Assessing variability of water quality in a groundwater-fed perennial lake of Kashmir Himalayas using linear geostatistics

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This paper presents a study on Manasbal lake, which is one of the high altitude lakes in the Kashmir Valley, India. Eighteen water samples were analysed for major ions and trace elements to assess the variability of water quality of the lake for various purposes. Geostatistics, the theory of regionalized variables, was then used to enhance the dataset and estimate some missing spatial values. Results indicated that the concentration of major ions in the water samples in winter was higher than in summer. The scatter diagrams suggested the dominance of alkaline earths over the alkali elements. Three types of water were identified in the lake that are referred to as Ca–HCO_3, Mg–HCO_3 and hybrid types. The lake water was found to be controlled by rock–water interaction with carbonate lithology as a dominant source of the solutes. The major (Ca^{2+}, Mg^{2+}, Na^+, K^+, NO_3 and HCO_3^-, CO_3 and Cl) and trace elements of the lake water were within the World Health Organization standards, therefore the lake water was considered chemically safe for drinking purposes. Although NO_3 concentration (ranging from 1.72 to 2 mg/L), is within the permissible limit and not very alarming, the gradually increasing trend is not acceptable. It is however, important to guard its spatio-temporal variability as the water is used for domestic as well as agricultural purposes. This study is significant as hydrogeological information on such high altitude lakes in India is scanty.

1. Introduction

Lakes are inland bodies of water which are formed in rock basins of various shapes and sizes. These play an important role in the economy of a region or country and are of tremendous academic, societal and economic importance. They act as natural water reservoirs and store a large quantity of water, which can be used for drinking, industrial, irrigation, aesthetic and other purposes including generation of hydro-electricity. Kashmir is blessed with a number of lakes with different hydrological settings such as Manasbal lake (fed mainly by groundwater), Dal lake (fed mainly by fresh water streams) and Wular lake (fed mainly by the river Jhelum) (Raza *et al* 1978; Keller 1985; Sharma and Bakshi 1996; Kapoor and Das 1997; Hussain 1998; Khan *et al* 2006). The origin of the lakes in Kashmir Valley is either tectonic (as the area is tectonically active) or fluviatile, as all the lakes lie on the flood plain of river Jhelum. Our study covers one of the important lakes in India on which much hydrogeological data is not available. Moreover, studies on lakes in Kashmir are very important as information on high altitude lakes is very rare in India (Hamilton and Schaldow 1997;

Subramanium 2000; Bhatt 2004). In the Kashmir Valley, tourism is the backbone of the economy and the lakes play an important role in increasing the economic status of the state. As the water quality of the lakes in Kashmir is not monitored regularly and data on the water quality of the Manasbal lake are very meagre, it is important to study the water quality of the lake and its use for various utilizations and to prevent the degradation of its quality. The purpose of this study was to assess the chemical quality of the Manasbal lake which is least influenced by anthropogenic inputs. The theory of regionalized variables was employed to augment the scarce data and has helped to improve the geochemical interpretation.

2. Description of the study area

Manasbal lake is the deepest ($\sim$12 m deep) of all the freshwater lakes fed by groundwater in Kashmir Valley (Lawrence 1895; Raina 1971). It is situated at an altitude of 1583 m amsl. It lies between $34°15'$N latitude and $74°40'$E longitude and covers an area of about 280 ha of which 25 ha is marshy (figure 1). The lake is surrounded by moderately high mountains on its eastern and southern sides. A few limestone quarries exist towards the eastern part. The northern bank of the lake comprises a raised land or Karewas. The oblong outline of Manasbal lake extends in a NE–SW direction with a maximum length and breadth of 3.5 and 1.5 km, respectively. The volume of water has been estimated as 12.8×106 m^3 Yousuf (1992). The lake is also fed seasonally by an irrigational stream; Larkul, on the eastern side, which is operational only during summer season. It drains into the river Jhelum through a 1.6 km Nunnyar Nalla near Sumbal village. The lake serves as an important natural water reservoir for the local population and its water is used for drinking and agricultural purposes.

3. Geology

The catchment of the Manasbal lake consists mainly of Triassic limestone, Quaternary karewas and Recent alluvium. Triassic limestone is made up of a thick series of compact blue limestone, slates and dolomites (Krishnan 1968; Wadia 1975). Karewas are the Lacustrine deposits of the Plio-Pleistocene age and are composed of fine silty clays with sand and boulder gravel (Bhat 1989). The Karewas series consists of blue, grey and bluff silts, sand, partly compacted conglomerates and embedded moraines (Wadia 1975). The alluvium consists of boulders, pebbles and sands.
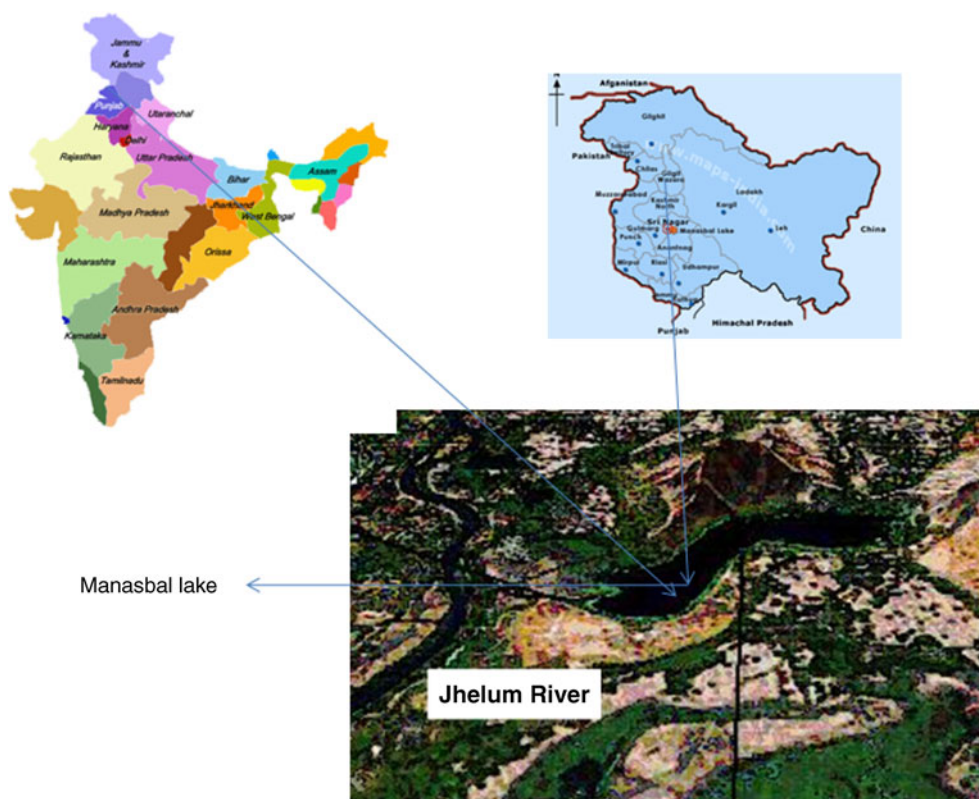

Figure 1. Location map.

