PROJECT REPORT

DST-SERB NO. SB/DGH-49/2013

Principal Investigator: Dr. M. K. Sharma

Ionic Enrichment Dynamics of Glacial Sediment and Meltwater of Gangotri Glacier

National Institute of Hydrology
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Project Completion Report

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(DST-SERB No. SB/DGH-49/2013 dated 13.01.2014)

Principal Investigator:	**Dr. M. K. Sharma**
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FOREWORD

Gangotri glacier is the biggest glacier in the Ganga basin as well as the origin of the sacred River Ganga. The meltwater of the rivers originating from the Himalayan glaciers are characterised by its low ionic concentrations and play a major role in diluting the high solute load emanating from Ganga plain catchments. Hence any change in the quality and quantity of the Himalayan tributaries of River Ganga under the climate change regime will impact the quality parameters of River Ganga as well. Understanding of low temperature solute acquisition processes is therefore very important for assessing the solute acquisition and pollutant loading further downstream. Therefore, the study of major ions and trace metals in snow and glacier meltwater from the Himalaya has a special significance. Considerable work has been carried out by different investigators on major ion chemistry of meltwater of Gangotri glacier but little is known about the chemical processes involved in glacial sediment and meltwater interaction in the Gangotri glacier catchment. To build credible knowledge on various aspects of Gangotri glacier system, the Science and Engineering Research Board (SERB), Department of Science and Technology (DST), New Delhi launched an initiative under "Integrated Programme on Gangotri Glacier". In view of the importance of low temperature chemical process in controlling the solute acquisition during suspended sediment-meltwater interaction, the project "Ionic Enrichment Dynamics of Glacial Sediment and Meltwater of Gangotri Glacier" has been sanctioned to NIH. Under this project, the study was carried out along the 14 km stretch from the source at Gomukh to Gangotri town.

The activities to meet the objectives of the project were started in the month of June 2014 by taking observations in the Gangotri Glacier during ablation period and analyzing the collected water and sediment samples from the study area. A Project Report titled "Ionic Enrichment Dynamics of Glacial Sediment and Meltwater of Gangotri Glacier" is prepared on the observed and analyzed data of the said project for the period of 3 years duration from 2014 to 2016 by Dr. M. K. Sharma, Scientist 'D' & Principal Investigator of the project, Environmental Hydrology Division of the institute. The study has succeeded in understanding the chemistry of glacier meltwater better during its transport from its source i.e. snout at Gomukh to Gangotri. The study has demonstrated a new insight of persisted closed system behaviour of meltwater from its origin at Gomukh to 14 km downstream at Gangotri. This has been concluded after processing the hydro-chemical data generated during the period 2014-2016. Further, inter-annual and seasonal variability of hydrological and hydro-chemical behaviour of the system has the significant effect on the characteristics of glacio-hydrological weathering environments. Anomalous response of the hydro-chemical characteristics of meltwater associated with delayed discharge peak during the year 2015 has been interpreted in terms of under development of the subglacial system favouring low sediment flux. The study has succeeded in building key knowledge gaps on the solute acquisition of glacier melt waters during its transit with high sediment load under prevailing low temperature conditions. The conclusions have been supported further by the results of dissolution experiments. Wealth of data generated with great accuracy during this study will be useful in future. National Institute of Hydrology, Roorkee has been actively involved in carrying out R&D studies in the area of snow and glacier hydrology.

A number of scientific studies on Himalayan cryospheric system, which includes the study of Dokriani and Gangotri Glaciers in Uttarakhand, Phuche and Khardung Glaciers in the Ladakh Range have been completed by NIH in the past. This project added one more feather in NIH cap. NIH would like to pursue such investigation in future.

(Sharad K. Jain)
Director

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In the end, PI is thankful to his family members Smt. Aparna, Mr. Mridul and Mr. Chakshu for their very valuable understanding of the life of a glaciologist and encouragement. Being a God believer, PI is thankful to blessings of the God to work in harsh and extreme environment of the Gangotri glacier.

(M. K. Sharma)
Principal Investigator

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RESEARCH HIGHLIGHTS

- One of the major findings of the study is that River Bhagirathi remains under closed system conditions from its origin at Gomukh to 14 km downstream at Gangotri, in which high $p(CO_2)$ closed system conditions dominates. The sediment concentration and subglacial activities play a major role in this process and influence of glacier system extend to downstream reaches as well.
- SO_4 is the dominant anion in the meltwater and highest concentration was observed at Gomukh followed by Gangotri and Bhojwasa during the complete ablation period of the year 2014, 2015 and 2016 suggesting that the sulphide oxidation dominates the water chemistry from glacier portal to downstream.
- Very low C-ratio for meltwater of River Bhagirathi at Bhojwasa and upto Gangotri indicates that the major proton producing reaction is oxidation of sulphide. The coupled reaction involving carbonate and CO_2 dissolution and oxidation of sulphide minerals derived protons control the chemistry of meltwater draining from Gangotri glacier.
- Comparatively high pH (>7.0) was observed in the year 2015 in the meltwater of River Bhagirathi at Bhojwasa, especially during the seasonal high flow period which may be attributed to the higher surface melt contribution from prolonged snow cover in the basin and also associated with under development of subglacial zone during the year, limiting the pyrite oxidation which results in less production of proton (H^+) ions and thereby increasing the pH. This is also associated with higher HCO_3 values and low $p(CO_2)$ closed system conditions and very low sediment evacuation during the year.
- Dissolution experiments of glacial meltwater- sediment interaction conducted on bed sediments of River Bhagirathi considering different operating variables viz; contact time, seasonality, different sediment particle sizes, different sediment dose, effect of pH, wetting and crushing of bed sediments revealed the role of sediment in low temperature solute acquisition process characterised by sudden release of ions from the sediment in the initial few seconds. Surface characteristics of sediments play an important role in solute acquisition during freshly grinded sediment-meltwater interaction, which is revealed from progressive increase in solute acquisition process.
- Inter-annual variability of the discharge characteristics in a glacial system has direct bearing on the sediment transfer characteristics, which is also linked with the development and progression of subglacial channel network as subglacial zone is the major source area of glacial sediments. The sediments, which got deposited throughout the winter period, gets evacuated during the early stages of subglacial channel development. In the year 2014 and 2016, this early evacuation of sediment is clearly visible in the data. However, the year 2015 did not experience any significant sediment evacuation neither during the initial stage nor later. Low sediment flux was observed in the year 2015, which may be attributed to the under development of subglacial drainage system.

