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Imprints of long-range-transported pollution on high-altitude Eastern Himalayan lake water chemistry

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Abstract Pangang Teng Tso Lake, located at an altitude of 3962 m in the Eastern Lesser Himalaya, was monitored for seasonal variation in hydrogeochemical processes, major ions and levels of trace elements to understand the imprints of long-range-transported contamination. Results revealed that major cations except Na decreased, whereas major anions except NO_3^- and PO_4^{3-} increased in the post-monsoon. ANOVA indicated that pH, EC, TDS, Na^+, HCO_3^-, Cl^- and NO_3^-, PO_4^{3-} showed significant seasonal variation in the P. T. Tso Lake. Wet precipitations of aerosols were found to be the most important source of major ions. Lake water chemistry is attributed to long-range transport of air pollutant through dry precipitation in the pre-monsoon, and by chemical weathering, biological and mineralization processes in post-monsoon. In pre-monsoon, trace elements were found to be in the order of Fe > Mn > Zn > Pb > Cu > Cr > Cd with slight change in Pb, Cd, Cr and Cu in post-monsoon. Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by NOAA's Air Resources Laboratory was used to understand the long-range transport and depositions of aerosols. The results of HYSPLIT back-trajectory model illustrate that air arriving in the vicinity of the lake has an origin from the southeast direction and the mid-Gangetic plain during pre-monsoon and post-monsoon season, respectively. The interrelationship among trace elements in the projection of factor 1 and 2 implies that natural weathering and metal-containing aerosols transported from elsewhere may be the governing processes for lake water chemistry. The study suggests that seasonal changes in water chemistry of high-altitude lakes can reflect the imprints of change introduced through long-range-transported pollution. Long-term monitoring programs are recommended for periodic evaluation of the high-altitude lakes worldwide in order to trace climate change impacts.

Introduction

High-altitude lake (HAL) research is of significant importance as change in the lake chemistry reflects global climate change (Thies et al. 2007; Zaharescu et al. 2009; Li et al. 2014; Deka et al. 2015a). This is especially because these lakes are located in pristine environment and in general lack direct anthropogenic impacts. Further, if certain pollutants such as major ions, trace elements, sulfur- or nitrogen-containing compounds are being added to such systems through mineralogical dissolution or atmospheric transport, there is limited opportunity for neutralization or uptake of such compounds (Deka et al. 2015b). This is due to limited buffering capacity of these lakes attributed to the purity of water and weak soil–water interaction. Therefore, HALs are known as sensitive indicators of changes in local, regional or global environment (Talbot 1996; Clow et al. 2002; Gopal 2005; Zaharescu et al. 2009).

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As most HALs are located in the pristine environment, there is no direct anthropogenic source of pollution. Thus, the changes occurring in the HAL water chemistry may be attributed to long-range transport of air pollution (LRTAP). LRTAP can affect lake chemistry through both dry and wet perception of aerosols. Thus, HAL water chemistry can be used as an indicator of changes introduced by LRTAPs. The hydrogeochemistry of HALs is primarily influenced by the seasonal changes in major ion chemistry which is further executed by the lithology, mineralogy, catchment area, weathering process and precipitation (Lewin and Macklin1987; Patrick et al. 1998; Anshumali and Ramanathan 2007; Zaharescu et al. 2009; Kumar et al. 2011; Deka et al. 2015a). Mineral weathering contributes to majority of base cations and alkalinity to HALs, and hence seasonal variations in such parameters along with trace elements can largely reflect differences in dominant mineral weathering reactions and atmospheric inputs. In a monsoon-dominated tropical country like India, seasonal variations can be significantly dominating enough to understand the imprints of LRTAPs in the different timescales. Numerous studies reported elevated inputs of trace element to lake systems due to LRTAP (Yang and Rose 2005; Han et al. 2007). Most frequently, Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model developed by NOAA's Air Resources Laboratory (ARL) was used to understand the long-range transport and depositions of aerosols because of its climate implications and deleterious health impacts (Cohen et al. 2002, 2007, Deka et al. 2015a). Thus, it is imperative to assess the level and source of such aerosols contributing various trace elements to the HAL water. The information will eventually lead to better understanding of the imprints of LRTAP on water chemistry in pristine environments.

The literature available pertaining to high-altitude lakes of the world is still weak and needs to be strengthened in the context of present environmental challenges. Since the Himalayan HALs have gained little attention so far in terms of studies carried out, they are becoming increasingly important under climate change scenario. Moreover, scientific information on the Eastern Himalayan high-altitude lakes is rare (Khadka and Ramanathan 2012). In light of the above discussion, we decided to monitor Pangang Teng Tso (P. T. Tso) Lake located at an altitude of 3962 meters above mean sea level (AMSL) in the Eastern Lesser Himalayas. The aim of this study was to: (a) understand the imprints of long-range-transported contaminants on lake water through seasonal variation in hydrogeochemical processes and estimation of seasonal variation in the major ions as well as metal concentration (Fe, Mn, Zn, Pb, Cu, Cr and Cd) in the lake water and (b) trace the source of aerosols through multivariate statistical technique and HYSPLIT back-trajectory model.

Materials and methods

Study area description and climatic condition

Pangang Teng Tso Lake in Arunachal Pradesh (India) is popularly known as P. T. Tso Lake and is located at 18 km from Tawang Township. P. T. Tso Lake is 3962 meters AMSL in the Eastern Lesser Himalayan region. The lake is located at latitude and longitude of 27°36′16.56″N and 91°51′18.95″N. A hydrogeomorphological map of the Tawang district is given in Fig. 1. The district is bounded by Lower Tibet in the north, Bhutan in the south and West Kameng district in the east. During winter months, the lake remains entirely frozen. The soil in the district is generally loamy or sandy loam mixed with coarser soil particles. In the forested regions, the soil generally contains high humus and nitrogen levels. Soils in the mountain are relatively poor in organic materials (CGWB 2009). This category of soil is reddish in color and acidic in nature. The soil found along the foothill areas is alluvial, loamy or sandy loam mixed with gravel and pebble.

The climatic condition of Arunachal Pradesh is governed by the Himalayan system. The climate of Tawang district is largely influenced by the nature of its terrain. The summer is moderate with an average temperature of 13 °C and extremely cold in winter with an average temperature of 11 °C below the freezing point. However, the mountain peaks are covered with perpetual snow. In winter, temperature falls below freezing point. In general, June to September is regarded as a monsoon period. Four months before the monsoon period are regarded as pre-monsoon, i.e., February to May, and 4 months after monsoon are regarded as post-monsoon, i.e., October to January. Monsoon is considered as summer, and rest period is considered as winter. Annual rainfall of Tawang district varies from 1500 to 2000 mm. Heavy rainfall occurs during summer and occasional rainfall/snowfall during winter. Most of the rainfall is received during monsoons from June to September. January and February are the driest months of the year. The summer rainfall is dominated by southwest monsoon.