4. Data and methodology

4.1 *Geostatistical methods*

Data requirement is an essential but conscientious need for any study and it is very difficult to establish its sufficiency and suitability conditions. The dataset available in this study (8 measurements in summer and 10 measurements in winter) is not sufficient to perform a meaningful statistical analysis and enhancement of data population was inevitable. We have adopted a novel and special approach of using the theory of regionalized variable (Matheron 1971). We have added a matching number of additional measurement points for enhancing the dataset. However, it was not possible to obtain measured values for the same time period as in the past and hence all the water quality parameters were estimated for both the seasons using the theory of regionalized variables at new/additional points and then taken as measured/known values with the following justifications.

- The water quality of a lake that is small in dimension; about 3×0.5 km with more or less steady flow has been studied. All the chemical constituents may be regarded as regionalized variables within the lake and theory of regionalized variables will be applied.
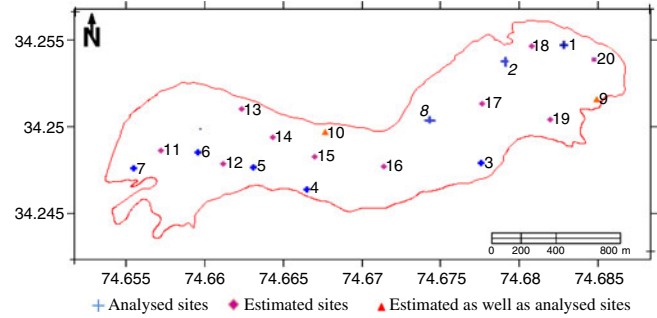

Figure 2. Sample sites (monitoring network).

- The new and additional points were taken close to the existing measurement points (figure 2) to minimize the variance of the estimation error and obtain the measured values close to the true value (Marsily and Ahmed 1987). Thus the revised dataset could consist of 20 values during June 2006 as well as 20 values during September 2006 allowing a reasonable application of graphical and statistical analyses of the water quality (Fetter 1980; Karanth 1987; Tebbutt 1998). All the observed values were first analysed for their basic statistics. Table 1 presents their minimum, maximum, variance as well as standard deviation. The basic step of applying the theory of regionalized

Table 1. *Statistics of the observed values as well as the corresponding variogram parameters.*

	min	max	mean	var	sd	mt	c0	c	a
Tempjune	27.9	29.5	28.8	0.332	0.576	2	0	0.332	2200
Tempsept	16.4	17	16.8	0.0296	0.172	2	0	0.0296	2200
pHjune	8.6	10.2	8.96	0.293	0.541	2	0	0.293	2000
pHsept	7.4	9.2	8.15	0.255	0.505	2	0	0.255	1600
ECjune	350	490	403	2290	47.8	2	0	2290	1600
ECsept	190	380	246	3740	61.2	2	0	3740	1600
Cajune	11.2	26.9	19.1	35.9	5.99	2	0	35.9	1600
Casept	18.9	31	23.4	17.5	4.19	2	0	17.5	1600
Mgjune	11.3	15.5	13.8	1.75	1.32	2	0	1.75	800
Mgsept	12.9	18.1	15.3	2.68	1.64	2	0	2.68	2400
Najune	5.68	9.69	7.49	2.14	1.46	2	0	2.14	2000
Nasept	7.63	18.1	10.2	9.06	3.01	2	0	9.06	2800
Kjune	0.571	1.98	1.62	0.195	0.442	2	0	0.195	400
Ksept	0.769	1.71	1.38	0.37	6.88	2	0	0.37	400
NO_3june	46.3	124	92.2	614	20.8	2	0	614	2000
NO_3sept	14.5	394	157	20100	142	2	0	20100	2000
HCO_3june	40	200	104	3170	56.3	2	0	3170	2000
HCO_3sept	20	290	169	5470	74	2	0	5470	2800
Cljune	2.13	4.97	3.46	0.934	0.967	2	0	0.934	2000
Clsept	2.13	6.39	3.67	1.67	1.29	2	0	1.67	2000
SO_4june	71.7	342	228	6590	81.2	2	0	6590	2000
SO_4sept	5.05	372	222	17100	131	2	0	17100	2800
CO_3june	20	120	76	1180	34.4	2	0	1180	1600
CO_3sept	60	80	73.3	88.9	9.43	2	0	88.9	2800
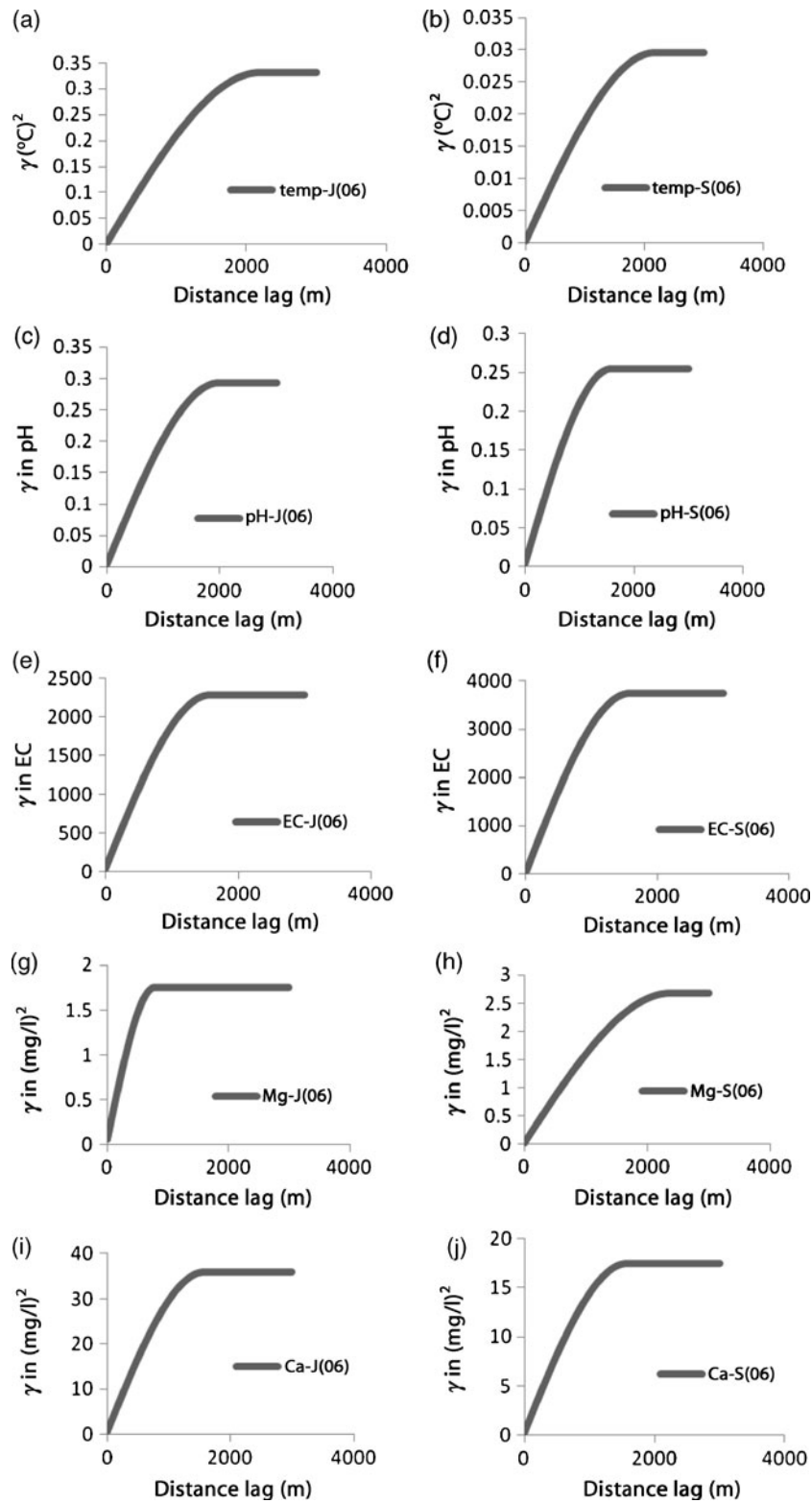
Figure 3. (**a–x**) Finalised variograms.