Chapter 1

INTRODUCTION

Mountain regions play a critical role in the water cycle, storing water in the form of snow and ice mainly during the cold/wet season, and releasing it as melt water during the dry/ warm season when it is greatly needed (Gino et al., 2009). Glaciers, especially mountain glaciers, are sensitive to climatic change (Li et al., 2007; Zhou et al., 2010). Since the 20thcentury, most of the global mountain glaciers have begun to retreat after the little ice age advancement and the trend of recession continue till date for most of the Himalayan region. These influences melt water discharge and much research has shown that this is affected by air temperature (Mingjie et al., 2013). The advancement or retreat of glaciers can influence the sea level within decades. This is the reason glaciers are considered as best indicator of climatic change (Singh et al., 2006).

Most of large river systems of the world originate from mountains where a significant quantity of fresh water is stored in the form of snow and glaciers. The Himalaya is the youngest and tallest mountain system which includes world's most erosion prone regions (Pandey et al., 1999). The glacier distribution in the Himalaya is uneven with higher concentration in northwest as compared to northeast Himalaya (Vohra, 1981; GSI, 1999). Seven great Asian rivers: Ganga, Indus, Brahmaputra, Yangtze, Huang He or Yellow River, Salween and Mekong are fed by Himalayan glaciers. Total number of glaciers in Indus, Ganga and Brahmaputra basins are 16,049, 6237 and 10,106 covering total glaciated areas of 32246.43, 18392.90 and 20542.75 km^2, respectively (SAC, 2011) and have substantial contribution of annual runoff from the melting of snow and glaciers. Along with meltwater, glaciers also deliver huge amount of sediment to the fluvial system. In the Himalayas, these active glaciers are located.

Geologically young mountain system, which is still undergoing uplift (Hasnain and Chauhan, 1993), the present estimates of uplift rate for different parts of Himalayas vary from 0.6–6 mm/yr (Gansser, 1983; Rajal et al., 1986; Nakata, 1989; Jackson and Bilham, 1994). This combination makes the Himalayan ecosystem fragile and susceptible to high erosion rate ranging from of 2–12 mm/yr (Burbank, 1996). This also facilitates high level chemical denudation rates of higher Himalayan region. To analyze these aspects, there is need to establish a long term database related to SSC (suspended sediment concentration) and SSL (suspended sediment load) for the glacierized basins in the Himalayan region, which is very limited at present. Dissolved materials fluxes carried by rivers are also regulated by chemical weathering of rocks and minerals, whereas particulate transport is determined by physical weathering (Krishnaswami and Singh, 2005). In the Himalayan region, Alaknanda and Bhagirathi rivers contribute high sediment and dissolved flux of the Ganga River (Sarin and Krishnaswami, 1984; Abbas and Subramanian, 1984; Burbank and Beck, 1991; Krishnaswami et al., 1992; Harris, 1995; Singh et al., 1999; Galy and France-Lanord, 2001; Dalai et al., 2002; Vance et al., 2003).

In the glacial areas, the interaction between dilute glacier water with fresh sediments takes place in a cold environment and further transported downstream. This makes the ionic enrichment of meltwater very unique. As these waters flows down through the mountains system and plains, more and more pollutant are added to the system. High level of pollutant load in the lower reaches of River Ganges is as an unresolved problem for the past many decades. In this perspective, contribution of Himalaya rivers originating from snow and glacier fields of higher Himalaya play an important role in controlling the solutes levels in the River Ganges. As these mountain waters with significant amount of snow, glacier meltwaters and rainfall is characterised by low ionic concentrations and play a major role in diluting the high solute load emanating from the Ganga plain catchments. Hence any change in the quality and quantity of the Himalayan tributaries of River Ganga under the climate change regime will impact the quality parameters of River Ganga. Hence a clear understanding of the characteristics and process driving the chemical enrichment of the glacial meltwater and its instream modification in the high altitude region is essential for evaluating the role of Himalayan component of the Ganga river system in maintaining the quality of the Ganges water.

Solute is defined as all ions, including base cations (e.g. Ca^{2+}, Mg^{2+}, K^+, Na^+), aqueous protons [H^+ (aq)] and anions (HCO_3^-, SO_4^{2-}, NO_3^-, Cl^-), and neutral species (e.g. O_2, N_2, CO_2, H_4SiO_4) dissolved in water (Stumm and Morgan, 1970). Solute acquisition (or chemical weathering) is therefore concerned with reactions which affect species in all phases: solid, liquid and gas. Solute may be derived from atmospheric deposition either contained in snow or rain, or from dry deposition on to the catchment surface (Barrie, 1991; Cadle, 1991). Snow and rain bring various chemicals from the atmosphere to mountain ecosystems throughout the year (Fenn et al., 1998). Because mountain snowpacks accumulate as much as 8 months of atmospheric deposition over the cold months and then release it over a relatively short time during late spring, large fluxes in chemicals occur where there are large snowpacks (Campbell et al., 2000). Glacier drainage system characteristics also control solute enrichment processes of meltwater during its passage through the glacier drainage system (Thayyen et al., 2003).

Melting of snow causes the migration of soluble and insoluble impurities. Since the solute composition of meltwater from a seasonal snowpack significantly affects the water quality of snow-fed streams and lakes, intensive work on the chemistry of seasonal snowpacks and meltwaters has been conducted at global level. It is well known that most of the soluble ions stored within a snowpack are removed by the first fractions of snowmelt, and that ionic concentrations of a snowpack and runoff water generally decrease as melting proceeds. The first derived snowmelt or rain-snow melt mixture is more concentrated than that derived from leached snow cover, since solute from snow readily fractionates into snowmelt and rainfall (Johannessen and Henriksen, 1978; Colbeck, 1981; Suzuki, 1982; Jones et al., 1989; Tranter, 1991). The chemical changes of a snowpack and runoff can be influenced by chemical composition of the snow and refreezing processes of the meltwater (Colbeck, 1981; Davies et al., 1987; Bales et al., 1990). The snowline retreats up-glacier as the ablation season proceeds and therefore snowpack leaching occurs later at higher altitudes. However, much of the solute found in the bulk meltwaters emerging at the portal is acquired by the chemical weathering in subglacial environments (Souchez and Lemmens, 1987).