Sampling

The sampling sites were selected in a way to bear maximum representativeness for the lake (Fig. 1). The number of surface water samples was 17 and 13 in the pre-monsoon (May, 2011) and post-monsoon (November, 2011) seasons, respectively. The number of sampling locations sampled in next season was reduced because there were very less variations observed among few close samples out of 17 sampled sites. The water samples were collected from the
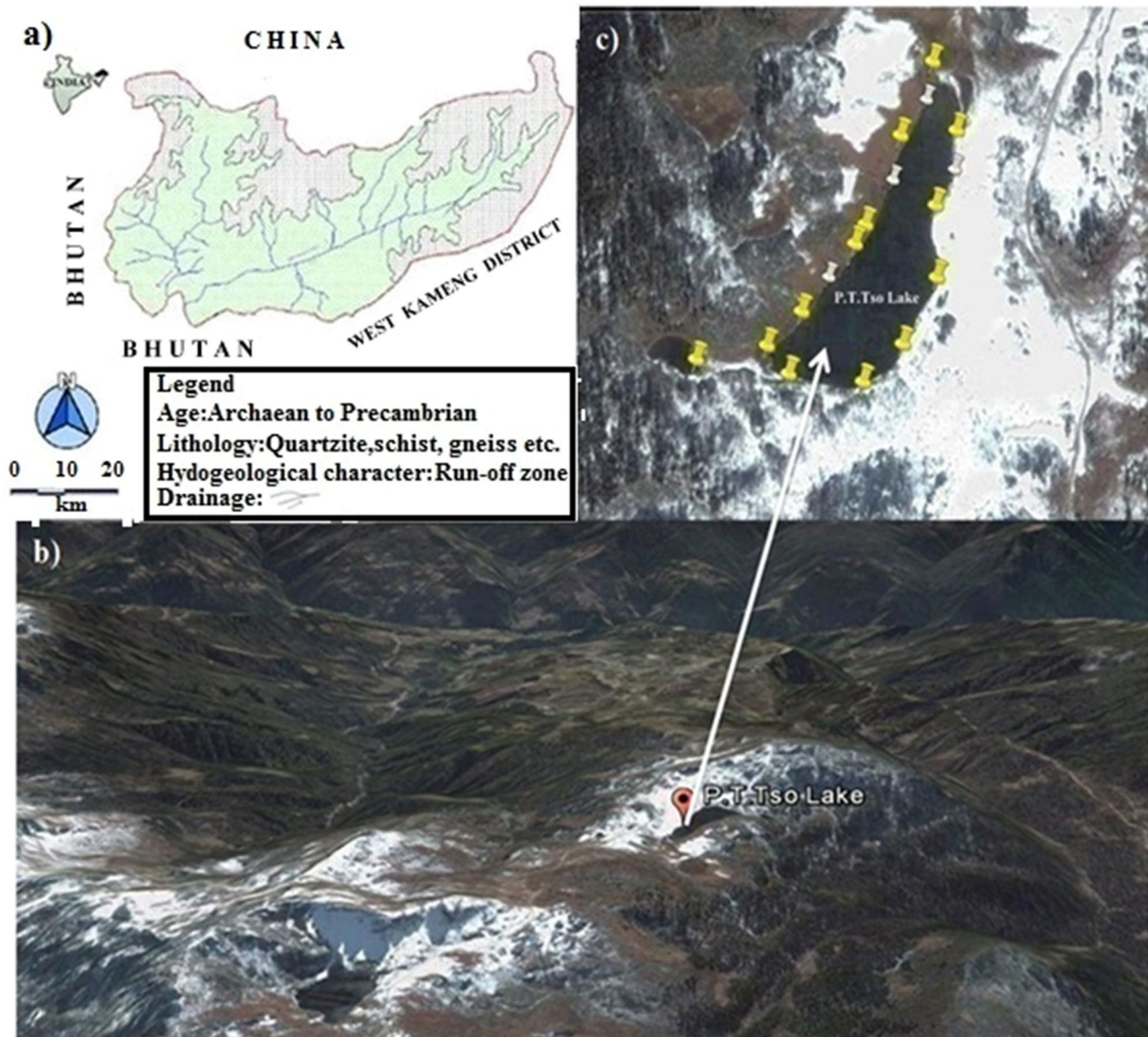
Fig. 1 Map showing **a** hydrogeomorphology of Tawang district, Arunachal Pradesh, **b** 3D view of P. T. Tso Lake, and **c** sampling location of the pre-monsoon ($N = 17$) indicated as *yellow* and *white* *thumbnails* and of the post-monsoon ($N = 13$) indicated by *yellow* *thumbnails* only (Courtesy: Google Earth)

periphery of lakes with a maximum depth of 20 cm below the water surface. The water samples were collected in two different polypropylene bottles of size 500 and 125 ml. The water samples collected in 125-ml bottles were filtered using 0.45-μm Millipore membrane filters with hand-operated vacuum pump. The filtered samples were acidified with 2–3 drops of concentrated HNO_3 in field to bring down pH less than two. The samples were preserved at 4 °C until further analyses. Samples were stored at 4 °C until the analyses. Unfiltered raw samples (500 ml) were used for major ion analyses, whereas acidified and filtered samples (125 ml) were used for trace metal analysis. On-

site measurements included electrical conductivity (EC) and pH using portable Orion Thermo water analyzing kit (Model Beverly, MA, 01915). Alkalinity was also measured in the field using a titration method (APHA 2005). For NO_3^- analysis, HBO_3 acid was used as a preservative (Kumar et al. 2009).

Elemental analyses

The major ion analyses were performed as per the standard techniques given by American Public Health Association (2005). Flame photometer (Systronics-EEL 128)

was used for analyzing sodium (Na^+) and potassium (K^+), and UV spectrophotometer (PerkinElmer 1700) for phosphate (PO_4^{3-}), dissolved silica (H_4SiO_4), sulfate (SO_4^{2-}) and nitrate (NO_3^-). The accuracy of the chemical analyses was carefully defined by checking ion charge balance, which was generally found to be within ±10 %. Dissolved metals {cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), zinc (Zn)} and calcium (Ca), magnesium (Mg) were measured using inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer Optima 2100 DV). Stock multi-element metal solutions of 5 and 50 mg/L were prepared from ICP-grade multi-element standard metal solutions "WAKO-138-13781" and "CertiPUR-1.11355.0100," respectively. The standards were prepared from the stock solutions. Internal standard, metal solutions used for Sc, In and Bi were "CertiPUR-1.70324.0100," "CertiPUR-1.70349.0100" and "CertiPUR-1.70306.0100," respectively (Gogoi et al. 2015). The internal standards were added to samples and standards to reach a final concentration of 200 μL^{-1} of each internal standard. The coefficient of variation in metal concentrations was found to be <10 % in all cases after three measurements of the samples (Deka et al. 2015b).

