Geochemical factors controlling the chemical nature of water and sediments in the Gomti River, India

L. P. Gupta · V. Subramanian

Abstract R-mode factor analysis of the recently acquired data on water and sediment chemistry has been performed. Basic chemical parameters have been merged together which aid in interpreting a few empirical geochemical factors controlling the chemical nature of water and sediments of the Gomti River, a major Himalayan tributary of the Ganges drainage basin. Water chemistry seems to be controlled by three factors: bicarbonate, rainfall and silicate and phosphate factors. Sediment chemistry is largely controlled by the following four factors: clay, adsorption/desorption, Fe-Mn hydroxide and mercury factors. These factors show spatial and temporal variability in terms of their R-scores.

Key words Water chemistry · Sediment chemistry · Factor analysis · Gomti River

Introduction

Rivers are, in a way, veins of continents draining ca. 35000 km^3 water (Milliman 1991), 15.5 billion tonnes sediment (Milliman and others 1995) and 3.5 billion tonnes total dissolved solids (Meybeck 1976) every year to the world oceans. The chemistry of river water is a cumulative reflection of catchment geology, rainfall, erosion processes and anthropogenic interventions. These factors will also be responsible for the chemistry of loose sediments being transported by the river. Weathering and erosion operate incessantly. The important physical processes are thawing and freezing, growth of roots, mineral expansion due to hydration, diurnal temperature change, etc. (Blatt and Middleton 1972; Krauskof 1979). The chemical processes are mainly chemical degradation of silicate minerals by various processes like dissociation, hydrolysis, oxidation and reduction. The basic chemical reactions take place among silicates, carbonates and rainwater (weak carbonic acid) giving rise to various ions and clay minerals. The release of solutes in weathering processes is fundamentally governed by the thermodynamics and kinetics of the reactions involved as well as by the residence time of water in soil or rock body (Walling 1980). From the point of view of water quality and pollution, critical evaluation of these factors becomes pertinent, so that sources of specific pollution can be identified. In this paper, an attempt has been made to achieve this objective by studying a major river, the Gomti, which is a tributary of the Ganges River.

Factor analysis, which is also a way of classifying manifestations or variables but not the producer of taxonomy (Cattel 1965) used in this study, helps explain the observed relations among numerous general water and sediment chemistry parameters in terms of simpler relations. Factor analysis has been used to understand a number of geochemical processes by several professionals (Dawdy and Feth 1967; Hitchon and others 1971; Ashley and Lloyd 1978; Lawrence and Upchurch 1983; Briz-Kishore and Murali 1992; Subbarao and others 1996; Jayakumar and Siraz 1997).

An R-Q mode programme written by DeMooy and others (1988) has been used for extracting factors governing the water and sediment chemistry of the Gomti River. The program first standardizes the whole data to have mean 0 and standard deviation 1, and then extracts the factors. Factor rotation gives values closer to –1, 0 and +1, which means negative, no and positive contribution, respectively, by a variable towards a factor (Briz-Kishore and Murali 1992). Communality attached to each row of the matrix gives an appreciation of how well each variable is explained by *m* factors. If many communalities are 0.8 or less, more factors are required (Klovan 1975). Factor score relates to the intensity of the chemical process described by each factor sample-wise. Extreme negative values denote areas essentially unaffected by the process, a positive score denotes areas most affected, and a near-zero score means areas affected to an average degree. This interpretation becomes otherwise if the varimax rotated factor has a negative value (Dalton and Upchurch

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1978). With this background information the factor analysis results of the Gomti River have been explained.