variables (i.e., geostatistics) is the estimation of experimental variograms from the measured values and their modelling using theoretical variograms. The extremely small dataset has restricted the calculation of a meaningful variogram and modelling them with unambiguous theoretical variograms. To overcome this difficulty, we have taken the aid of the cross-validation test (Ahmed and Gupta 1989). Following assumptions were made to generate initial variograms to perform the cross-validation tests.

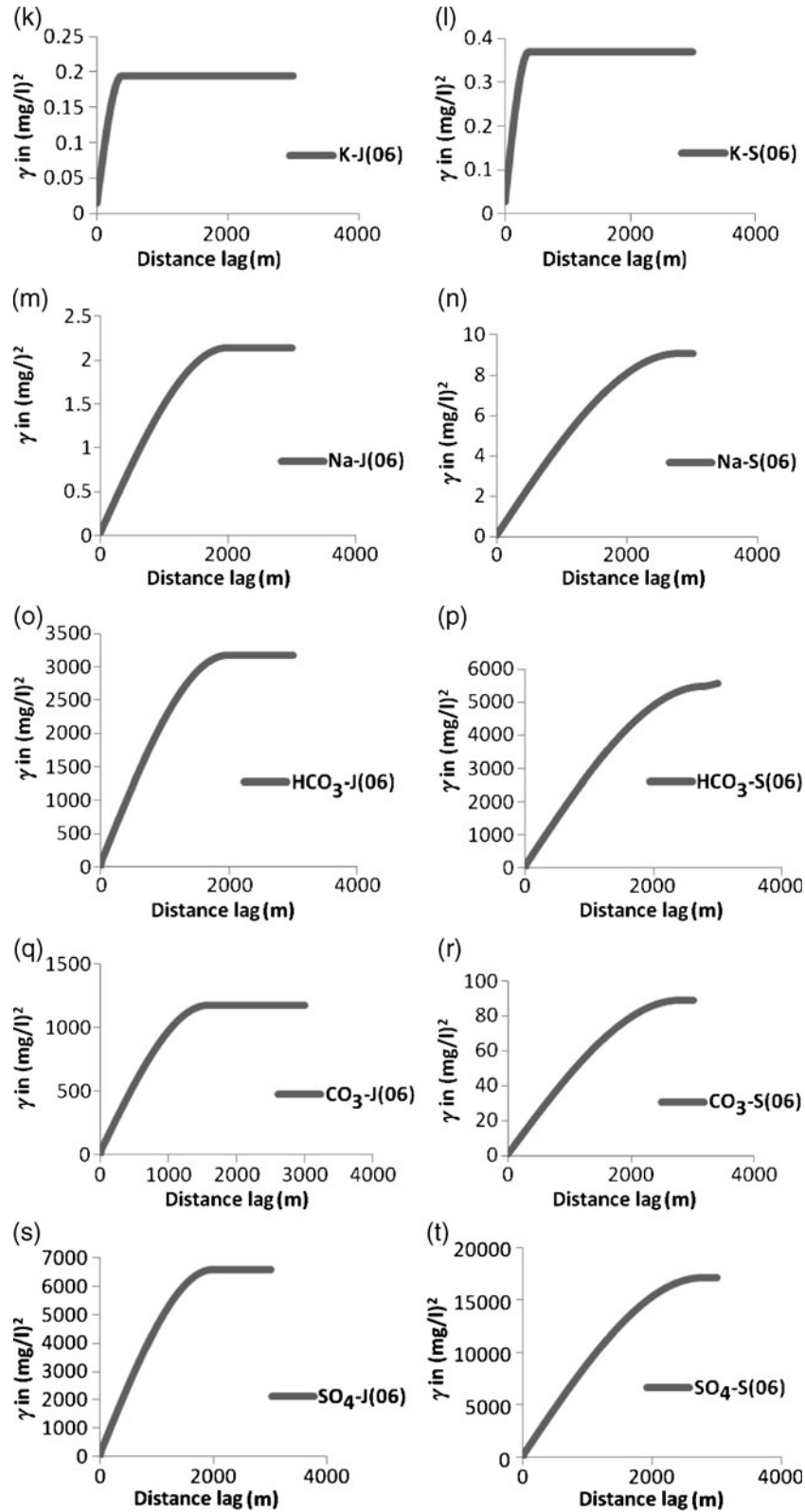Figure 3. (*Continued*).