Statistical analyses

All statistical analyses were performed using "Statistical Package for the Social Sciences (SPSS), version 16.0" (SPSS, Inc., Chicago, IL, USA). Pearson's correlation matrix was used as the measure of correlation between the different physicochemical parameters of both seasons. Factor analysis for water samples was performed to deduce factor controlling nutrient chemistry in the river basin. "Principal component analysis" and "varimax rotation" were used for extraction and deriving factors, respectively (Jha and Minagawa 2013). One-way ANOVA was used to determine significant seasonal variations in chemical parameters in the P. T. Tso Lake.

Application of HYSPLIT back-trajectory model

The HYSPLIT model can be accessed at the Web site of Air Resources Laboratory (ARL) (http://www.arl.noaa.gov/ready.html). For the purposes of our study, reanalyses archived data from the NCEP/NCAR were utilized. The trajectories were initialized at three different heights of 500, 1000 and 1500 m. They are modelled backward 96 h from the geographic coordinates of the lake. Preset perturbation already programmed into HYSPLIT was used for this purpose keeping the initial trajectory unaltered.

Results and discussion

Hydrogeochemistry of the lake water

The average chemical composition of the P. T. Tso Lake is given in Table 1. The pH of lake water ranged from slightly alkaline in the pre-monsoon season to slightly acidic in the post-monsoon season. This may be due to the increase in SO_4^{2-} and Cl^- levels in the post-monsoon. Electrical conductivity (EC) is a measure of the ionic strength and is dependent on the concentration, volume and rate of movement of ionic species (Das and Kaur 2001). The conductivity of the lake was very less with an average of 15.6 ± 17.53 μS/cm in the pre-monsoon season and an average of 3.53 ± 3.53 μS/cm in the post-monsoon season. Such low EC indicates that the lake had very little dissolved ions. The order of the concentration of major cations was $Ca^{2+} > Mg^{2+} > Na^+ = K^+$ in the pre-monsoon and $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ in the post-monsoon. This is probably due to silicate weathering that leads to addition of more Na^+ to the system after pre-monsoon.

The order of the concentration of major anions in the lake water was $HCO_3^- > SO_4^{2-} > Cl^- > NO_3^- > PO_4^{3-}$ for both seasons. Higher NO_3^- and PO_4^{3-} concentration during pre-monsoon samples is attributed to the atmospheric contribution in the form of dry deposition. SO_4^{2-} concentration variation in the P. T. Tso Lake can be explained by the increased dissolution of secondary minerals in the lake surface sediments derived from the black shales (Das and Kaur 2001). SO_4^{2-} in P. T. Tso Lake may be derived from atmospheric deposition and oxidation of S-based compounds in the bottom sediments at the boundary between aerobic and anaerobic environment. Such processes are common at the surface of reduced sediment that gets covered by oxygenated water (Jones 1982). The major cation that characterized the lake water was Ca^{2+} in the monsoon season and Na^+ in the post-monsoon season. $Ca^{2+} + Mg^{2+}$ together accounted for about 79.4 and 37.3 % of all the major cations in pre-monsoon and post-monsoon, respectively.

Overall, the results reveal that major cations in the lake except Na^+ decreased in post-monsoon season, whereas major anions except NO_3^- and PO_4^{3-} increased during post-monsoon season, although the variation was not too high. Such trends are indicative of addition of cations during monsoon directly from either the rain or runoff water of the catchment. The decrease in NO_3^- and PO_4^{3-} concentration may be attributed to consumption in biological processes and mineralization of the N- and P-containing compounds by microorganism. The increase in other anion may be the result of enrichment due to evapotranspiration processes. Not much variation in the water

Table 1 Statistical summary of the hydrogeochemical parameters of the lake water in Pre-monsoon and post-monsoon seasons [all units are in mg/L except metals (μg/L), ratio (Eq/Eq), EC (μS/cm) and pH]

| Parameter	Pre-monsoon		Post-monsoon	
	Range	Avg ± SD	Range	Avg ± SD
pH	6–7.6	7.08 ± 0.08	4.41–6.29	5.86 ± 0.49
EC	6–40	15.6 ± 17.5	1.5–4.9	3.53 ± 0.9
Na^+	0–0.6	0.4 ± 0.15	3.6–4.6	4.3 ± 0.3
K^+	0.1–9	0.7 ± 2.15	0.3–0.4	0.32 ± 0.04
Ca^{2+}	0.5–6.2	2.2 ± 1.9	1.3–2.0	1.5 ± 0.2
Mg^{2+}	0.28–1.6	0.6 ± 0.5	0.4–0.7	0.5 ± 0.09
HCO_3^-	6–10	8.2 ± 0.9	20–24	21.8 ± 1.5
Cl^-	0.3–0.8	0.5 ± 0.2	0.6–0.8	0.7 ± 0.1
SO_4^{2-}	3.1–6.5	4.1 ± 0.95	4.1–8.7	4.7 ± 1.2
NO_3^-	0.95–1.4	1.06 ± 0.1	0.28–1.25	0.5 ± 0.3
PO_4^{3-}	0.09–0.4	0.14 ± 0.12	0.07–0.13	0.09 ± 0.03
SiO_2	1.15–2.68	1.77 ± 0.45	1.36–2.82	1.85 ± 0.37
Cu	2.0–8.0	4.2 ± 5.0	ND	ND
Cd	ND–1.0	6.0 ± 0.5	ND–2.0	1.0 ± 0.08
Cr	2.0–4.0	3.1 ± 2.0	ND	ND
Fe	51–328	164 ± 122	1.0–46	18.0 ± 9.1
Mn	9.0–21	15 ± 5.0	5.0–28	15 ± 2.0
Pb	ND–21	7.0 ± 11	ND–7.0	2.0 ± 2.6
Zn	1.0–23	11 ± 8.0	1.0–21	8.0 ± 6.1
$(Ca^{2+}+Mg^{2+})/Tz^+$	0.14–0.97	0.76 ± 0.28	0.33–0.44	0.37 ± 0.04
$(Na^++K^+)/Tz^+$	0.03–0.86	0.2 ± 0.18	0.57–0.65	0.63 ± 0.03
Mg^{2+}/Ca^{2+}	0.27–0.52	0.44 ± 0.09	0.49–0.57	0.55 ± 0.03
Ca^{2+}/Mg^{2+}	1.9–3.7	2.48 ± 0.63	1.8–2	1.89 ± 0.097
$SiO_2/(Na^++K^+)$	0.20–18.4	3.83 ± 4.31	0.30–0.66	0.40 ± 0.09
$(Ca^{2+}+Mg^{2+})/(Na^++K^+)$	0.17–36.3	10.55 ± 12.67	0.48–0.79	0.59 ± 0.10
$HCO_3^-/(Ca^{2+}+Mg^{2+})$	0.29–3.2	1.3 ± 0.9	2.12–3.61	3.05 ± 0.56
Ca^{2+}/SO_4^{2-}	0.3–5.2	1.55 ± 1.64	0.37–1.1	0.83 ± 0.25

ND not detected

chemistry was observed among the different locations as evident from low standard deviation. This is because water characteristics remain relatively uniform due to mixing by winds (Kaushal et al. 2001). Other factors responsible for the abundance and variation in major cations (Na^+, Ca^{2+}, Mg^{2+} and K^+) and anions (Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, PO_4^{3-}) in surface water are weathering, atmospheric precipitation and possible atmospheric activities (Anshumali and Ramanathan 2007).