Materials and methods

As a major tributary of the Ganges River, the Gomti River has a unique geological setting, in the sense that the whole of its catchment area lies in recent alluvium, that is geologically monotonous (alluvium and gravel formations). Climatological conditions are similar over the whole basin, having temporal variations in annual rainfall from 87 to 125 cm and in temperature from 0 to 47 °C. The soils in the basin show spatial variation and are mainly high-base brown soil, shallow black brown and alluvial soils, Tarai soils, Bhabar alluvium and Usar soils (Census 1989). There are patches of tropical dry and moist deciduous forests, scrubs and grassland. Four major towns (Hardoi, Sitapur, Lucknow and Jaunpur) with population exceeding 1 million are the major human settlements, but small towns and villages are spread throughout the river basin. In addition to municipal waste, wastes from some sugar mills, breweries, distilleries and other industries are released directly into the river water.

Water and bed sediment samples were collected at the riverbank from 15 locations (Fig. 1) throughout the river basin during second half of October 1991, a period immediately after the monsoon season. The details of the sampling procedure and analysis are described elsewhere (Gupta 1993). In brief, 1 l running water was collected in the polyethylene bottles. The top 5–7-cm layer of the bed sediments was scooped out with a stainless-steel vessel and immediately transferred into the polyethylene bags. The samples were stored at 1–4 °C temperature prior to analysis in the laboratory. Water samples were filtered through 0.45-μm membrane filter paper (Millipore®) using an all-glass filtration unit, then the filters were dried and weighed for total suspended solid (TSS) estimation; pH and conductivity were measured with the glass electrodes; bicarbonate content was measured by titrating it against 0.02 N HCl to the pH 4.5, and sulfate content against 0.0005 M barium perchlorate solution; chloride was measured with Radelkis® ion selective electrode and fluoride with Radiometer® ION 85 ion analyser; phosphate content was estimated with the ascorbic acid method and silica with the molybdosilicate method as described in APHA (1985). Calcium, magnesium, potassium and sodium were analysed with the GBC® 902 AAS. The bed sediments were dissolved following the solution A method (Shapiro and Brannock 1962; Shapiro 1975) for silica and phosphate estimation with the Cecil® 594 double beam UV/Vis spectrophotometer, and following the solution B method for elemental analysis with the GBC® 902 AAS. Kjeldahl nitrogen was estimated by microdistillation method (Trivedi and Goel 1984). The basic data on water and sediment chemistry of the Gomti River have already been published by Gupta and Subramanian (1994).