Solute in the meltwater is derived during the passage of meltwater through the sub-glacier channel at the rock-ice and meltwater interface (Trudgill, 1986). The rate and mechanism responsible for dissolved ion release in the meltwater of glacier streams vary with lithology (Collins, 1979). Weathering of bedrock is likely to occur when water flows at the ice-rock interface. In glacial environment, proton (H^+) appears to be accountable for the weathering of rock-forming minerals. The carbon dioxide reacts with water and form the weak carbonic acid, which dissociates into H^+ and HCO_3^-. Sulphide oxidation is another mechanism, which is responsible for the production of hydrogen ions (Garrels and Mackenzie, 1971).

Seasonal variations in the concentration and flux of dissolved major, minor and trace elements, and sediment bound species are controlled by the dynamic nature of the subglacial hydrological system and associated changes in meltwater discharge, suspended sediment concentrations and conditions of water–rock interaction over seasonal timescales (Brown et al., 1996a,b; Mitchell et al., 2001). About 90% of the annual discharge is generated (Ro¨thlisberger and Lang, 1987) and ~90% of dissolved and particulate- associated major ions and minor and trace elements (Collins, 1983; Metcalf, 1986; Sharp et al., 1995a,b; Mitchell et al., 2001) and suspended sediments (Gurnell, 1987) are exported during the 4–5 month summer ablation period. Over the ablation season, discharge exhibits rising and falling flow in response to diurnal changes in surface ablation and meltwater generation and routing, during which large magnitude changes in the concentration and flux of suspended sediments and major ions have been observed (Gurnell, 1987; Brown et al., 1994a; Singh et al., 2005). However, short-term diurnal fluctuations in the mode of minor and trace element export in glacierized catchments have not been investigated, despite their potential as markers for assessing the short-term controls on minor and trace element transport, and the utility of minor and trace elements for hydrological flow-path studies (Mitchell and Brown, 2007).

Chemical models for the evolution of glacial meltwaters (Raiswell and Thomas, 1984; Raiswell, 1984) suggest that kinetic factors exert a critical control on the nature and magnitude of sediment-water interactions and thus on the composition of bulk meltwaters (those emerging from the portal). Solute acquisition in the glacial system may follow two distinct chemical pathways, where carbon dioxide dissolution is the principal source of the hydrogen ions consumed during the weathering and dissolution of rock minerals. A closed-system pathway occurs where the rate of CO_2 consumption by weathering reactions exceeds the rate of CO_2 renewal by dissolution (Raiswell and Thomas, 1984) while the chemical evolution of bulk melt waters is said to be open system characteristics when rates of CO_2 consumption by weathering equal to rates of renewal by dissolution. The development of open- or closed-system characteristics in a glacial system depends, in the first instance, on whether dissolution/weathering reactions occur when chemically aggressive englacial waters are mixed with solute and sediment- rich subglacial melt. Occurrence of dissolution/weathering reactions leads to closed system conditions; otherwise open systems are observed. Such closed system characteristics may be modified by re-equilibration with atmospheric CO_2 or ground water mixing to give bulk meltwaters with open-system characteristics (Thomas and Raiswell, 1984). In otherwords, a glacial system is said to be open when the $p(CO_2)$ in the gas phase is in equilibrium with the amount of dissolved CO_2 in the liquid phase (i.e. $p(CO_2){\sim}K_H\ (CO_2)\ (aq)$). The system is said to closed when this is not the case (i.e. $p(CO_2) \neq K_H\ (CO_2)\ (aq)$). Open- and closed-system weathering regimes are kinetic phenomena and depend on the rate at which CO_2 diffuses into or out of solution relative to the rate of other chemical-weathering reactions (Raiswell, 1984; Raiswell and Thomas, 1984; Thomas and Raiswell, 1984).

Further, hydrological interpretation of the solute content of glacial meltwater is dependent on a knowledge of the processes and rates at which meltwater acquires solute in the subglacial environment. To date, this has been limited because there are no independent studies of i) the chemical processes involved in solute acquisition by sub-glacial meltwater, ii) the rate at which they occur, iii) the parameters that control the reaction rates in the Himalayan glacier environment. Therefore, laboratory dissolution experiments needs to be carried out directly to improve hydrological interpretations such as; a) the prediction of meltwater residence times in subglacial reservoirs; b) definition of the rate and magnitude of post-mixing reactions (the possibility of solute uptake from suspended sediments is a serious limitation to the validity of simple mixing models that assume conservative mixing); c) improving hydrograph separation techniques, solute provenance studies and calculations of chemical denudation rates; d) assessment of the controls on chemical weathering processes so that the nature of the different subglacial environments (open channels, linked cavities, discrete water pockets) can be defined in terms of open or closed system characteristics (Raiswell, 1984), redox potential, effective gas pressure and turbulence, and e) assessment of the impact of the 'acid-flush', associated with preferential elution during spring snowmelt of the winter snowpack, on the rate and magnitude of subglacial weathering processes (Brown et al., 1996a).

Understanding of low temperature solute acquisition processes is therefore very important for assessing the solute acquisition and pollutant loading further downstream. Higher sediment load in the glacier fed streams play a significant role in solute acquisition by its interaction with dilute glacial and snow melt waters. Further downstream, higher sediment load due to anthropogenic activities added another dimension to the problem. Hydrology of mountainous areas, especially snow and glacier hydrology, is lagging behind in proportion due to greater difficulty in collection of data at higher altitudes. However, the status of hydro-meteorological data has been improved in the recent times for few selected glaciers, more extensive work on some selected representative glaciers is needed. Very limited hydrological investigations have been done in the high altitude Himalayan glacierized basins (Singh et al., 2006).