Evaluation of hydrogeochemical processes in the lake environment

The chemical compositions of low-salinity waters are controlled by the amount of dissolved salts furnished by atmospheric precipitation and chemical weathering (Kumar et al. 2006; Gibbs 1970). During monsoon, the major ions are the result of atmospheric precipitation, but in winter they are the consequence of chemical weathering processes (Bricker and Garrels 1967; Garrels 1967; Hem 1985; White 2002; Das and Kumar 2014). Various ionic ratios and scatter plots are shown in Table 1 and Fig. 2, respectively, which are indicative of different hydrogeochemical processes occurring in the lake. The ratio $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ varied from 10.55 during pre-monsoon season to 0.59 during post-monsoon season. The $HCO_3^-/(Ca^{2+} + Mg^{2+})$ ratio for both seasons was >2, indicating contribution of carbonate weathering into the lake water. A cross-plot of Ca^{2+} versus SO_4^{2-} was drawn in order to visualize whether gypsum is a common source for both Ca^{2+} and SO_4^{2-} ions (Fig. 2a). Since both ionic species do not increase simultaneously, we can reject the hypothesis. Further, the Ca^{2+}/SO_4^{2-} ratio was >1 for pre-monsoon, indicating that H_2SO_4 does not replace H_2CO_3 as a source of protons for rock weathering (Stallard and Edmond 1983). The ratio of $(Ca^{2+} + Mg^{2+})$ by summation of major cation (Tz^+) ratio was 0.76 for the pre-monsoon season and 0.37 for the post-monsoon season. The ratio indicated the

Fig. 2 Different scatter plots expressing hydrogeochemical processes. a Ca^{2+} versus SO_4^{2-}; b Tz^+ versus $Ca^{2+}+Mg^{2+}$; c Tz^+ versus Na^++K^+; d EC versus Na^+/Cl^-; e Cl^- versus Na^+; and f $SO_4^{2-}+HCO_3^-$ versus $Ca^{2+}+Mg^{2+}$ in P. T. Tso Lake
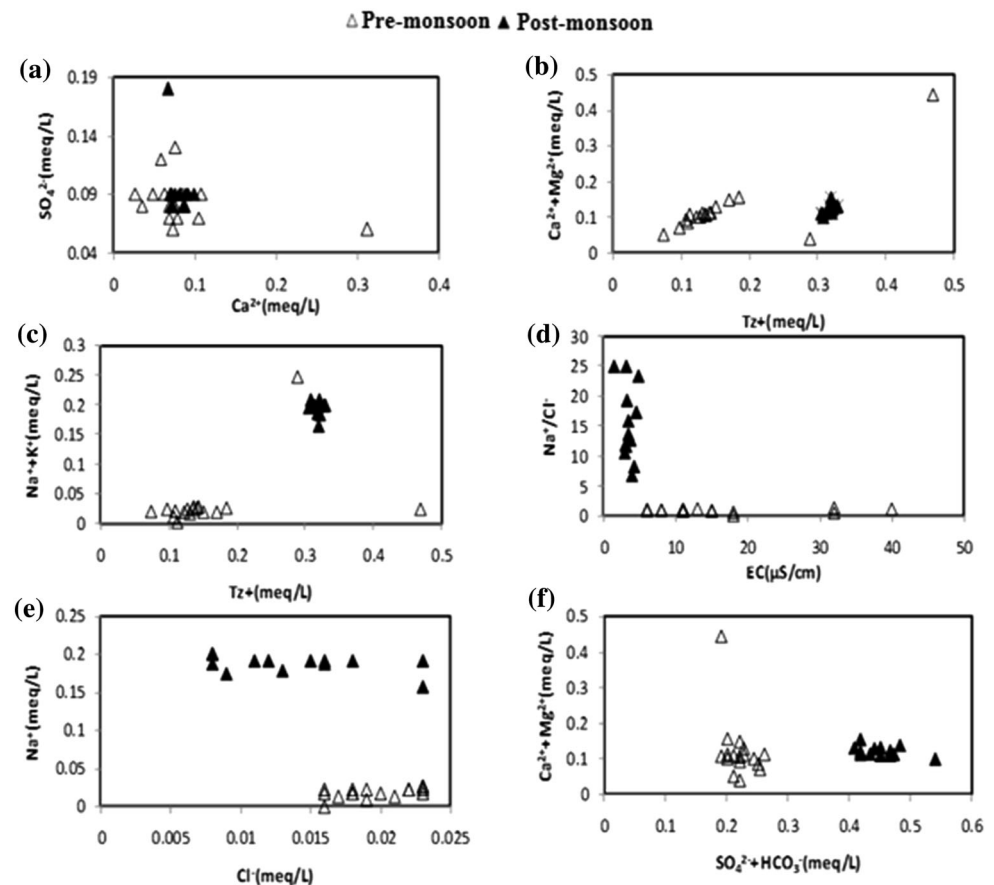
abundance of Ca^{2+} and Mg^{2+} in the pre-monsoon season, which could be the result of carbonate weathering. $Ca^{2+} + Mg^{2+}$ versus Tz^+ plot (Fig. 2b) suggests that Ca^{2+} and Mg^{2+} were the major cations in the pre-monsoon though, which supports the occurrence of carbonate weathering during pre-monsoon. However, Ca^{2+} and Mg^{2+} do not constitute a large share in the cations during the post-monsoon period, which could be the result of observed shift in major hydrogeochemical processes.

High percentage of $Na^+ + K^+$ during the post-monsoon season (Fig. 2c) supports silicate weathering. Mg^{2+}/Ca^{2+} ratio was <0.5 for the pre-monsoon samples, which suggests low saturation index resulting in carbonate precipitation (Anshumali and Ramanathan 2007). During both seasons, P. T. Tso was enriched with HCO_3^- accounting for 50–60 % of all anions in the lake. The occurrence of carbonate minerals in lake sediment could be the reason for this high percentage of carbonate during both the seasons. In general, it is expected that the evaporation process would cause an increase in concentration of all species in water. If evaporation is dominant, assuming that no mineral species are precipitated, the Na^+/Cl^- ratio would be unchanged (Kumar et al. 2006). Hence, the plot of Na^+/Cl^- versus EC (Fig. 2d) would give a horizontal line if

enrichment of ions occurs because of evaporation and evapotranspiration, which is not found in this lake system. In the present study, the molar ratio of Na^+/Cl^- generally ranged from 0 to 0.023 in pre-monsoon season and from 0.11 to 0.48 in the post-monsoon season. All the ratios of Na^+/Cl^- for both seasons indicate that ion exchange was the major process prevalent in the lake. The Na^+ versus Cl^- plot (Fig. 2e) indicates that all samples lie below 1:1 ratio that supports the above inference that silicate weathering is not dominant. Lower 1:1 ratio indicates higher chloride concentration probably because of rise in water level, in pre-monsoon season by snow melt. Water level rise causes more salt dissolution from the soil.