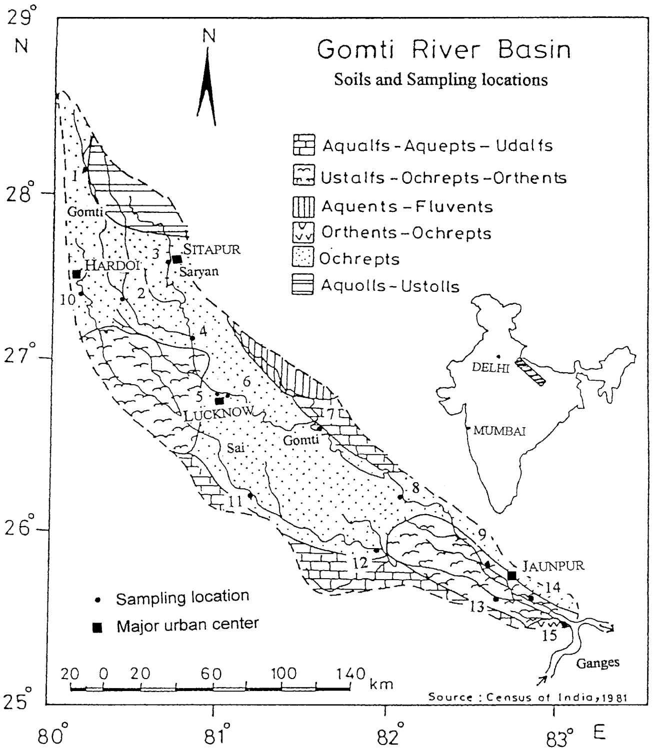

Fig. 1
Sampling locations and major soil groups in the Gomti River basin

Results and discussion

Before discussing the actual results obtained by factor analysis of the water and sediment chemistry data of the Gomti River, a brief explanation of the various mathematical terms, inherent in the factor analysis, will simplify the interpretation and understanding of the factors extracted. Factor analysis is an attempt to reveal simple underlying structure that presumably exists within a set of multivariate observations. The raw data standardized to have a mean of zero and standard deviation of 1 gives a matrix '*R*' containing correlation coefficients among '*m*' variables. The matrix '*R*' is produced when a matrix of raw data (X), having m columns and n rows, is multiplied with its transpose (X'). Principal factor matrix (or principal components) are nothing more than the eigenvectors of a correlation or a variance-covariance matrix. Total variance in a data set is sum of the individual variances. Communality provides an index to the efficiency of reduced set of factors. The magnitude of communality depends upon the number of factors retained. Varimax rotation moves each factor axis to positions so that projections from each variable onto the factor axes are either near the extremities (± 1) or near the origin (0). The method operates by adjusting the factor loadings. Interpretation, in terms of original variables, is thus made easier. Some analysts recommend retaining all factors of eigenvalue greater than 1, which means retaining all factors containing greater variance than the original standardized variables. Eigenvalues are quantities arising in a set of simultaneous equations dealing with the matrix operation. Eigenvalues greater than 1 account for greater variance than the standardized variables. However, if the original variables are only weakly correlated or uncorrelated, the number of factors with eigenvalue >1 increases with many of them uninterpretable anyway, which means the factor model is probably inappropriate for the given set of variables (Davis 1986).

Factors governing water chemistry

Three factors with eigenvalue >1 have been extracted from the principal factor matrix after varimax rotation (Table 1). Factor 1 is explicitly a bicarbonate factor, which contains variables HCO_3^-, Ca^{2+}, Mg^{2+}, K^+ and conductivity. This factor explains dissolution of carbonates as the dominant chemical process in the Gomti River basin. The upper reaches of the river show predominance of Shiwalic (tertiary) sediments, limestones, dolomite and calcareous shales (Sarin and Krishnaswamy 1984), and further downstream they account for as much as 30% of the surface geology (Wadia 1981) in the form of $CaCO_3$ nodules and Na- and K-carbonates (Kumar and Singh 1978). Kaolinization of K-feldspar and consequent production of bicarbonate ions are also explained by this factor. The chemical reaction may be expressed as:

$$2\text{K–feldspar} + 2CO_2 + 11H_2O = \text{Kaolinite} + 2K^+ + 2HCO_3^- + 2H_4SiO_4$$

The bicarbonate ions, which make up ca. 92% of the total anions, and corresponding cations, which together make up ca. 60% of cations, are to a large extent responsible for the conductivity of the river water. Factor 1 dominates (accounts for 40% variance in the data matrix) over the other factors in controlling the water chemistry of the Gomti River.

Factor 2 accounts for 32% variance in the data matrix. This factor consists of variables F^-, Cl^-, SO_4^{2-} and Na^+ ions and pH. Cl^-, SO_4^{2-} and Na^+ are grouped together because of their origin from similar sources, for example atmospheric precipitation, groundwater seepage and to a lesser extent chemical weathering in the basin. Contribution from atmospheric precipitation is expected to be higher during the monsoon season. Sporadic occurrence of alkaline and saline soils in the river basin may contribute these ions through dry deposition especially during the peak period of summer season. This factor also explains pH controlled dissolution of fluorite minerals. Silica shows a negative contribution (R-score –0.76) to the factor, that is, silica concentration decreases with increase in any other variable contained in this factor. This factor may be termed rainfall and silicate weathering factor.

In comparison with Factors 1 and 2, Factor 3 is less significant, and accounts for 12% of the total variance. This factor contains negatively correlated phosphate with respect to pH and TSS. The factor indicates that lower pH increases dissolution of phosphate minerals, and vice versa. The total suspended solids (TSS) content in the river water seems to have a similar influence on the dissolution of phosphate minerals. In other words, higher TSS leads to an increase in pH and, in turn, reduces dissolution of phosphate minerals. This factor may be termed *phosphate factor*.