Now Himalayas are under increasing pressure due to growing demand for fresh water in the country due to population growth, urbanization and industrial development. Hydrological investigations of Himalayan glaciers become inevitable because of their importance in terms of source of water for irrigation, drinking water supply and hydroelectric power generation. A number of important multipurpose projects in India exist on Himalayan rivers and many are under construction or proposed. The power generation from several projects like Salal, Bhakra, Tehri, Maneri Bhali etc. depends heavily on the melt runoff generated from melting of snow and glacier (Singh et al., 2006). Little work has been carried out on the chemical processes involved in glacial sediment and meltwater interaction in Gangotri glacier catchment. Being the biggest glacier in the basin as well as the importance of low temperature chemical process in controlling the solute acquisition during suspended sediment-meltwater interaction, understanding the ionic enrichment dynamics of glacial sediment and melt water of Gangotri glacier is very important. Therefore, a project study was conceptualized with the following objectives:

i. To characterize the seasonal variability of the major-ion chemistry of glacial meltwater
ii. Chemical characterization of the suspended sediment of Gangotri glacial system
iii. To study ionic enrichment dynamics of meltwater-glacial sediment interaction
iv. To investigate open- and closed-system low temperature ionic enrichment process

Chapter 2

STUDY AREA

The Gangotri glacier is one of the biggest and most important glaciers in the Himalayan region. This valley type glacier is situated in the Uttarkashi district of Uttarakhand state in central Himalaya. Geographically this glacier lies between 30º43'22"-30º55'49" (latitude) and 79º4'41"–79º16'34" (longitude) (Naithani et al., 2001) (Fig. 1). The snout of Gangotri glacier, known as Gomukh (meaning mouth of the cow) is located at about 4000 m above mean sea level elevation (Singh et al., 2012), from where the Bhagirathi River originates and is a religious place for Hindu pilgrims. The Gangotri glacier system is a cluster of many small and large glaciers comprising three main glacier tributaries, namely, Raktvarn glacier (length 15.90 km; area 55.30 km^2), Kirti glacier (length 11.05 km; area 33.14 km^2) and Chaturangi glacier (length 22.45 km; area 67.70 km^2) with main Gangotri glacier as the trunk part of the cluster system (length 30.20 km; area 86.32 km^2) (Naithani et al., 2001; Singh et al., 2006, 2011). The gradient of Kirti glacier is highest (0.317), whereas Gangotri glacier gradient is lowest (0.045) followed by Chaturangi (0.146) and Raktvarn (0.210) glacier, respectively (Naithani et al., 2001). The total catchment area of the Gangotri glacier basin up to the snout at Gomukh is 513 km^2, up to the discharge gauging site established downstream of the snout by NIH at Bhojwasa is about 556 km^2, out of which about 286 km^2 (51.4%) is glacierized area (Haritashya et al., 2006; Singh et al., 2006; Arora, 2008) and up to Gangotri is 691 km^2. The Bhagirathi River and its tributaries drain mostly through the Lesser and Central Crystallines rocks (Agarwal and Kumar, 1973; Pandey et al., 1999; Jain et al., 2002; Singh et al., 2014).

The Gangotri glacier system geologically falls in the higher and Tethys Himalayan zone (Kumar et al., 2009). One of the largest bodies of the Higher Himalayan Leucogranite belt located in the Garhwal Himalaya is Gangotri granite (Heim and Gansser, 1939; Gansser, 1964; Le Fort, 1975; Yin, 2006). It is fine grained (1–2 mm), comprising quartz + K-feldspar + tourmaline + Plagioclase + muscovite ± biotite ± garnet ± beryl with most abundant accessory mineral apatite (Scaillet et al., 1990; Jowhar, 2010). All along the upper reaches of the Bhagirathi River around the area of Gangotri glacier, Gangotri granite is exposed (Jain et al., 2002). The Gangotri glacier system geology comprises granite (tourmaline rich), sericite schist, mica schist, quartzite, phyllite, sulphide minerals like pyrite, chalcopyrite and arsenopyrites at the contact of quartz veinlets and massive, banded fine grained limestone (Bhatt, 1963). In the Gomukh–Gangotri shrine section both $CaSO_4$ and $MgSO_4$ are found. Normally sulphate minerals are expected to be associated with carbonate rocks, likely to have same packets particularly due to the presence of evaporites such as anhydrite and gypsum (Srivastava et al., 2004). Geologically, the glacierised area of Bhagirathi valley contains mainly of crystallines with the presence of phyllites, carbonates and pyritous shales (Singh et al., 2014).

For hydro-meteorological study of any glacier, the first and foremost requirement is availability of continuous and reliable flow data of at least ablation period (May–October) every year. In India, regular streamflow monitoring sites are not available in the high altitude region, as is also the case of Gangotri Glacier until 2000. Most of the studied glaciers are monitored only during specific project duration. Thus, keeping in view of the importance of the Gangotri glacier, and its hydrology, a discharge observation site and a meteorological observatory were established at Bhojwasa near the snout of the Gangotri Glacier in the year

2000 by the National Institute of Hydrology, Roorkee. Keeping in view several requirement, such as, round the clock accessibility to the site, flow of water in a single channel, minimum turbulence in flow etc. a suitable gauging site was selected about 4 km downstream of the snout of glacier (Fig. 1)(Singh et al., 2006).

Fig. 2.1 Satellite imagery view of the study area showing sampling sites along River Bhagirathi

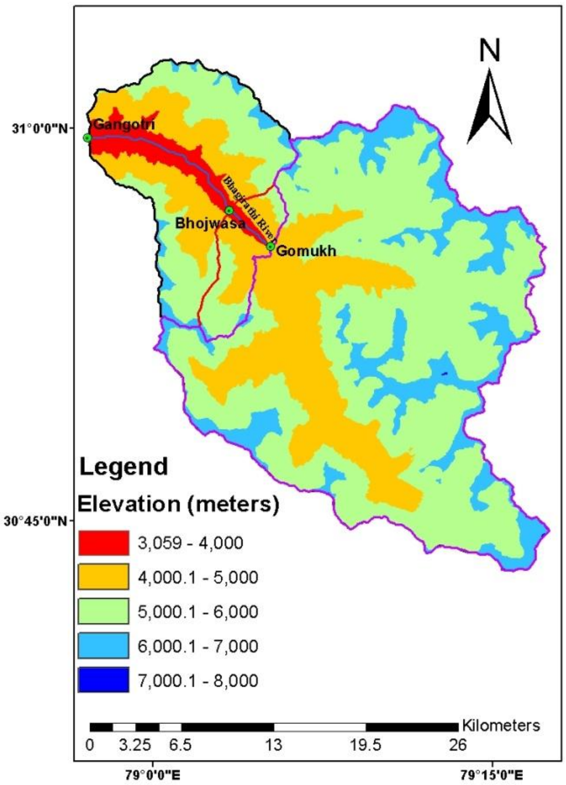


Fig. 2.2 Digital elevation map (DEM) of the study area

Chapter 3

EXPERIMENTAL METHODOLOGY

The most important mechanism responsible for rock mineral weathering in a glacial subsystem is acid hydrolysis (Raiswell, 1984). In the bulk stream water, the relative proportions of HCO_3^- and SO_4^{2-} reflect the dominance of the two major sources of aqueous protons driving subglacial chemical weathering reactions (Raiswell, 1984; Trainter et al., 1993; Brown et al., 1996b).