The Ca^{2+}/Mg^{2+} ratio for both pre-monsoon and post-monsoon samples lies between 1 and 2 (except one, which is 3.7), which indicates greater input from calcite dissolution into the lake water chemistry (Table 1). The plot of $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$ (Fig. 2f) for both seasons tends to the right, which indicates ion exchange to be the dominant process except during pre-monsoon. Comparatively higher concentrations of silica during the post-monsoon season may be attributed to the weathering of silicate minerals (Kaushal et al. 2001; Helgeson 1968.

Overall, considering very low TDS and EC of this pure lake water as well as resistant quartzitic rocks of the Himalaya, contribution of ions from chemical weathering still needs to be substantiated further with more data set and under the light of other rare geological indicators such as rare earth element data. This is also because weathering is a slow process and thus unlikely to contribute to the change significantly just within 6 months of time.
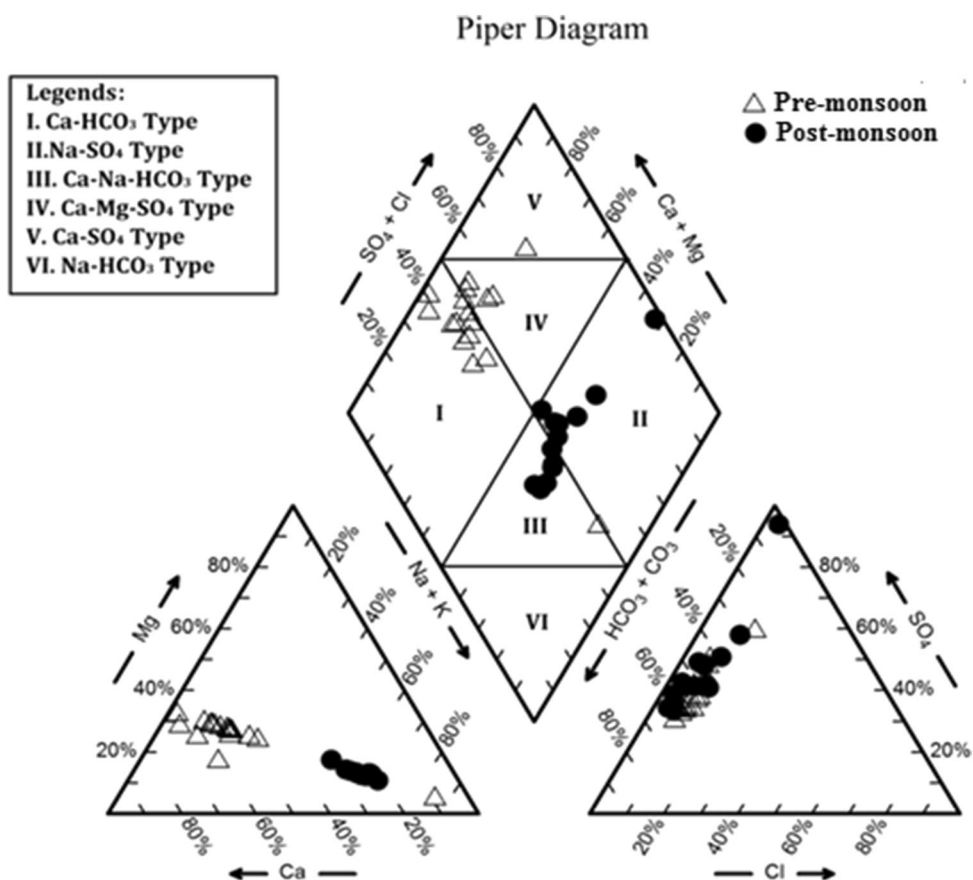
Graphical representation of the hydrogeochemical data

The hydrogeochemical characterization of lake water system is presented through Piper trilinear diagram (Piper 1944) (Fig. 3). During the pre-monsoon season, the lake water chemistry is of Ca^{2+}–HCO_3^- and Ca^{2+}–Mg^{2+}–SO_4^2 type, whereas during the post-monsoon season, water chemistry shifts to Na^+–SO_4^{2-} and Ca^{2+}–Na^+–HCO_3^{--} type. This result suggests that alkaline earths exceed alkali metals and weak acidic anions exceed strong acidic anions in the studied lake as Ca^{2+} and SO_4^{2-} remains dominant during both seasons. Such water has temporary hardness. These changes in overall chemistry support the previous interpretation of carbonate weathering operative during

pre-monsoon and consequent shift to silicate weathering during the post-monsoon.

From the discussion above, considering the low TDS and ions chemistry, the equilibrium state of the lake water with respect to the possible reactants and product minerals was evaluated by Gibbs (1970) plot (Fig. 4). The graphical approach describes the mineral stability fields of minerals in equilibrium with water, in terms of activity ratios of ions in water (Helgeson 1968; Kramer 1968; Paces 1972). The stability fields of crystalline minerals serve as reference points to predict which mineral will react with water, and the direction and the extent of the reaction (Rogers 1989). It was found that precipitation was the most important source of major ions in the water of the P. T. Tso Lake governing the water chemistry of the lake (Fig. 4). Further, lower TDS than the average Indian rain water indicates that the lake water originally receives majority of the water from snow melt. While, during pre-monsoon season, the addition of bicarbonate by rain water decreased $Cl^-/(Cl^- + alk)$ weight ratio, in the post-monsoon season there is a decrease in alkalinity, which leads to higher $Cl^-/(Cl^- + alk)$ weight ratio. Along with this, an increase in TDS is evident in pre-monsoon as well.