- The parameters under study, i.e., the small area of the lake and the chemical constituents determining the water quality of the lake and it was assumed that there may not be any small-scale variability and the random part may be neglected taking the values of nugget effect as zero (de Marsily and Ahmed 1987) for all the parameters.
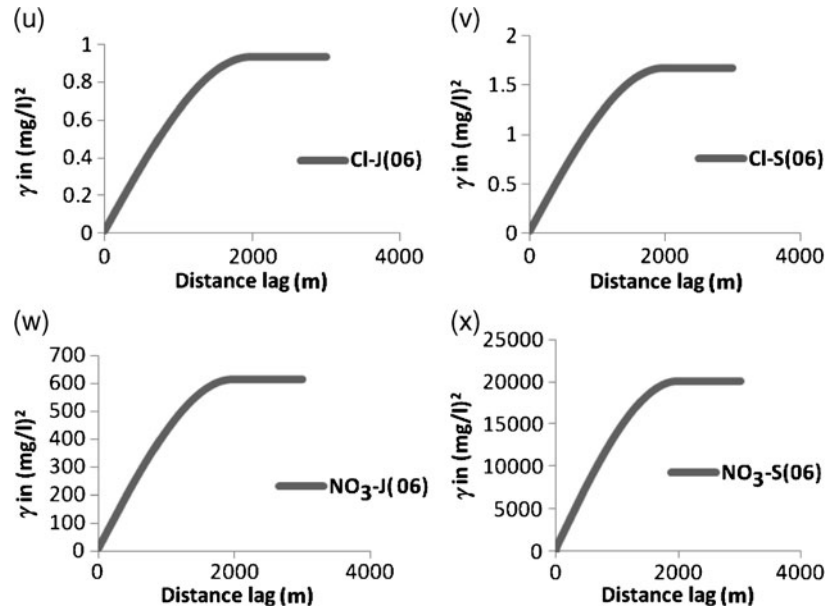
Figure 3. (*Continued*).

- The sill value is usually close to the variance of the parameter and hence the respective variances of the water quality parameters were taken as the corresponding sill values (c).
- For simplicity and as applicable in most cases, the model type of the variogram was taken as spherical.
- The range initially varied from the least to the maximum distance possible in the lake and was finalized based on the least square difference procedure called jack-knifing.

Thus all the possible components of the variogram/ structures, viz., trend, correlation as well as noise were estimated. The cross-validation tests were performed systematically on all the parameters and suitable variograms that have satisfied the norms given by earlier studies (e.g., Ahmed and Gupta 1989) were completed. The finalized variograms of the parameters are shown in figure (3a–x) and table 1. Finally, all the additional measurement points for the two seasons were estimated using respective variograms and the corresponding datasets using ordinary kriging (Journal and Huijbirgts 1978). As stated above, the estimated values have been taken as measured values as the variance of the estimation error obtained was low. Thus an integrated data set was prepared for further analysis and interpretation (table 2) including correlation matrix preparation. As indicated, figure 2 contains three types of data supports: 8 sites represented by (+), where measurements were made for both the seasons; 10 sites represented by (♦), where values were estimated for both the seasons; and 2 sites represented by (▲), where values were

estimated only for June 2006, but were available for September 2006.

4.2 *Analytical methods*

Eighteen water samples from the lake were collected in summer and winter seasons of 2006 across the Manasbal lake (figure 2), in pre-cleaned (acid washed) HDPE bottles (Scalf *et al* 1987). Water samples were filtered with 45 μm filters and collected in two sets. One set was immediately acidified with concentrated HCl and ultrapure HNO_3. All the chemical constituents were analysed following standard methods (APHA 1995). Temperature, electrical conductivity (EC) and pH were measured *in situ* using a potable water analysis kit. Alkalinity was determined by acid titration with 0.1 N HCl. Chloride was determined by acid titration with $AgNO_3$. Major cations, trace and ultra-trace elements were determined by ICP-MS on the acidified set of samples. Spectrophotometry was used to determine concentration of SO_4 and NO_3. The normalized inorganic charge balance (NICB=$(TZ_+ -TZ-)/TZ_+ +TZ-)$) was used to estimate overall analytical uncertainty and it should be close to zero. NICB is within ± 0.5.

5. Results and discussions

5.1 *Physico-chemical characteristics of the lake water*

The results of physico-chemical analyses of the Manasbal lake water samples collected in summer

Table 2. *Physico-chemical analysis.*

Sl. no.	Temp	pH	EC	TDS	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	NO₃ (mg/L)	Cl (mg/L)	SO₄ (mg/L)	CO₃ (mg/L)	HCO₃ (mg/L)
1. (J)	28	8.6	471	301	23.5	11.3	6.7	1.4	0.007	2.13	0.317	120	40
2. (J)	28	8.6	350	224	21.9	15.2	9.6	1.9	0.009	3.55	0.216	80	60
3. (J)	27	9.4	490	314	11.2	13.9	5.9	1.6	0.005	4.97	0.168	60	70
4. (J)	29	10	370	237	13.4	13.7	8	1.9	0.008	4.26	0.341	0	150
5. (J)	28	8.7	380	243	26.8	14.8	5.7	1.8	0.006	2.86	0.189	100	80
6. (J)	29	8.8	370	237	15.7	15.5	9.7	1.9	0.009	3.55	0.071	0	170
7. (J)	29	8.7	380	243	13.3	12.7	7.7	1.8	0.008	4.26	0.257	0	200
8. (J)	29	8.7	410	262	26.9	13.6	6.5	0.6	0.007	2.13	0.263	20	60
9. (J)	27	8.9	471	301	18.9	9.6	6.3	3.2	0.9	2.91	0.279	112	49
10. (J)	29	9.4	375	240	18	6.23	7.1	3.5	0.06	3.3	0.281	28	109
11. (J)	28	8.7	376	241	14.4	13.5	8.7	3.5	0.09	3.97	0.173	0.464	187
12. (J)	28	8.7	372	238	21.3	15.6	7.5	3.7	0.08	3.19	0.141	52	124
13. (J)	28	8.6	376	241	25.5	13.1	6.5	3.7	0.07	2.73	0.192	75	85
14. (J)	28	9.2	375	240	21.8	8.1	6.7	3.9	0.07	3.28	0.256	56	104
15. (J)	29	9.5	377	241	20	5.7	7.1	3.6	0.08	3.37	0.284	33	110
16. (J)	29	9.7	383	245	18.7	4.3	7.3	3.6	0.08	3.54	0.302	17	116
17. (J)	28	8.9	419	268	19.8	14.8	7.2	2.6	0.09	3.56	0.216	52	61
18. (J)	28	8.7	427	273	21.6	12.7	9.4	2.8	0.07	4.01	0.189	102	71
19. (J)	28	8.9	459	294	18.7	11.8	8.2	3.2	0.08	4.43	0.186	101	65
20. (J)	28	8.8	472	302	20.5	10.5	8.3	3.2	0.07	4.29	0.187	115	65
1. (S)	17	7.7	340	217	29.7	17.3	18	1.1	0.02	4.97	0.005	0	200
2. (S)	16	9.2	200	128	18.9	14	9.6	1.4	0.009	2.84	0.329	80	20
3. (S)	16	8.2	260	166	20.7	14.2	9.6	1.5	0.009	3.55	0.371	0	190
4. (S)	16	8	230	147	21.7	14.5	7.6	1.5	0.008	2.13	0.311	0	220
5. (S)	16	7.9	200	128	19	12.9	8	1.3	0.008	4.97	0.085	0	180
6. (S)	16	8.5	190	121	20.4	14.7	7.6	1.4	0.008	3.55	0.132	60	160
7. (S)	16	8	220	141	21.1	14.7	9.7	1.5	0.009	2.84	0.3	0	160
8. (S)	16	7.4	240	153	26.9	18.1	12	1.7	0.01	2.13	0.278	80	60
9. (S)	16	8.7	200	128	24.9	15.7	11	1.7	0.01	2.84	0.051	0	210
10. (S)	17	7.7	380	243	30.9	17.4	8.4	0.8	0.008	6.39	0.352	0	290
11. (S)	16	8.3	201	128	20.4	14.4	8.7	2.7	0.02	3.15	0.222	27	159
12. (S)	16	8.2	191	122	19.4	13.7	7.8	2.6	0.04	4.21	0.114	26	169
13. (S)	16	7.9	253	162	23.3	14.7	8.5	2.6	0.3	5.47	0.154	17	191
14. (S)	16	7.9	271	173	23.8	14.8	7.9	2.6	0	4.96	0.227	0	230
15. (S)	16	7.9	342	219	28.5	16.5	8.2	2.6	0.002	5.63	0.322	0	272
16. (S)	16	7.8	322	206	27.7	16.6	8.5	2.6	0.4	4.53	0.342	6	249
17. (S)	16	8.3	232	148	22	15.5	11	2.3	1.7	0	0.335	53	88
18. (S)	16	8.4	275	176	24.5	13.6	14	2.9	2	0	0.161	30	130
19. (S)	16	8.4	260	166	24	13.4	13	2.8	1.7	0	0.166	10	171
20. (S)	16	8.2	266	170	26.5	13.4	14	3.1	2	0	0.057	0.417	201