$$\mathrm{CaCO_3(s) + CO_2(aq) + H_2O(aq) = Ca^{2+}(aq) + HCO_3^-(aq)} \quad (1)$$
(calcite)

$$\mathrm{CaAl_2Si_2O_8(s) + 2CO_2(aq) + 2H_2O(aq) = Ca^{2+}(aq) + 2HCO_3^- + H_2Al_2Si_2O_8(s)} \quad (2)$$
(Ca-feldspar) (partially weathered feldspar)

$$\mathrm{4FeS_2(s) + 16CaCO_3(s) + 15O_2(aq) + 14H_2O(aq) =}$$
(pyrite) (calcite)

$$\mathrm{16Ca^{2+}(aq) + 16HCO_3^-(aq) + 8SO_4^{2-}(aq) + 4Fe(OH)_3(s)} \quad (3)$$

The relative importance of two major proton producing reactions - carbonation and sulphide oxidation can be evaluated on the basis of the C-ratio. Brown et al. (1996b) proposed estimation of C-ratio as

$$\mathrm{C - ratio = HCO_3^-/(HCO_3^- + SO_4^{2-})} \quad (4)$$

If C-ratio is 1.0, it indicates the significance of carbonation reaction involving acid hydrolysis and pure dissolution, consuming protons from atmospheric CO_2 (equation 1 and 2) and if C-ratio is 0.5, it suggests coupled reaction involving carbonate weathering and protons derived from oxidation of sulphide (equation 3).

Effective CO_2 pressure or internal CO_2 pressure [log $p(CO_2)$] can be estimated from pH values and HCO_3^- concentration (Ford and Williams, 1989). The $p(CO_2)$ of a solution reflects the rate at which CO_2 diffuses into and out of the solution relative to the rate of other chemical weathering reactions (Raiswell, 1984; Raiswell and Thomas, 1984; Thomas and Raiswell, 1984). The $p(CO_2)$ signature of meltwater can be used to characterize different glacial hydrological weathering environments (Sharp, 1991; Wadham et al., 1998). When proton supply equals the consumption, the $p(CO_2)$ of the solution remains in the equilibrium with the atmosphere $i.e. p(CO_2)(aq) = p(CO_2)(g)$, the system is said to be open. If pCO_2 of solutions are not equal to atmospheric pCO_2 ($10^{-3.5}$atm) $i.e. p(CO_2)(aq) \neq p(CO_2)(g)$, it can be said to be in disequilibrium with respect to the atmosphere. When the supply of protons is more than their consumption, then high $p(CO_2)$ conditions arise. Low $p(CO_2)$ conditions arise when the demand of protons for chemical weathering is more than the rate of CO_2 diffusion into the solution (Wadham et al., 1998) indicating closed system weathering.

3.1 Sampling and Chemical Analysis

Reconnaissance survey of Gangotri Glacier was carried out from 26th June to 2nd July, 2014 and fixed the sites at Gomukh, Bhojwasa and Gangotri for collection of meltwater, suspended and bed sediment samples (Table 3.1). Fieldwork at the selected Gangotri glacier sites were carried out during ablation period from 28th June to 16th October, 2014, 10th May to 11th October, 2015 and 15th May to 2nd October, 2016. Meltwater samples were collected using grab sampling method from River Bhagirathi at Gomukh, Bhojwasa and Gangotri during these periods and immediately filtered the samples for suspended sediment concentration through 0.45 µm membrane Whatman filter paper by using hand operated vacuum pump (Tarson make) and filtration apparatus. The bed sediments were also collected from the bed of River Bhagirathi at Gomukh, Bhojwasa and Gangotri monthly in polyethylene begs. The observations were taken as details given below:

At Gomukh (Glacier snout) **(GMK)*:*** From the selected site at Snout and measured water temperature at 0830 hours (8.30 A.M.) and 1730 hours (5.30 P.M.) every Sunday on weekly basis.

At Bhojwasa (4 km downstream of snout) **(BJW):** Just near NIH Hut and measured water temperature at 0830 hours (8.30 A.M.) and 1730 hours (5.30 P.M.) daily. Hourly samples were also collected on 30th or 31st of every month.

At Gangotri (14 km downstream of snout)**(GNT):** Just before Bathing Ghat near Gangotri Temple and measured water temperature at 0830 hours (8.30 A.M.) and 1730 hours (5.30 P.M.) every Sunday on weekly basis

Table 3.1 Details of the sampling sites

Sampling site	**Location**	**Elevation**	**Stream distance from Gomukh (km)**	**Drainage area (km^2)**
Gomukh	30°55′29″N 79°04′52″E	4000	0	513
Bhojwasa	30°56′57″N 79°03′03″E	3800	4	556
Gangotri	30°59′38″N 79°56′30″E	3060	14	691

Insitu parameters like water temperature, pH and electrical conductivity (EC) were measured at the time of sampling using pH meter (Model: HQ11d, Make: Hach, USA) and EC meter (Model: HQ14d, Make: Hach, USA). Filtered water samples were brought to Water Quality laboratory, National Institute of Hydrology (NIH), Roorkee and kept in Deep freezer (Model: RQV-600 Plus Make: Remi) maintaining 3°C temperature till the analysis. Total suspended sediment (TSS) concentration was measured in the collected suspended sediment samples after drying in the oven in the laboratory. The bed sediments were dried at 50ºC before weighing. Size fractions 0-75, 75-150, 150-210, 210-250, 250-300, 300-425, 425-600 micron were derived by dry-sieving the bed sediment through sieves using a sieve shaker for 10 minutes and kept in polyethylene bags for later dissolution experiments. Discharge was observed and calculated by establishing a rating curve for the gauging site at Bhojwasa.