These three factors taken together explain about 84% of the total variance in the data matrix, indicating that the determined variables, which control the water chemistry of the Gomti River, are not only linearly correlated with each other but also in another way. For instance, chemical weathering generates proportionate amount of ions in

Table 1
Principal and varimax rotated R-mode factor loading matrix (water chemistry)

principal factor matrix			Communality	varimax rotated factor matrix			Variable
Factor 1	Factor 2	Factor 3		Factor 1	Factor 2	Factor 3	
0.42	0.81	0.30	0.93	0.05	0.92	0.13	Cl^-
0.51	0.71	0.17	0.80	0.18	0.87	0.02	SO_4^{2-}
0.86	−0.37	−0.12	0.90	0.94	−0.00	−0.12	HCO_3^-
0.46	−0.41	0.68	0.84	0.59	−0.06	0.70	PO_4^{3-}
0.89	−0.25	−0.09	0.86	0.91	0.12	−0.11	Ca^{2+}
0.87	−0.35	−0.17	0.90	0.93	0.01	−0.18	Mg^{2+}
0.56	0.75	0.17	0.91	0.20	0.93	0.01	Na^+
0.77	−0.58	0.13	0.96	0.94	−0.18	0.17	K^+
0.23	0.71	−0.02	0.56	−0.08	0.73	−0.15	F^-
−0.02	−0.86	0.11	0.76	0.34	−0.76	0.25	SiO_2
0.38	−0.20	−0.72	0.70	0.42	−0.15	−0.70	TSS
0.40	0.53	−0.56	0.76	0.15	0.54	−0.66	pH
0.97	0.03	0.11	0.96	0.87	0.44	0.03	conductivity
		Eigenvalue		5.17	4.13	1.53	
		Variance %		39.80	31.77	11.76	
		Cumulative %		39.80	71.56	83.32	

water, but due to common ion effect, coprecipitation, conditions of saturation and undersaturation, the original proportion of the ions will be changed. It seems that with the current set of variables an approach has to be used which should be based on complex interactions, besides the linear relationships, among the variables. Then it may become possible to account for the 100% variance in the data matrix, but it may generate a larger number of factors whose contribution to the water chemistry may not be very significant, as the existing number of factors explains ca. 84% of the total variance.

Factors governing sediment chemistry

Table 2 lists the major principal and varimax rotated factors governing the sediment chemistry of the Gomti River. Factor 1 explains 37% variance in the data and comprises aluminum, magnesium, potassium and Kjeldahl nitrogen. Although silicon is not included in this factor, Factor 1 stands for illite and montmorillonite clay minerals dominating the sediment chemistry of the Gomti River. Kjeldahl nitrogen indicates indirectly the association of organic matter with these clay minerals. This factor may be termed the clay factor.

Factor 2 accounts for 21% of the total variance and consists of phosphorous, calcium, copper and sodium. This factor emphasizes the role of apatite minerals in controlling the sediment chemistry. Inclusion of copper in this factor indicates its adsorption on the apatite probably due to substitution of calcium by copper. Sodium shows a negative contribution towards Factor 2. This factor may be termed the *adsorption/desorption factor*.

Factor 3 consists of iron, manganese and silicon, which exhibits a negative relationship with the factor. This factor signifies theoretically the role of iron-manganese hydroxides deposited on silicates in determining the chemistry of bed sediments of the Gomti River. No direct observation of these hydroxides has been attempted in the present study. It accounts for 12.7% of the total variance in the data matrix. This factor may be termed as the Fe-Mn hydroxide factor, or better, the colloidal factor, since Fe, Mn and Si in the aquatic system are influenced by the colloidal properties of their ligands.