and winter seasons of 2006 are presented in table 2. The lake water is characterized by medium to high alkalinity (pH: 7.7–10), medium electrical conductivity (EC: 191–490 μS/cm) and medium total dissolved salts (TDS: 122–314 mg/L). Ca, Mg and Na are the most abundant cations with the concentrations ranging from 11.2–29.7, 4.3–18.1 and 5.7–18 mg/L, respectively. Potassium is the least abundant major cation with an average value of 2.36 mg/L. Bicarbonate is the most dominant anion with an average value of 20–230 mg/L followed by Cl with an average value

of 3.36 mg/L. The concentration of sulphate and nitrate ranges from 0.005–0.371 to 0.018–2.014 mg/L, respectively. All the major ions show obvious spatial variations (figure 2a–x). Ca is the dominant cation, which contributes 46% to the major cation budget while HCO₃ is the dominant anion contributing 76% to the major anion budget. Thus the lake water composition is dominated by Ca and HCO₃ ions. In general, most of the major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, NO_3 and HCO_3^-) show higher concentration in winter and lower concentration in summer, while CO₃ and Cl

show lower concentration in winter and higher concentration in summer with Ca as a dominant cation.

5.2 *Trace and ultra-trace element chemistry*

There are some trace elements which are considered important for the human metabolism within the WHO limits and a few are carcinogenic. The concentration of all the trace elements in the lake water are within the permissible limits of WHO standards (1998). Details of the trace and ultra-trace elements of the lake water samples are given in table 3. The concentration of Fe^{2+} (0.48–0.16 mg/L), Mn^{2+} (0.001–0.036 mg/L),

Ba^{2+} (0.008–0.029 mg/L) and Sr^{2+} (0.24–0.39 mg/L) among the trace elements is higher in the lake water and also exhibit temporal variations, in contrast to the low Al^{2+} (0.003–0.208 mg/L) concentration in the lake water. The trace elements are important for both human and plant health as well. Trace elements such as Mn, Fe, Zn and Cu are vital to plant metabolism as they play an essential function in processes such as respiration and photosynthesis. In humans, trace elements play a vital role in metabolic processes such as activation of enzymes, glucose metabolism, red blood cell formation, normal growth and development of body and immune system, etc. (Berner and Berner 1987).

Table 3. *Trace elements.*

Sl. no.	Cu	Li	Be	B	Al	Si	V	Cr
1. (J)	0.010547	0.002416	0.000018	0.031561	0.085516	0.001821	0.002474	0.001483
2. (J)	0.008596	0.003547	0.000035	0.070702	0.208346	0.001186	0.002014	0.001439
3. (J)	0.003099	0.003159	0.000008	0.02546	0.031607	0.000207	0.000968	0.000722
4. (J)	0.001125	0.00314	0.00001	0.050438	0.017054	0.000995	0.000663	0.000753
5. (J)	0.004277	0.002844	0.000009	0.024128	0.045316	0.001532	0.001872	0.001522
6. (J)	0.012135	0.003466	0.000006	0.067138	0.028452	0.000616	0.001936	0.001074
7. (J)	0.005177	0.002801	0.000018	0.046198	0.051148	0.000785	0.001923	0.001234
8. (J)	0.001601	0.003127	0.000002	0.039069	0.0034	0.00069	0.000307	0.000955
1. (S)	0.005806	0.003535	0.000006	0.081338	0.007804	0.006597	0.000842	0.002089
2. (S)	0.00783	0.003043	0.000006	0.049226	0.037147	0.003241	0.002104	0.001197
3. (S)	0.005876	0.003305	0.000004	0.08118	0.024429	0.003233	0.000713	0.001033
4. (S)	0.007128	0.003316	0.00003	0.062023	0.068112	0.003152	0.002129	0.00119
5. (S)	0.004283	0.002996	0.000002	0.061248	0.016757	0.002668	0.000657	0.000766
6. (S)	0.006649	0.003307	0.000024	0.054408	0.187008	0.003027	0.002137	0.002039
7. (S)	0.007319	0.003288	0.000009	0.077949	0.038076	0.003316	0.002026	0.001641
8. (S)	0.003891	0.003994	0.000002	0.143562	0.063514	0.004745	0.001243	0.001549
9. (S)	0.007411	0.004181	0.00001	0.071981	0.049906	0.00486	0.001788	0.001382
10. (S)	0.004138	0.00454	0.000012	0.065237	0.010132	0.006163	0.002727	0.001102