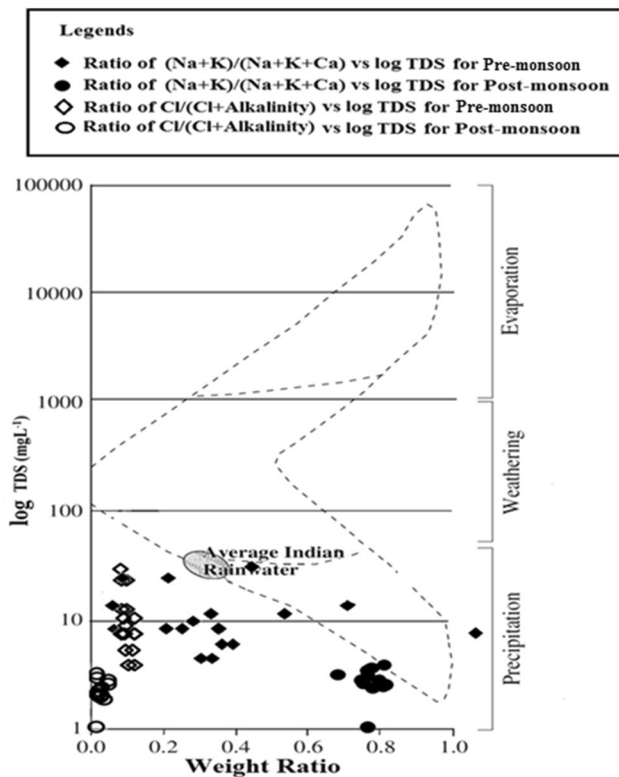**Fig. 3** Piper plot showing the types of water of P. T. Tso Lake in pre-monsoon and post-monsoon seasons

Legends

◆ Ratio of (Na+K)/(Na+K+Ca) vs log TDS for Pre-monsoon
● Ratio of (Na+K)/(Na+K+Ca) vs log TDS for Post-monsoon
◇ Ratio of Cl/(Cl+Alkalinity) vs log TDS for Pre-monsoon
○ Ratio of Cl/(Cl+Alkalinity) vs log TDS for Post-monsoon

Fig. 4 Gibbs plot showing the mechanisms controlling the water quality of P. T. Tso Lake in pre-monsoon and post-monsoon seasons

Multivariate statistical analyses to identify governing processes

The Pearson's correlation matrices are given in Table 2, exhibiting the correlation among different hydrogeochemical parameters of lake water samples. During the pre-monsoon season (17 sampling locations data), significant relationships were observed between Ca^{2+}–EC, Mg^{2+}–EC, Ca^{2+}–Mg^{2+} and NO_3^-, K^+. Strong correlations were found between Ca^{2+}–EC and Mg^{2+}–EC, suggesting that the Ca^{2+} and Mg^{2+} cations contribute to the EC of the lake water. It also supported the carbonate weathering theory during the pre-monsoon season. Moderately strong correlations (>0.5) were also observed between Mg^{2+}–pH, Na^+–Cl^-, NO_3^-–SO_4^{2-}, SO_4^{2-}–HCO_3^- and HCO_3^-–SiO_2 in the pre-monsoon season. Such interrelationships between pH^-, NO_3^-, SO_4^{2-} and HCO_3 were attributed to rainfall contribution and the effect of LRTAP. During the post-monsoon season (13 sampling locations data), significant and positive relationships were observed between EC–NO_3^-, Mg^{2+}–Cl^-, PO_4^{3-}–SO_4^{2-}, PO_4^{3-}–SiO_2 and SO_4^{2-}–SiO_2. Strong negative correlations were found between pH–PO_4^{3-}, pH–SO_4^{2-}, EC–PO_4^{3-}, Ca^{2+}–Cl^-, Ca^{2+}–Mg^{2+} and Mg^{2+}–SiO_2. In/post-monsoon season, geochemical processes such as chemical weathering and

the local environment govern the water chemistry (Das and Kumar 2014).

For factor analysis, data were normalized before analysis, and both pre- and post-monsoon data were incorporated as one set of data. The number of significant factors within the data is established by considering only those with an eigenvalue >1.0. The degree of association between each variable and each factor is given by its loading on that factor (Jha et al. 2009). Factor analysis of major ions along with physicochemical parameters of P. T. Tso Lake indicates four trends (Fig. 5). Factor 1 accounted for 35.60 % of variance in the data, and it shows a strong geochemical association between EC, pH, Cl^- and NO_3^-, indicating the effect of anthropogenic influence (LRTAPs) and precipitation. Factor 2 attributing 18.93 % of the variation in data represents association between SO_4^{2-}, PO_4^{3-} and SiO_2, which indicated anthropogenic sources, mineralization and precipitation of organic compounds. Factor 3 accounted for 17.70 % variation with two closely placed loadings for Ca^{2+} and Mg^{2+} as well as Na and HCO_3^-. Such clustering represents contributions from rainfall and watershed of a particular lake.

ANOVA indicated that pH, EC, TDS, Na^+, HCO_3^-, Cl^- and NO_3^-, PO_4^{3-} showed significant seasonal variation in the P. T. Tso Lake as indicated by higher F calculated values compared to F critical values (Table 3). Significant variance of pH, EC and Na^+ showed evaporative enrichment. Significant variance of HCO_3^- and Cl^- showed enrichment due to melt water. Significant variance of NO_3^- indicated the anthropogenic influence on the lake chemistry attributed due to rainfall contribution and the effect of LRTAP. Ca^{2+}, Mg^{2+}, K^+, SO_4^{2-} and SiO_2 did not show significant seasonal variation in the P. T. Tso Lake as indicated by lower F calculated values compared to F critical values (Table 3). This indicates that ions contribution from rock weathering not varied much due to seasonal change in study area.

Occurrence and source of trace elements

The concentration of the different metals (Cu, Cd, Cr, Fe, Mn, Pb and Zn) as found in the lake during pre-monsoon and post-monsoon seasons are presented in Table 1. There is a general trend indicating decrease in the concentration of various metals from monsoon to post-monsoon season. During the pre-monsoon season, trace elements indicate concentration Fe > Mn > Zn > Pb > Cu > Cr > Cd, which remains same during post-monsoon with slight change in the order of Fe > Mn > Zn > Pb > Cd. Higher Fe, Mn and Zn compared to Cd, Pb and Cd may be due to their higher content in the local materials/rock and greater solubility or weathering of such metal-bearing minerals

Table 2 Correlation matrix of the hydrogeochemical parameters of P. T. Tso Lake in the pre-monsoon season and post-monsoon season