Hydro-chemical analysis of filtered meltwater samples collected from River Bhagirathi was carried out using Ion Chromatograph with Auto Titrator (Metrohm, Switzerland) in Water Quality laboratory, NIH, Roorkee. The charge balance errors were <5% for each analysis determined by the formula $[\{(TZ^+ - TZ^-)/(TZ^+ + TZ^-)\}x100]$ confirming the reliability and quality of the analytical results. For metal analysis, suspended and bed sediments were digested using conc. HNO_3 on hot plate and analyzed using Voltametry (VA) technique.

3.2 Dissolution Experiments

Dissolution experiments of glacial meltwater-suspended and bed sediment interaction considering different operating variables viz; contact time, seasonality (different months), different sediment particle sizes, different sediment dose, effect of pH, effect of wetting and crushing of sediment were carried out maintaining glacier environment condition in the Water Quality Laboratory, NIH, Roorkee.

Dissolution experiments were carried out on 0-75 micron size fraction of bed sediments. The solution-sediment mixture was in free contact with the laboratory atmosphere for the duration of the experiments. The duration of the experiments is kept as1 hour, considering to be representative of bulk meltwater residence times in arterial channels during the latter part of the ablation season. The temperature (0-3ºC) is realistic of field condition maintained by keeping solution-sediment mixture in a HDPE plastic beaker in the ice bath. Water to sediment ratios (8.0 g/L) were derived from the maximum suspended sediment concentration sampled during diurnal cycles in the field. Ultra pure water was used as a surrogate for icemelt with very low ionic concentration. Different pH of ultrapure water was maintained using 1 N HCl and 1 N NaOH solution. Experiments were conducted in a HDPE grade plastic beaker containing 250 ml (±2 ml) of ultrapure water on a shaker with magnetic stirrer maintaining with a speed of 500±20 rpm. pH, electrical conductivity and temperature were measured continuously during the experiment. The samples (20 ml) were collected at set intervals during the course of the experiment, immediately syringe-filtered through Whatman 0.45 µm cellulose nitrate membranes and refrigerated at 4ºC for later analysis of major cations and anions on Ion Chromatograph.

3.3 Geochemical Analysis

Dried suspended and bed sediment collected from the River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016 were analysed for surface characteristics using Scanning Electron Microscope (SEM) technique and oxides of major and trace element using X-Ray Fluorescence (XRF) technique.

For SEM analysis, suspended and bed sediments (0-75 µm) were sprinkled on the carbon tape, which was further gold coated to make the sample conducting. The sample was then inserted into the vacuum chamber of SEM (Model LEO 435 VP) and micrographs were recorded at different magnifications upto 10K at Institute Instrumentation Centre (IIC), Indian Institute of Technology (IIT), Roorkee. For XRF analysis, the powdered suspended and bed sediment samples were kept in air tight plastic containers. 6.5 g of sediment sample and 4-5 drops of PVA solution (poly vinyl alcohol) were properly mixed. PVA solution was used as binder for oxides of major and trace element analysis of sediment samples. The mixture was taken in a collapsible alluminium cups and powder filled cups were pressed under a hydraulic press at 13-20 tons pressure to gets pellets of 40 mm diameter. Analysis of oxides of major and trace element was done using Bruker-S4 Pioneer Sequential Wavelength Dispersive X-Ray Fluorescence coupled with automatic sample charger in the Institute Instrumentation Centre (IIC), IIT, Roorkee.

Fig. 3.1 Sampling site on River Bhagirathi at Gomukh

Fig. 3.2 Sampling site on River Bhagirathi at Bhojwasa

Fig. 3.3 Sampling site on River Bhagirathi at Gangotri

Fig. 3.4 pH measurement at Gomukh

Fig. 3.5 EC measurement at Gomukh

Fig 3.6 Water temperature measurement at Gomukh

Gomukh 2014

Gomukh 2015 **Gomukh 2016**

Fig. 3.7 A view of Gangotri glacier snout at Gomukh during the year 2014, 2015 & 2016

Fig. 3.8 A view of Bhojwasa

Fig. 3.9 On-site water sample filtration for suspended sediment

Fig. 3.10 Water sample processing in Fibre Hut at Bhojwasa

Fig. 3.11 EC measurement at Bhojwasa

Fig. 3.12 Water sample collection and temperature measurement at Gangotri

Fig. 3.13 Dissolution experiment in Water Quality Laboratory, NIH, Roorkee

Fig. 3.14 Analysis on Ion Chromatograph at Water Quality Laboratory, NIH, Roorkee

Chapter 4

HYDRO-CHEMICAL CHARACTERISTICS OF GLACIAL MELTWATER

Field observations to assess the variations of meltwater chemistry of proglacial stream from its origin at the Gomukh (4000 m a.s.l.) and along the stream continuum at Bhojwasa (3800 m a.s.l.) and at Gangotri (3060 m a.s.l.) were carried out during the ablation periods of the year 2014, 2015 and 2016. Water temperature, pH and electrical conductivity were measured at the time of sampling from 28th June to 16th October, 2014, 10th May to 11th October, 2015 and 15th May to 2ndOctober, 2016. Total suspended sediment (TSS) concentration was also measured at these sampling locations. The meltwater samples were filtered at the site soon after the collection and stored at 3°C in the laboratory till the analysis. The hydro-chemical analysis of collected filtered meltwater samples was carried out using Ion Chromatograph with Auto-Titrator and the data for the year 2014, 2015 and 2016 is being presented here. Summary of the data is also given in Table 4.1, 4.2 and 4.3 respectively.

4.1 Variations of Hydrological and Hydro-chemical Parameters at Gomukh, Bhojwasa and Gangotri

4.1.1 Variation of water temperature at Gomukh, Bhojwasa and Gangotri

The water temperature is an important parameter responsible for the solute acquisition process during interaction of meltwater and freshly grinded glacial sediments in the high altitude cold environment. Variation of water temperature at Gomukh, Bhojwasa and Gangotri is shown in Fig. 4.1(a) & (b) during the period of investigations of 2014-2016 respectively. Water temperature varies from 0.3 to 1.4ºC at 0830 hours and 0.5 to 1.5ºC at 1730 hours in the meltwater of River Bhagirathi at Gomukh, 0.1 to 2.5ºC at 0830 hours and 0.1 to 4.0ºC at 1730 hours in the meltwater of River Bhagirathi at Bhojwasa and 1.0 to 7.0ºC at 0830 hours and 2.9 to 7.0ºC at 1730 hours in the meltwater of River Bhagirathi at Gangotri respectively during the period of investigation of 2014-2016.