Sl. no.	Mn	Fe	Ni	Co	Zn	As	Se	Rb
1. (J)	0.017457	0.129763	0.003853	0.000223	0.049458	0.001176	0.000137	0.001157
2. (J)	0.036005	0.163471	0.004581	0.000368	0.115186	0.00148	0.00018	0.001409
3. (J)	0.007357	0.048284	0.001427	0.000108	0.008398	0.001329	0.000144	0.00105
4. (J)	0.011206	0.05107	0.003058	0.00014	0.017365	0.001319	0.000171	0.001417
5. (J)	0.006016	0.108942	0.003364	0.000161	0.054281	0.001257	0	0.001478
6. (J)	0.026018	0.072483	0.004164	0.000171	0.018373	0.001599	0	0.001426
7. (J)	0.018356	0.06203	0.005688	0.000259	0.019407	0.001395	0	0.001481
8. (J)	0.000698	0.133878	0.003118	0.000199	0.005232	0.000451	0.000208	0.000523
1. (S)	0.001439	0.095607	0.003801	0.000107	0.007664	0.001409	0.000528	0.001015
2. (S)	0.005351	0.082173	0.002805	0.000123	0.025875	0.001549	0.000373	0.001089
3. (S)	0.018684	0.081234	0.002947	0.000132	0.028322	0.00152	0.000285	0.001235
4. (S)	0.024941	0.097964	0.013255	0.000155	0.020094	0.001872	0.000305	0.001233
5. (S)	0.018225	0.07488	0.002866	0.000131	0.015998	0.001495	0.000122	0.001016
6. (S)	0.022792	0.107884	0.02242	0.000331	0.023867	0.001888	0	0.001144
7. (S)	0.035253	0.089716	0.007979	0.000197	0.019428	0.001705	0	0.00122
8. (S)	0.015853	0.131464	0.003511	0.000348	0.013425	0.001371	0.000309	0.001411
9. (S)	0.016998	0.168828	0.00413	0.000295	0.016909	0.001179	0.000266	0.002178
10. (S)	0.001332	0.112748	0.003207	0.000114	0.005699	0.000947	0	0.000791

Table 3. *(Continued.)*

Sl. no.	Sr	Mo	Ag	Cd	Sb	Ba	Pb
1. (J)	0.240516	0.000366	0.000064	0.000125	0.000104	0.014116	0.02685
2. (J)	0.31093	0.0004	0.00007	0.000168	0.000149	0.017879	0.085029
3. (J)	0.289097	0.000283	0.000126	0.000028	0.000055	0.008385	0.000833
4. (J)	0.299978	0.000449	0.000038	0.000046	0.00008	0.0104	0.001057
5. (J)	0.336426	0.000154	0.000156	0.00008	0.000058	0.022126	0.003609
6. (J)	0.355932	0.000213	0.000043	0.000039	0.00007	0.019209	0.001292
7. (J)	0.29333	0.000282	0.000101	0.001056	0.000086	0.01656	0.001482
8. (J)	0.249764	0.000738	0.000025	0.000016	0.000249	0.013014	0.00006
1. (S)	0.333438	0.001949	0.000035	0.000044	0.000117	0.014517	0.000141
2. (S)	0.325619	0.000304	0.000058	0.000049	0.000087	0.019885	0.012978
3. (S)	0.350658	0.000403	0.000019	0.000072	0.000074	0.01423	0.000716
4. (S)	0.383809	0.001001	0.000071	0.000084	0.000091	0.019293	0.002758
5. (S)	0.32688	0.000303	0.000055	0.000048	0.000067	0.01183	0.001692
6. (S)	0.37535	0.00072	0.000069	0.000116	0.000095	0.019592	0.004854
7. (S)	0.374489	0.000563	0.000033	0.000123	0.000079	0.02143	0.003982
8. (S)	0.395257	0.000433	0.000041	0.000066	0.000081	0.015573	0.001507
9. (S)	0.330537	0.000469	0.000045	0.000129	0.000079	0.015012	0.000658
10. (S)	0.369616	0.001271	0.000033	0.000023	0.000068	0.029814	0.000084

Note: Units in mg/L.

5.3 *Water types*

Using Piper trilinear diagram (figure 4), three main water types were identified: Ca–HCO_3, Mg–HCO_3 and hybrid. Most of the samples (85%) are of hybrid type, followed by the Ca–HCO_3 type (13%) and the remaining 2% are of Mg–HCO_3 type. The dominance of hybrid type indicated the role of multiple lithology including carbonates and silicates in controlling the chemistry of the lake water. As discussed above, the catchment of the lake consists of both carbonate rocks (Triassic limestone) and silicates (Karewas deposits), which support the interpretation. The plotting of the water samples near the left corner of the diamond in the Piper trilinear diagram shows that the lake water is rich in Ca^{2+}, Mg^{2+} and HCO_3 and possesses temporary hardness (Hounslow 1995). This pattern also shows that the lake water is dominated by alkaline earth (Ca^{2+}, Mg^{2+}) and weak acids such as HCO_3. No significant seasonal change in the hydrochemical facies was found indicating that the origin of most of the natural ions is lithogenic.

Figure 4. Piper trilinear diagram.

5.4 *Source of the solutes*

Use of Gibbs formula (Gibbs 1970) indicated that the major mechanism controlling the water chemistry of the Manasbal lake is the rock–water interaction (TDS: 122–314 mg/L and weight ratio of $Na/(Na+Ca)$:(0.1–0.3). To determine the dominant sources (carbonate or silicate rocks) of major ions, HCO_3 is plotted against Ca, Cl against Na, $Ca+Mg$ against HCO_3 and ($Ca+Mg$) against (HCO_3+SO_4) in figure 5. The figure indicates carbonate and dolomite lithology as the dominant source of major ions respectively. The decreased concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+ and HCO_3 in summer and the negative correlation (table 4) between Ca^+ (June) and Cl^- (June), SO_4^- (June) and Mg^+ (June), NO_3 (September) and Cl^- (September) can be attributed to increased uptake and exchange of these ions by the planktons in summer. The trace elements Fe^{2+}, Mn^{2+}, Ba^{2+} and Sr^{2+} show higher concentration in the lake water. As pH and redox conditions influence the
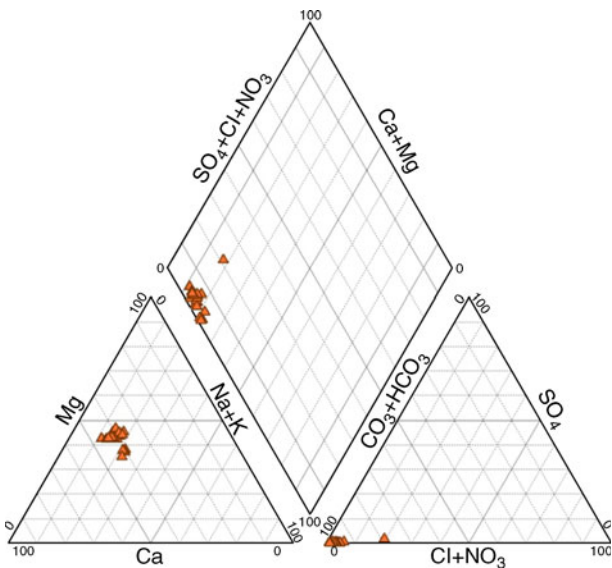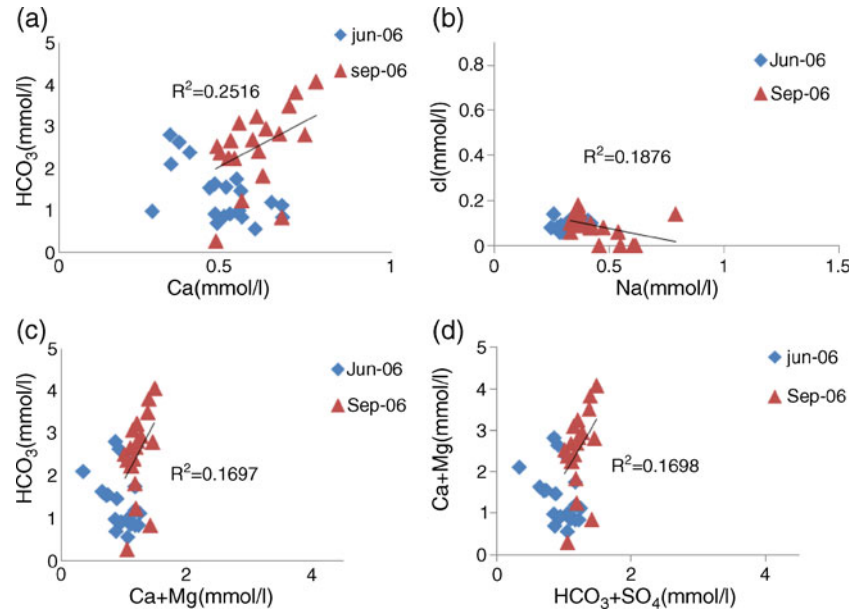
Figure 5. Scatter diagrams showing possible liganding of major ions.