Parameters	pH	EC	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}	Mg^{2+}
Pre-monsoon											
EC	0.736										
Cl^-	−0.452	−0.607									
NO_3^-	−0.226	−0.368	−0.302								
PO_4^{3-}	0.231	0.162	0.135	−0.243							
SO_4^{2-}	−0.712	−0.72	0.443	0.651	−0.042						
HCO_3^-	−0.921**	−0.463	0.354	0.082	−0.308	0.561					
Na^+	−0.207	−0.199	0.584	−0.048	−0.3	0.345	0.367				
K^+	−0.064	−0.202	−0.471	0.897**	−0.263	0.332	−0.167	−0.061			
Ca^{2+}	0.442	0.853*	−0.295	−0.395	−0.084	−0.454	−0.112	0.175	−0.383		
Mg^{2+}	0.571	0.917**	−0.359	−0.423	−0.015	−0.558	−0.250	0.108	−0.354	0.987**	
SiO_2	−0.675	−0.365	−0.155	0.261	−0.676	0.213	0.726	0.053	0.226	−0.233	−0.315
Post-monsoon											
EC	0.738										
Cl^-	0.318	0.365									
NO_3^-	0.730	0.954**	0.408								
PO_4^{3-}	−0.916**	−0.805*	−0.456	−0.785*							
SO_4^{2-}	−0.881**	−0.753	−0.456	−0.743	0.991**						
HCO_3^-	−0.349	−0.144	−0.392	−0.282	0.128	0.126					
Na^+	0.268	0.082	−0.377	−0.079	−0.290	−0.346	0.183				
K^+	0.350	−0.104	0.070	−0.234	−0.193	−0.135	0.117	0.095			
Ca^{2+}	0.334	0.444	−0.840*	0.609	−0.387	−0.378	−0.626	−0.581	−0.254		
Mg^{2+}	0.509	0.535	0.742	0.718	−0.570	−0.554	−0.470	−0.539	−0.151	−0.931**	
SiO_2	0.181	0.167	−0.527	−0.279	−0.287	0.183	0.462	0.680	0.478	−0.809	−0.893*

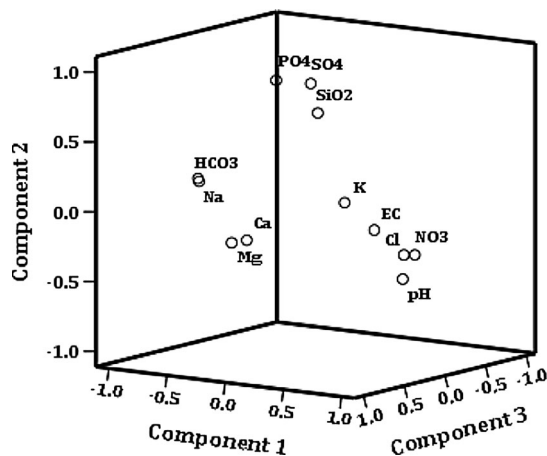** Correlation is significant at 0.01; * Correlation is significant at 0.05

Fig. 5 Three-dimensional representation of water quality parameters alignment obtained from multivariate factor analysis of P. T. Tso Lake water

Table 3 Single-factor ANOVA of P. T. Tso Lake for significant mean variation

Parameters	F critical	F calculated
pH	4.26	48.43
EC	4.26	19.70
Ca^{2+}	4.26	0.20
Mg^{2+}	4.26	0.05
Na^+	4.26	2410.17
K^+	4.26	0.56
HCO_3^-	4.26	831.48
Cl^-	4.26	12.79
SO_4^{2-}	4.26	1.96
NO_3^-	4.26	45.42
PO_4^{3-}	4.26	4.52
H_4SiO_3	4.26	2.31

compared to others elements (Horowitz et al. 1999; Zaharescu et al. 2009). The source of Pb is generally anthropogenic. There are few military settlements near the lake from where the road runoff carrying petrol remains or wear and tear from the vehicles can introduce Pb, Cu and Cd to the lake (Kumar et al. 2013a, b). Fe, Cu and Zn seem to come from natural mineral weathering (Lavilla et al. 2006).

The interrelationship among the elements is displayed in the projection of factor 1 and factor 2 for pre-monsoon and post-monsoon seasons (Fig. 6a, b). It is evident from Fig. 6a that Fe, Cu, Zn cluster together on the positive side of the factor 1 and factor 2 along with anthropogenic chalcophiles, i.e., Pb. Clustering of Fe, Cu and Zn shows that the elements are of geogenic origin as evident from mineralogical analyses too. Positive loading for Pb in factor 1 may be attributed to plate tectonics as chalcophiles are known for their enrichment in high plateau and mountain area which have been uplifted through plate collision (Raymo and Ruddiman 1988; Edmond et al. 1995).

The highest loading on the second component (factor 2) for Pb in pre-monsoon switched to Mn in post-monsoon. This change signifies that pre-monsoon introduces Pb-containing aerosols through wet precipitation. This is also evident from high loading of Cd in pre-monsoon for factor

2 and negative factor loading for Cd in post-monsoon (Fig. 6b). The switch over in factor loading of Pb and Cd is largely due to their source which may be either anthropogenic or local mobilization process. In the post-monsoon season, Mn is identified as factor 1 and it has a mineral source. The second factor is identified to be the set of Cu, Cr and Pb which seem to be due to the anthropogenic influence. Assessment of the metal burden in lake sediments and their relationship with minerals and physico-chemical characterizations of the sediment can be an additional approach for further investigation.

Overall, it seems that long-range transport of aerosols and their wet depositions during monsoon is the reason for the addition of heavy metals to the lake system. This assertion of long-range transport of aerosol deposition to this pristine environment has further been verified by HYSPLIT back-trajectory model for both seasons.

Tracing the source of aerosols through HYSPLIT back-trajectory model

In order to trace the input source of the aerosols to the lake system, trajectories were obtained from HYSPLIT model (Draxler and Rolph 2013; Rolph 2013). The results obtained are shown Fig. 7a, b illustrating the origin and possible source of aerosols in pre-monsoon (May 30, 2011) and post-monsoon (November 25, 2011). Results illustrate that air arriving in the vicinity of the lake has an origin from the southeast direction (Fig. 7a) and the mid-Gangetic plain (Fig. 7b) during pre-monsoon and post-monsoon season, respectively. Such clear difference in the origin of air parcel arriving over the lake substantiates the earlier findings, viz. (1) high HCO_3 and (2) high Cd and Pb loading in the post-monsoon. The reason may be attributed to large-scale post-harvest agricultural waste burning during late November in the mid-Indo-Gangetic plain to quick release of nutrients and clearing the fields for next crop. This leads to release of high carbonaceous aerosol and associated metals in the air which eventually transported over to the high-altitude lakes such as P T Tso Lake in the northeastern India. During pre-monsoon season, origin of air parcel is from southeastern region—east of Burma Mountains—due to which the nature of contamination associated with aerosol is different than that of the mid-Gangetic origin. The results show that P. T. Tso Lake has significant impacts of long-range transport of air pollutants rather by local interferences. This finding should further be tested through long-term monitoring of the fluctuation in key parameters. Overall, high-altitude lakes like P. T. Tso can reflect the change in regional as well as global scale; therefore, it becomes a sensitive environmental system for climate change-related research.
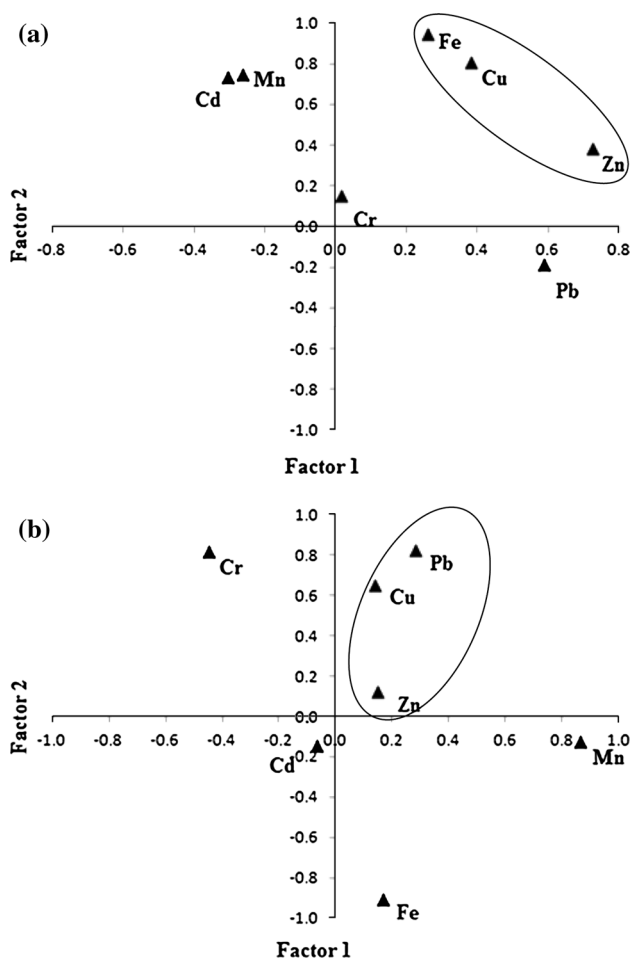

