, the major ion chemistry of the Yamuna, Chambal and Gomti Rivers is influenced by the weathering of carbonates, silicates and soil salts in varying proportions. In these rivers, Na^+, Ca^{2+} and Mg^{2+} are equally significant in the cation balance and HCO_3^- accounts for over 70 % of the anions. The SO_4:Cl equivalent ratio varies between 0.5 to 1.1. The major ion composition of these rivers show large seasonal variations. The TDS content varies between 173 to 461 mg/l, low values occurring during peak flow conditions. The $(Na^*+K):TZ^+$ ratio (Na^* signifies sodium corrected for chloride) has been used as an index of silicate weathering in these river drainage basins. The $(Na^*+K):TZ^+$ ratio in these river waters is about 0.2, which seem to suggest that the silicate weathering is of minor importance in these river basins. During peak flow, the chemistry of Yamuna and Chambal Rivers is dominated by carbonate weathering, as evident from the high abundances of Ca^{2+} and HCO_3^- . During lean flow (in summer months), the contribution from alkaline and saline salt-affected soils is more pronounced. This is reflected upon the high abundances of Na^+, Cl^- and SO_4^{2-} during lean flow.

During lean flow, the Betwa River is also characterised by high TDS content, 388 mg/l. However, unlike Yamuna and Chambal Rivers, the effects of silicate weathering in this river basin are more pronounced, $(Na^*+K):TZ^+$ ratio is 0.5. The (Ca+Mg):(Na+K) equivalent ratio is 1:1 and HCO_3^- accounts for about 90 % of the anions. Both Ken and Son

The regional and seasonal variations of δD and $\delta^{18}O$ have been studied, for the first time, in these river waters. During peak flow conditions, the highland rivers show remarkable similarities in δD values, the extreme values being -60 ‰ and -70 ‰, very similar to that of the precipitation samples. This suggests that the isotopic imprint of these surface waters during peak flow represent the direct run-off of seasonal precipitation. During lean flow in summer months, the highland rivers show a marginal enrichment in Deuterium and Oxygen-18 contents. In contrast, the lowland rivers show large seasonal and regional variations in δD and $\delta^{18}O$ values. During peak flow, δD varies from -19 ‰ to -60 ‰ , significantly higher than those of the highland rivers. Several environmental factors such as isotopically heavier precipitation, effluent seepage of groundwaters and the evaporation effects can contribute to the enrichment of Deuterium in the lowland rivers. The relative significance of evaporation losses, and hence the isotopic enrichment, can be deduced from the linear relationship between δD and $\delta^{18}O$ values. A plot of δD and $\delta^{18}O$ values yield a slope 6.1, significantly lower than the slope of the meteoric water line. This seems to suggest that the isotopic enrichment in these waters is mainly caused by evaporation losses from the reservoir and dam systems.

The ^{238}U concentration and $^{234}U/^{238}U$ activity ratio have been measured in water and suspended sediments to evaluate the interrelationship between them and to obtain the fluxes of these nuclides to the estuaries. The dissolved ~~^{238}U concentration shows a linear relationship with~~ ΣCations and the $^{238}U/\Sigma$Cations ratio in these river waters is similar to that in the river suspended sediments suggesting congruent dissolution for major cations and uranium. The distinct difference between the lowland and highland rivers is in the $^{234}U/^{238}U$ activity ratio. In the lowland rivers, activity ratios vary between 1.16±0.03 to 1.84±0.03 which are significantly higher than those of the highland rivers, 1.02±0.02, an observation consistent with the regional lithologies of the drainage basins.

The Ganga and Brahmaputra River constitute the major source of dissolved uranium to the oceans. These two rivers transport annually $9.4X10^8$g of uranium to the Bay of Bengal, about 10 % of the global river input to the oceans. The high intensity of weathering of uranium in the Ganga and Brahmaputra River drainage basins has also been evaluated from the $^{238}U/^{232}Th$ and $^{230}Th/^{232}Th$ activity ratios in the suspended sediments. The ^{230}Th is enriched in suspended sediments by 30 to 40% compared to ^{238}U. This disequilibrium is most likely caused by the preferential leaching of ^{238}U from the suspended sediments. The flux of excess ^{230}Th added to the Bay of Bengal via suspended sediments is computed to be 8.5×10^{14} dpm/yr, which is significantly higher than the production rate of ^{230}Th in the entire Bay of Bengal.

The work carried out in this thesis represents a detailed integrated study of the major ion chemistry, stable isotopes and radionuclide abundances in the Ganga and Brahmaputra Rivers and their major tributaries. The results of this study have provided important information on the geochemical processes regulating the major ion and radionuclide abundances in these two major river systems of the country. Future studies should focus on the chemistry of regional precipitation and of groundwaters which would enable a quantitative interpretation of the data obtained during this geochemical investigation.

APPENDIX

Chemical composition of river suspended sediments.

Table 1. Ganga main stream: Major and minor element composition of river suspended sediments

Sample Code*	Na	KK	Mg	Ca	Al	Fe	Cr	Mn	Ni	Cu
	°/o						ppm			
26.Hardwar	1.36	2.99	1.84	2.01	7.68	4.21	91	582	45	49
35.Garhmuk-teshwar	1.21	3.34	2.14	1.44	8.94	5.41	110	819	80	76
27.Kanpur	0.81	2.89	1.77	1.44	8.60	4.76	120	710	60	51
29.Allaha-bad	0.70	2.79	1.76	1.29	8.73	4.94	123	694	50	53
31.Varanasi	0.41	2.14	1.72	2.21	8.74	5.87	130	754	101	65
33.Patna	0.52	2.37	1.63	2.70	8.2	4.7	106	676	70	49

* Sample Code indicates Station No. and Location, to be used in conjunction with Figure and Table

Table 2. Ganga Tributaries: Major and minor element composition of river suspended sediments

Sample Code*	Na	K	Mg	Ca	Al	Fe	Cr	Mn	Ni	Cu
			°/o					ppm		
24.Yamuna	0.76	2.55	1.57	2.02	8.17	4.53	94	741	52	47
30.Yamuna	0.56	1.90	1.62	3.44	8.23	5.65	138	839	87	62
25.Chambal	0.47	1.34	1.66	3.90	8.21	6.92	150	1034	115	103
34.Son	0.13	1.55	0.95	0.74	10.9	6.67	174	739	102	90
14.Gomti	0.75	2.36	1.24	1.21	6.75	3.76	83	515	34	40
28.Ghaghara	0.76	2.56	1.97	3.75	7.35	3.94	80	599	33	39
32.Gandak	0.74	2.87	1.73	5.57	7.52	3.83	79	573	49	41

* Sample Code indicates Station No. and Tributary, to be used in conjunction with Figure and Table

Table 3 Brahmaputra River: Major and minor element composition of river suspended sediments

Sample Code*	Na	K	Ca	Mg	Al	Fe	Cr	Mn	Ni	Cu
	o/o						ppm			
20.Dibrugarh	1.79	1.60	3.79	2.85	6.42	4.52	226	850	150	64
21.Gauhati	1.48	1.97	2.52	1.81	6.68	4.27	113	723	72	50
22.Goalpara	1.41	2.12	2.00	1.92	7.59	4.76	183	801	95	66
23.Goalpara+	1.15	2.37	1.54	1.63	7.69	4.21	101	674	81	52

* Sample Code indicates Station No. and Location, to be used in conjunction with Figure and Table

+Manas River at Goalpara, before confluence with Brahmaputra

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