behaviour of various trace elements, the correlation matrix for June (table 5) and September (table 6) was prepared to determine their correlation with each other in different seasons (June and September). It shows that there exists a strong negative correlation between pH–Fe, pH–Ba, pH–Cr, pH–Vn, and pH–Ca+Mg as well as a positive correlation between pH+Mn, Fe+Cr, Mn+Vn, Al+Vn, Al+Cr, Al+Fe, Ba+Sr, Ba+Cr, Ba+Vn, Cr+Vn and Ca+Mg against Ba, Ca+Mg against Cr and Ca+Mg against Fe. Whereas, in September the pH of the water samples shows a strong correlation with Mn^{2+} but negative correlation with Sr^{2+} and Ca+Mg. The higher concentration of these trace elements in September shows the reducing environment of lake which facilitates the dissolution of

these trace elements. In the oxidizing environment, these trace elements get scavenged and move to sediments responsible for their lower concentration in the lake water in June. The reasons of these temporal variations are connected to the hydrological conditions in the watersheds as well as biological productivity in the lakes. The increased plankton production during summer favours an increased sedimentation of metals bound to particles and a subsequent decrease in the content of most elements in the water column (Salbo and Steinnes 1995). The concentration of Al^{2+} is low because aluminium is highly insoluble in natural water, and also because of the alkaline water of the lake. The weathering of the Fe^{2+}- and Mn^{2+}-bearing minerals as well as sewage effluents are the main sources

Table 4. *Correlation among different variables (major elements in June and September 2006).*

	Ca_J	Ca_S	Na_J	Na_S	Mg_J	Mg_S	Cl_J	Cl_S	NO₃_J	NO₃_S	SO₄_J	SO₄_S	HCO₃_J	HCO₃_S
Ca_J	1.000													
Ca_S	0.215	1.000												
Na_J	−0.264	−0.237	1.000											
Na_S	0.279	0.441	0.045	1.000										
Mg_J	0.235	−0.523	0.135	0.168	1.000									
Mg_S	0.167	0.741	−0.326	0.178	−0.346	1.000								
Cl_J	−0.774	−0.337	0.391	−0.168	−0.098	−0.581	1.000							
Cl_S	0.135	0.206	−0.452	−0.433	−0.216	0.377	−0.458	1.000						
NO₃_J	−0.027	0.122	−0.229	0.038	−0.113	0.106	−0.163	−0.058	1.000					
NO₃_S	0.098	0.115	0.335	0.480	0.127	−0.338	0.367	−0.782	−0.039	1.000				
SO₄_J	0.052	0.586	−0.362	0.168	−0.755	0.601	−0.264	0.215	0.169	−0.233	1.000			
SO₄_S	−0.418	−0.008	0.024	−0.465	−0.289	0.254	0.363	0.077	−0.318	−0.174	0.261	1.000		
HCO₃_J	−0.579	−0.312	0.327	−0.588	−0.149	−0.147	0.325	0.207	−0.235	−0.360	−0.139	0.261	1.000	
HCO₃_S	−0.240	0.510	−0.370	−0.214	−0.688	0.197	0.066	0.533	0.171	−0.189	0.344	−0.043	0.212	1.000

Table 5. *Correlation matrix of trace elements in June 2006.*

	pH	Fe	Mn	Ba	Sr	Cr	Vn	AL	Ca+Mg
pH	1.000								
Fe	−0.653	1.000							
Mn	−0.342	0.383	1.000						
Ba	−0.663	0.392	0.374	1.000					
Sr	0.028	−0.273	0.298	0.591	1.000				
Cr	−0.747	0.645	0.359	0.778	0.068	1.000			
Vn	−0.562	0.273	0.568	0.635	0.252	0.815	1.000		
AL	−0.381	0.646	0.780	0.310	0.055	0.559	0.553	1.000	
Ca+Mg	−0.912	0.729	0.154	0.597	−0.001	0.634	0.338	0.316	1.000

Table 6. *Correlation matrix of trace elements in September 2006.*

	pH	Fe	Mn	Ba	Sr	Cr	Vn	Al	Ca+Mg
pH	1.000								
Fe	−0.008	1.000							
Mn	0.690	−0.385	1.000						
Ba	−0.025	0.035	0.170	1.000					
Sr	−0.512	0.152	−0.191	0.406	1.000				
Cr	−0.107	0.246	−0.072	0.044	0.250	1.000			
Vn	0.266	0.261	0.333	0.879	0.373	0.110	1.000		
Al	0.257	0.209	0.067	0.050	0.435	0.480	0.317	1.000	
Ca+Mg	−0.595	0.513	−0.575	0.309	0.254	0.379	0.124	−0.243	1.000

of Fe^{2+} and Mn^{2+} in the lake water. Mn^{2+} is likely to be related from minerals along with Fe^{2+} and Ca^{2+}. Sr^{2+} and Ba^{2+} belong to the same group and may have similar characters. However, $Be(OH)_2$ is almost insoluble, whereas $Sr(OH)_2$ and $Ba(OH)_2$ are sparingly soluble. Sr^{2+} and Ba^{2+} exist in nature as sulphates or carbonates, which have very limited solubility in water (Liptrot 1989). The relative concentrations of these elements in groundwater are controlled by the solubility of their sources. The oxides of Sr and Ba react with water to form strong bases (Mahan 1966). Theses oxides also react with acids and dissolve in water to give stable Sr^{2+} and Ba^{2+} ions which could be leached from the host rock and other minerals into the groundwater. Strontium is strongly coupled to calcium in primary source rocks and is mostly abundant in Ca-rich sources such as limestone. Sr^{2+} occurs primarily in dolomites and limestone. The plots of (Ca+Mg) against HCO_3 and (Ca+Mg) *versus* (HCO_3+SO_4) (figure 5) suggest dolomite lithology as the main source of major ions.