Factor 4 exclusively highlights the role of mercury in defining the bed sediment chemistry. In correlation data matrix, mercury does not show association with any other variable studied. Factor 4 accounts for 10% of the total variance in the data matrix. With respect to other minor elements the concentration of mercury in sediments is considerably high and, therefore, this factor may be termed a *mercury enrichment* or *anthropogenic* factor.

The water chemistry of a river cannot be independent of its sediment chemistry. Therefore, some overlapping is expected among the three factors controlling water chemistry and the four factors controlling the sediment chemistry of the Gomti River. For instance, dissolution of calcium from sediments to water affects Factor 2 of sediment chemistry and Factor 1 of water chemistry. Similar interactive relationship could be worked out for all major chemical species, for example, Mg, Na, K, Fe, HCO_3^- etc. in water, which have their origins in sediments.

Spatial variability in the magnitude of factors

Water chemistry

The extent of influence of a factor on the overall water and sediment chemistry at a particular location has been inferred from the sheer magnitude of R-score computed in the process of factor analysis. Figure 2 depicts the downstream variations in the magnitude of all three factors controlling the river water chemistry. At the origin of the river, Factor 1 is least significant, but in downstream Factor 1 starts playing a large role, which slowly becomes of minor importance just before confluence of the Gomti River with the river Ganges. The left-bank tri-

Table 2
Principal and varimax rotated R-mode factor loading matrix (sediment chemistry)

principcal factor matrix				Communality	varimax rotated factor matrix				Variables
Factor 1	Factor 2	Factor 3	Factor 4		Factor 1	Factor 2	Factor 3	Factor 4	
0.36	−0.44	0.54	−0.48	0.84	0.13	0.70	−0.32	0.49	P
0.77	0.44	0.03	−0.13	0.89	0.91	0.19	0.03	0.15	Al
−0.44	−0.09	0.63	−0.18	0.63	−0.19	0.10	−0.77	0.03	Si
0.67	−0.48	0.08	−0.14	0.70	0.17	0.72	0.29	0.26	Ca
0.85	0.39	−0.00	−0.11	0.89	0.86	0.14	0.33	0.18	Mg
0.83	−0.19	−0.42	0.07	0.90	0.34	0.39	0.79	0.12	Fe
0.68	−0.44	0.16	0.33	0.80	0.23	0.78	0.32	−0.20	Cu
−0.34	0.66	−0.36	−0.31	0.78	0.09	−0.84	−0.02	0.24	Na
0.67	0.68	−0.02	0.09	0.93	0.91	−0.16	0.26	−0.06	K
0.50	−0.57	−0.46	−0.03	0.79	−0.15	0.48	0.70	0.22	Mn
0.59	0.49	0.35	0.12	0.73	0.83	0.11	−0.06	−0.14	Kjel. N
−0.15	0.04	0.27	0.84	0.80	−0.01	0.08	−0.14	−0.88	Hg
			Eigenvalue		4.45	2.48	1.52	1.24	
			Variance %		37.09	20.70	12.66	10.38	
			Cumulative %		37.09	57.79	70.45	80.83	

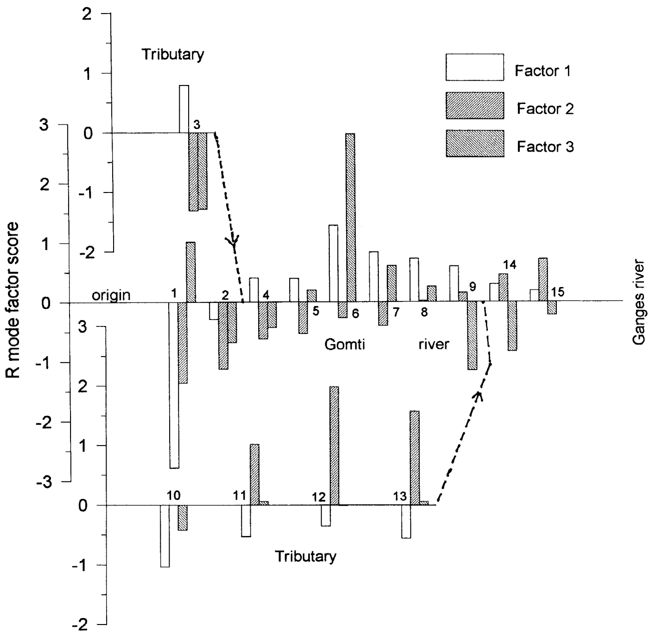

Fig. 2
Spatial distribution of the factors controlling the water chemistry of the Gomti River