4.1.2 Variation of Total Suspended Sediment (TSS) concentration at Gomukh, Bhojwasa and Gangotri

Suspended sediment load in the glacier fed streams play a significant role in solute acquisition by its interaction with dilute glacial and snow melt waters. Variation of Total suspended sediment (TSS) concentration in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri is shown in Fig. 4.2(a) & (b) during the period of investigation of 2014-2016. Suspended sediment concentration varies from 0.054 to 3.501 g/L with average value 0.947 g/L at 0830 hours and 0.112 to 5.703 g/L with average value 1.453 g/L at 1730 hours in the meltwater of River Bhagirathi at Gomukh, 0.048 to 6.866 g/L with average value 1.244 g/L at 0830 hours and 0.056 to 13.003 g/L with average value 1.644 g/L at 1730 hours in the meltwater of River Bhagirathi at Bhojwasa and 0.068 to 7.898 g/L with average value 1.420 g/L at 0830 hours and 0.071 to 8.803 g/L with average value 1.691 g/L at 1730 hours in the meltwater of River Bhagirathi at Gangotri respectively during the period of investigation of 2014-2016.

Table 4.1 Hydro-chemical data of meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during ablation period of 2014

Parameter	**Site: Gomukh**			
	Time: 0830 hours			
	Min	**Max**	**Mean**	**SD**
Water Temp.(ºC)	0.4	1.3	0.66	0.20
TSS (g/L)	0.054	1.424	0.697	0.429
pH	6.66	8.50	7.27	0.54
EC, µS/cm	71.3	125.6	92.6	14.4
Na^+, µeq/L	21.7	70.4	38.8	12.1
K^+, µeq/L	43.0	61.1	49.9	5.9
Ca^{2+}, µeq/L	367.0	646.8	543.9	81.3
Mg^{2+}, µeq/L	118.9	205.7	165.3	24.1
HCO_3^-, µeq/L	11.8	249.0	93.7	66.7
Cl^-, µeq/L	7.6	45.6	18.0	9.8
SO_4^{2-}, µeq/L	507.7	920.8	731.3	129.0
NO_3^-, µeq/L	0.0	6.1	3.4	2.0
TZ^+, µeq/L	556.2	952.9	802.5	108.3
TZ^-, µeq/L	553.8	1034.0	860.6	144.0
TDS, mg/L	38.2	69.1	57.9	9.4
C-ratio	0.02	0.32	0.11	0.08

Parameter	**Site: Bhojwasa**							
	Time: 0830 hours				**Time: 1730 hours**			
	Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Water Temp.(ºC)	0.1	2.5	1.03	0.38	0.1	4.0	1.21	0.47
TSS (g/L)	0.048	6.866	1.256	1.238	0.056	13.003	1.838	2.086
pH	6.49	8.11	7.14	0.32	5.98	8.08	6.82	0.44
EC, µS/cm	63.7	145.0	89.4	14.6	38.2	147.4	63.8	21.2
Na^+, µeq/L	4.9	86.5	43.5	14.5	6.5	86.9	31.2	15.2
K^+, µeq/L	0.0	71.6	41.6	9.2	13.0	65.2	31.1	11.1
Ca^{2+}, µeq/L	344.0	795.0	454.0	79.8	202.9	805.0	337.9	114.1
Mg^{2+}, µeq/L	4.9	338.5	136.6	50.2	22.1	368.03	118.0	59.3
HCO_3^-, µeq/L	50.4	408.6	135.6	44.9	12.0	270.4	99.1	36.4
Cl^-, µeq/L	0.3	41.7	25.1	14.4	1.4	51.6	11.0	9.6
SO_4^{2-}, µeq/L	383.6	1060.2	576.0	103.4	235.3	1084.4	422.0	144.5
NO_3^-, µeq/L	0.0	21.6	8.6	7.8	0.0	19.7	3.0	3.9
TZ^+, µeq/L	448.9	1288.1	676.5	141.1	307.4	1325.2	520.8	190.7
TZ^-, µeq/L	487.0	1290.2	752.9	120.8	348.2	1310.4	545.1	170.9
TDS, mg/L	31.1	88.3	50.9	8.4	24.0	89.7	37.3	11.9
C-ratio	0.14	0.23	0.18	0.03	0.14	0.26	0.18	0.03

Table 4.1 Contd.

Parameter	Site: Gangotri							
	Time: 0830 hours				Time: 1730 hours			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Water Temp. (°C)	1.0	7.0	4.19	1.17	3.0	7.0	5.19	1.11
TSS (g/L)	0.085	2.735	1.056	0.828	0.071	3.738	1.199	0.957
pH	6.82	8.20	7.61	0.31	7.22	8.33	7.60	0.27
EC, µS/cm	66.4	114.9	86.0	14.2	59.5	117.4	81.4	16.7
Na^+, µeq/L	27.0	84.8	40.5	15.0	17.0	675.0	74.8	160.9
K^+, µeq/L	29.1	55.8	46.9	6.4	29.4	66.0	42.4	10.1
Ca^{2+}, µeq/L	331.0	792.0	541.8	119.1	308.5	668.5	500.6	125.5
Mg^{2+}, µeq/L	120.5	222.9	158.9	25.5	77.1	235.3	154.0	45.4
HCO_3^-, µeq/L	84.0	317.4	170.9	78.5	75.6	833.2	215.4	181.7
Cl^-, µeq/L	10.5	29.9	16.3	4.8	3.9	29.1	14.5	5.4
SO_4^{2-}, µeq/L	397.1	823.2	646.2	138.4	328.1	986.3	592.5	205.9
NO_3^-, µeq/L	0.0	10.7	1.9	3.2	0.0	6.5	1.9	2.5
TZ^+, µeq/L	560.8	1035.9	788.1	143.7	510.9	1179.2	772.7	203.7
TZ^-, µeq/L	535.6	1171.5	864.5	178.3	487.3	1328.4	854.1	259.0
TDS, mg/L	37.3	79.3	58.3	11.8	34.9	98.4	58.2	17.9
C-ratio	0.11	0.40	0.21	0.08	0.11	0.68	0.26	0.15

TSS = Total Suspended Sediment (g/L); EC = Electrical Conductivity (µS/cm); TZ^+ = Total Cations (µeq/L); TZ^- = Total Anions (µeq/L); TDS = Total Dissolved Solids (mg/L); All cations and anions concentrations are in µeq/L.