5.5 *Anthropogenic inputs into the lake water system*

Nitrate is an important pollutant in the environment, being generally derived from the agricultural fertilizers, atmospheric input, human and animal excreta, bio-combustion, etc. (Prospero and Savoie 1989; Agarwal *et al* 1999; Jeong 2001; Xiao and Liu 2002; Liu *et al* 2006). The distribution trend of NO_3 in the Manasbal lake clearly indicates anthropogenic inputs. Higher concentrations are observed near the periphery towards eastern side of the lake with more anthropogenic activities. The concentration of NO_3 was 0.01–2 mg/L in winter and comparatively lower (0.002–0.9 mg/L) in summer (figure 6). The higher NO_3 concentration along the shore reflects the pollution due to human and animal excreta. The desirable limit of nitrate in drinking water is 45 mg/L according to WHO norms. Higher concentration of nitrate in drinking water makes it toxic and causes blue baby disease methaemoglobinaemia in children and gastric carcinomas. However, regarding NO_3 contamination (1.72–2 mg/L), although the values are within the permissible limit and not very alarming, the gradually increasing trend is certainly not acceptable. It is however, important to guard its spatio-temporal variability as the water is used for domestic as well as agricultural purposes.

6. Water quality of the lake

A major objective of the study of the hydrochemistry of the Manasbal lake was to find out whether the lake water is fit for drinking, irrigation and other purposes (Todd 1980; Chow *et al* 1988). The
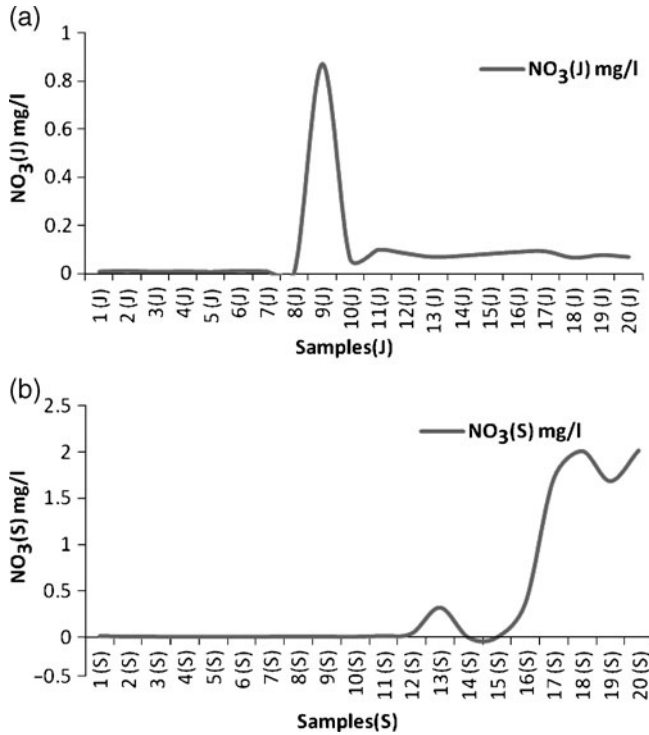
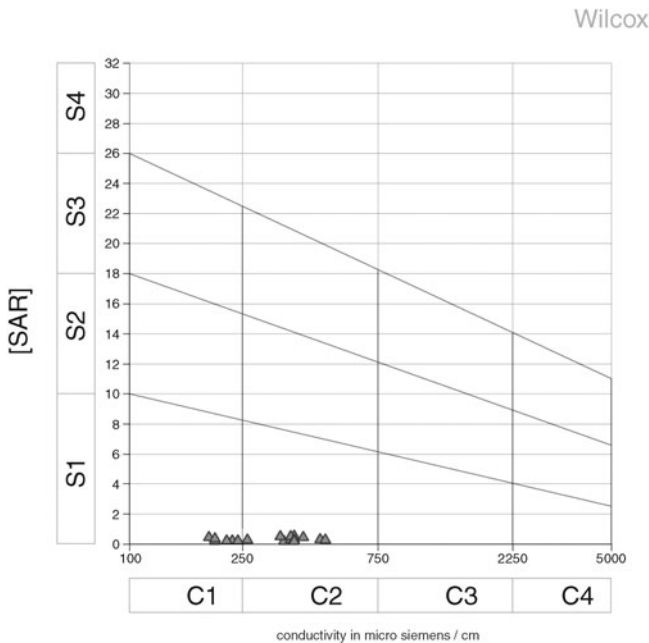Figure 6. Showing nitrate trend in (**a**) June 2006 and (**b**) September 2006.

Figure 7. Salinity hazard diagram.

quality of the lake water with respect to major ion chemistry and trace elements is safe for drinking purposes according to the guidelines proposed by WHO (1998). The relative activity of sodium ion in the exchange reaction with soil is expressed in terms of a ratio known as sodium adsorption ratio (SAR). The Salinity Laboratory of the US Department of Agriculture recommends SAR because of its direct relation to the adsorption of sodium by soil. The salinity hazard diagram (figure 7) was used for the classification of water samples at various sites from Manasbal lake to study its suitability for irrigation. The diagram shows that water samples of eight sites are from the C2S1 field and possess medium salinity and low sodium hazards. Therefore, the water from those sites can be considered suitable for plants with moderate salt tolerance and can be used for irrigation. Further, 50% of samples from the lake water (approx. 8) are from the C1S1 field of the diagram, possess low sodium and low salinity hazards which indicates that water from these sites does not pose any threat to vegetation, crops and soil. Hence, the water of the study area can be considered suitable for irrigation. The crop growth is very high and the plant growth is very good in these soils.

7. Conclusions

The primary data were generated using the chemical analyses of the water samples and the data scarcity was overcome by making precise estimates at additional locations using the theory of regionalized variables. The lake water was found to be alkaline with low total dissolved salts. Calcium was the dominant cation and bicarbonate, the dominant anion. Three types of water found in the lake (Ca–HCO_3, Mg–HCO_3 and hybrid water), reflect the initial stage of evolution of the lake water. Significant temporal variation was found in the trace elements Fe^{2+}, Mn^{2+}, Ba^{2+} and Sr^{2+}, which may be due to the hydrological conditions in the watershed as well as biological productivity in the lake. The sources of solutes were found to be lithogenic with carbonate (Triassic Limestone) and silicate (Karewas) as the dominant sources of solutes. All the chemical constituents were found to be within the WHO permissible limits indicating that the lake water is potable and suitable for other purposes. Linear geostatistics could successfully be applied to enhance the dataset using the continuity of the lake water and the absence of turbulence found in major fast flowing rivers. However, regular monitoring using an optimal monitoring network at a suitable frequency is recommended to detect any unacceptable variability of pollutants and adopt appropriate remedial measures.

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