butary of the Gomti River drains water from an area where Factor 1 plays quite a significant role. But in the right-bank tributary of the river Factor 1 remains essentially insignificant to river water chemistry. This leads to the conclusion that the river's main channel and its upper northern watershed receive water from terrain rich in carbonate minerals.

Factor 2 has the lowest factor score near the origin of the river. There is a gradual increase in the factor score downstream. This trend indicates that contribution of Factor 2 to the water chemistry of the main channel of the river becomes gradually significant. A similar trend, of larger magnitude, can be seen in the right-bank tributary, too; it is insignificant in the left-bank tributary of the river. From the distribution pattern of Factor 2 it appears that rainfall and associated silicate weathering are important processes in the right-bank tributary of the river; the right-bank tributary assumes a significant role in the main channel only after mid-course of the river. The direct influence of right-bank tributary water chemistry on the main channel water is evident at the Sites 14 and 15.

Factor 3 has an insignificant influence on the water chemistry of the tributaries. In the main channel, however, it becomes significant from Site 5 onwards, with a maximum at Site 6 and then rapidly diminishes to insignificance. This factor is exceptionally high near the origin of the river. Intensive agriculture is practised in the watershed around the river origin. Therefore, phosphorous may be contributed from run-off from croplands. Site 5 is located just upstream the biggest metropolitan city, Lucknow, in the river watershed. Perhaps some point source of water pollution from the city exists upstream the sampling location. The very high value at Site 6 can be explained by sewage waste being discharged from the city. The gradual decrease in the factor score from Site 6 onwards is due to dilution of municipal waste by the river water and natural recovery by the river.

Sediment chemistry

Factor 1 is prominent in accounting for sediment chemistry of the left-bank tributary (Fig. 3). This prominence dampens after confluence of the tributary with the main channel. There is some recovery in this factor after first half of the main channel, but it remains almost insignificant. In the right-bank tributary, however, there is no regular change in the contribution of Factor 1 towards sediment chemistry. In the case of both the tributaries near their origin, there exists shallow marshy terrain with plenty of water and extreme variations in annual temperatures, located in the foothills of the fast-eroding Himalayas. The geochemical setting of the sites seems to be appropriate for the formation of clay minerals (Velde 1992). The signature of this factor can be felt even after confluence through Site 5. As indicated by the low factor scores (lowest at Site 7) in the mid-course of the river, favourable conditions for clay formation do not exist to any appreciable extent.

Near the origin of the river the contribution of Factor 2 to sediment chemistry is very little. There is significant increase from –1.22 to 0.89 in the contribution by this factor in the downstream sediments. The sediment transport by the left-bank tributary is affected by Factor 2 to a more than average degree. After confluence there is a lowering in the intensity of Factor 2, which increases