Fig. 6 Factor 1 versus factor 2 of trace metal data for **a** monsoon, **b** post-monsoon of P. T. Tso Lake
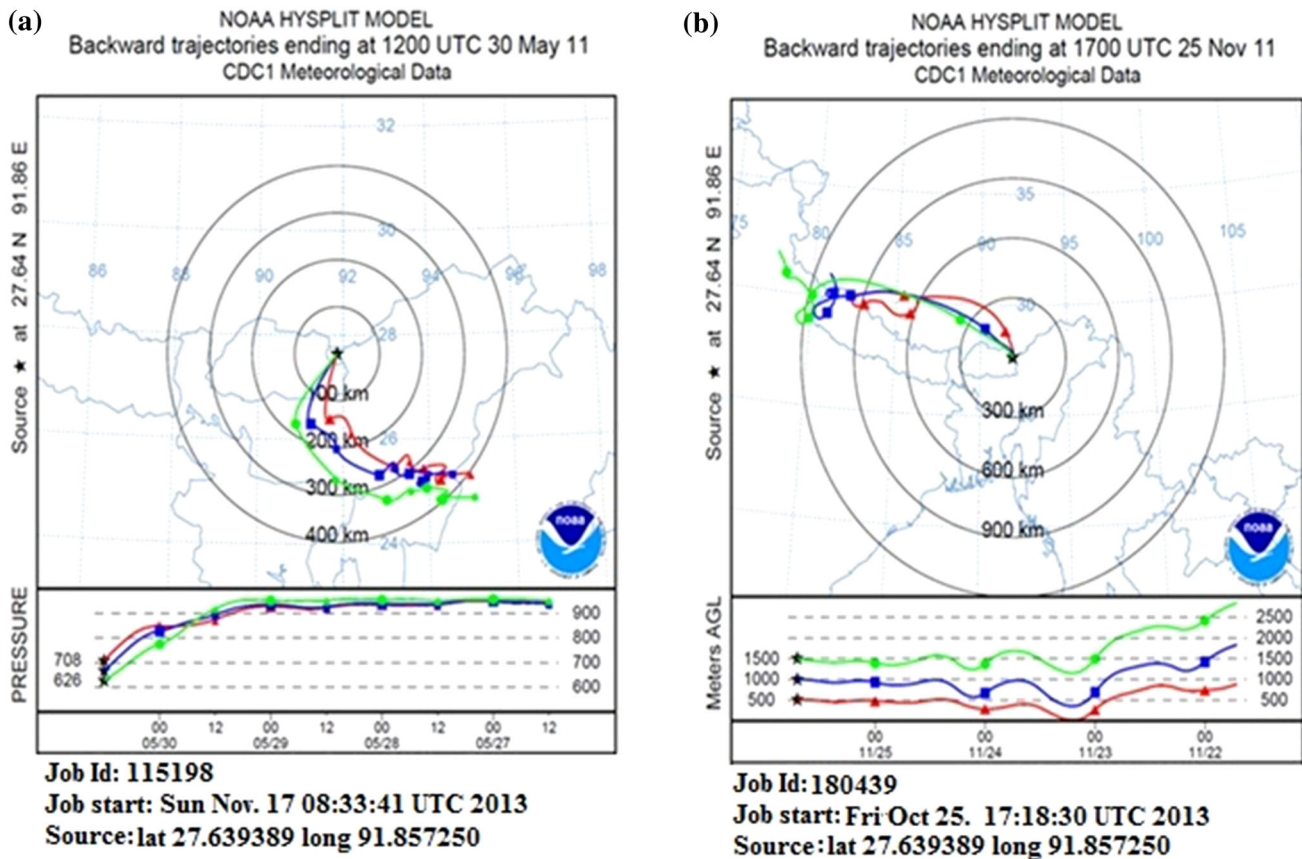
Fig. 7 HYSPLIT backward-trajectory model for **a** pre-monsoon, **b** post-monsoon of P. T. Tso Lake

Conclusion

The study presents the first hand report on geochemical processes, effective CO_2 pressure, level of trace elements of Lake Pangang Teng Tso, in the Eastern Lesser Himalaya. The hydrogeochemical evaluation of the lake water suggested that the lake is not influenced by direct anthropogenic activities in the vicinity but long-range-transport-induced contaminants. Lower TDS than the average Indian rain water indicated that lake water originally receives majority of the water through snow melt. Statistical analyses aptly revealed that the lake water chemistry is attributed to long-range transport of air pollutant through wet precipitation in monsoon, and by biological and mineralization processes in the post-monsoon. ANOVA indicated that pH, EC, TDS, Na^+, HCO_3^-, Cl^- and NO_3^-, PO_4^{3-} showed significant seasonal variation in the P. T. Tso Lake as indicated by higher F calculated values compared to F critical values. The interrelationship among the trace elements in the projection of factor 1 and factor 2 for different seasons implies that natural weathering and metal-containing aerosols may be the source of trace elements in the lake system.

The variability with respect to geological settings, climate, water chemistry and biological activities in different Himalayan lakes limits generalizations about processes operative and mechanism controlling the overall lake water chemistry. The dominance of the atmospherically derived sources on lake water implies that the quality of dry or wet depositions majorly depends on the nature of aerosols, as evident from the HYSPLIT back-trajectory model, which varies due to the difference in the population density, lifestyle and biomass burning. Therefore, long-term monitoring programs are recommended for periodic evaluation of the high-altitude lakes worldwide in order to trace climate change impacts.

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