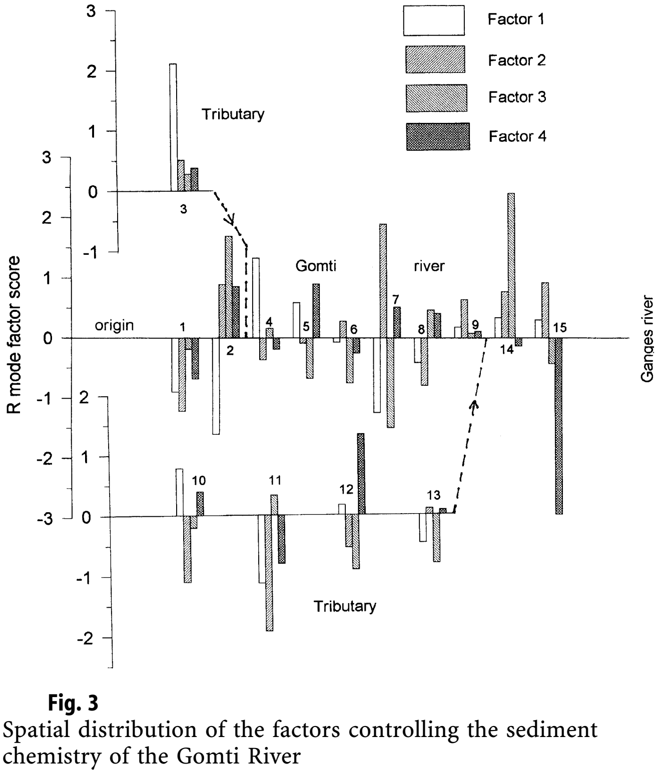

Fig. 3
Spatial distribution of the factors controlling the sediment chemistry of the Gomti River

again in downstream, reaching a high value of 1.89. This high value might be a reflection of sediments from a small tributary which joins the main channel just before the sampling point 7. The area through which the right-bank tributary traverses seems to be least affected by Factor 2. Just before the confluence with the main channel, there is a perceptible increase in the intensity of Factor 2. The main channel in the downstream shows steady increase in R-score, reflecting the sediments considerably affected by Factor 2.

In the upper reaches of the river Factor 3 increases rapidly and plays an important role in controlling the sediment chemistry at Site 2. The left-bank tributary transports sediments with an average degree of influence of this factor. After the confluence, Factor 3 loses importance gradually; at Site 8 only, it shows little increase. The major right-bank tributary sediments are not affected by Factor 3. After the confluence with right-bank tributary, however, the main channel's sediments are initially influenced by the Factor 3 (very high factor score); but the influence seems to be highly localized; further downstream, Factor 3 is reduced to a negative value.

Factor 4 has highly localized influence on the sediment chemistry of the Gomti River. There are sharp variations in its magnitude from site to site. However, downstream, from Site 7 to 15, there is a gradual reduction in the magnitude of this factor with extremely negative value, ca. –3, at Site 15. This factor exclusively reflects mercury concentration in the sediments. Application of pesticides on farm lands may be a source of mercury. As there are scattered agricultural activities in the basin, wide variations in the distribution of Factor 4 are expected. In the vicinity of Site 15, a small drain from nearby city delivers urban and industrial waste, perhaps rich in mercury content, directly into the river which is reflected in high R-score value at this site.

Conclusion

The factor analysis of the major ion chemistry data of the river water extracts three prevalent factors operating in the Gomti River basin. The factors are (1) bicarbonate, (2) rainfall and silicate weathering, and (3) phosphate. The water chemistry is dominated by carbonates, prevalent in the catchment of the river. The factor analysis of sediment chemistry data yields four factors: (1) clay, (2) adsorption/desorption, (3) Fe-Mn hydroxide, and (4) mercury enrichment. Phosphate minerals are important contributors to the water and sediment chemistry of the river. Water chemistry reflects influence of tributaries on the main channel, because water is a dynamic medium which provides physical and chemical continuation among tributaries and the main channel of the river. Therefore, whatever changes take place in water chemistry upstream are also reflected downstream for a considerable distance. Bed sediments are rather less mobile, and therefore any change in their physico-chemical properties tends to be localized. Although there are some trends for a short distance in tributaries and main channel as well, the factors governing the sediment chemistry of the river are almost unique to each location.

In order to establish a more meaningful interpretation of these factors, the data on river water discharge at various points, equilibrium constant (*K*) of the possible chemical reactions taking place in the river basin, temperature and rainfall distribution, relative chemical and physical stability index for the common minerals in the basin, etc., will be required.

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