Table 4.2 Hydro-chemical data of meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during ablation period of 2015

Parameter	Site: Gomukh							
	Time: 0830 hours				Time: 1730 hours			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Water Temp.(ºC)	0.3	1.4	0.93	0.27	0.5	1.3	0.98	0.17
TSS (g/L)	0.097	2.641	0.811	0.721	0.112	2.438	0.871	0.738
pH	6.63	8.53	7.16	0.39	6.13	7.80	7.03	0.32
EC, µS/cm	49	108.7	76.5	16.0	39.6	95.6	65.9	17.3
Na^+, µeq/L	25.3	102.0	54.3	18.4	21.7	65.2	41.0	15.4
K^+, µeq/L	20.2	133.2	49.9	22.7	17.3	65.2	37.4	13.7
Ca^{2+}, µeq/L	376.7	806.9	553.3	118.2	272.2	676.6	483.5	134.3
Mg^{2+}, µeq/L	101.8	251.2	182.3	43.5	105.3	231.1	153.2	43.5
HCO_3^-, µeq/L	66.3	200.4	137.4	35.7	71.7	325.5	145.9	75.6
Cl^-, µeq/L	10.4	66.5	20.0	14.8	10.3	22.8	14.7	3.5
SO_4^{2-}, µeq/L	391.4	981.8	727.2	169.7	371.3	878.7	599.4	190.5
NO_3^-, µeq/L	0.0	26.1	12.7	5.1	3.9	16.7	10.8	3.6
TZ^+, µeq/L	579.3	1141.6	844.5	177.8	433.8	999.6	719.8	189.9
TZ^-, µeq/L	637.8	1212.9	931.2	191.8	497.9	1096.6	794.7	203.7
TDS, mg/L	43.9	77.7	62.2	12.4	33.2	73.2	53.4	13.6
C-ratio	0.09	0.34	0.16	0.05	0.08	0.43	0.20	0.09
Parameter	Site: Bhojwasa							
	Time: 0830 hours				Time: 1730 hours			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Water Temp.(ºC)	0.5	2.0	1.27	0.29	0.9	2.7	1.49	0.29
TSS (g/L)	0.061	6.039	0.843	0.787	0.093	5.366	0.950	0.742
pH	5.73	8.90	7.29	0.55	6.00	8.70	7.15	0.55
EC, µS/cm	31	129	69.7	22.5	18	115	60.3	22.9
Na^+, µeq/L	2.1	115.5	43.1	24.3	0.4	140.8	38.5	26.3
K^+, µeq/L	0.03	107.2	36.0	21.3	0.0	148.4	32.6	23.0
Ca^{2+}, µeq/L	61.1	1224.7	454.6	191.8	48.4	1455.7	442.1	219.8
Mg^{2+}, µeq/L	1.56	262.8	129.6	70.7	4.8	309.8	123.7	71.3
HCO_3^-, µeq/L	54.0	1198.5	152.1	139.8	51.9	920.0	141.4	118.9
Cl^-, µeq/L	0.11	187.6	15.5	20.0	0.14	85.8	14.8	15.7
SO_4^{2-}, µeq/L	31.7	1142.9	534.3	251.1	46.3	1240	501.7	260.7
NO_3^-, µeq/L	0.0	29.2	6.8	7.1	0.0	45.1	6.4	7.4
TZ^+, µeq/L	110.9	1455.6	670.8	286.5	105.1	1706.1	646.3	317.5
TZ^-, µeq/L	126.2	1740.2	730.5	309.5	126.4	1528.8	686.5	314.2
TDS, mg/L	8.8	126.59	49.6	21.2	8.6	111.5	46.8	21.7
C-ratio	0.07	0.82	0.24	0.14	0.07	0.71	0.24	0.14

Table 4.2 Contd.

Parameter	**Site: Gangotri**							
	Time: 0830 hours				**Time: 1730 hours**			
	Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Water Temp.(ºC)	2.5	6.0	4.13	0.86	3.0	6.0	4.41	0.73
TSS (g/L)	0.068	4.553	0.981	0.993	0.094	3.819	1.113	0.817
pH	6.39	7.72	7.13	0.32	6.17	7.45	7.09	0.28
EC, µS/cm	53.0	125	77.3	18.7	41.7	108	74.1	17.25
Na^+, µeq/L	30.9	136.2	56.9	25.8	23.5	99.7	47.9	22.5
K^+, µeq/L	29.7	95.9	45.9	14.7	19.2	65.4	38.8	12.3
Ca^{2+}, µeq/L	379.1	847.3	530.4	136.4	299.0	788.5	454.7	131.9
Mg^{2+}, µeq/L	123.5	220.6	165.7	29.0	89.8	238.0	152.8	43.6
HCO_3^-, µeq/L	55.3	379.1	182.3	96.3	64.3	393.0	142.5	77.3
Cl^-, µeq/L	11.3	76.5	20.6	14.2	11.4	38.9	19.1	8.2
SO_4^{2-}, µeq/L	472.9	960.5	644.1	161.0	314.0	908.1	571.0	172.4
NO_3^-, µeq/L	2.8	23.2	11.9	5.4	0.0	18.5	10.9	5.0
TZ^+, µeq/L	606.3	1179.7	813.0	183.9	473.4	1150.1	707.0	192.6
TZ^-, µeq/L	649.4	1253.8	889.6	198.3	553.7	1276.9	772.5	206.4
TDS, mg/L	44.0	86.1	60.2	13.7	36.2	87.7	51.9	13.9
C-ratio	0.05	0.38	0.22	0.09	0.08	0.47	0.20	0.09

TSS = Total Suspended Sediment (g/L); EC = Electrical Conductivity (µS/cm); TZ^+ = Total Cations (µeq/L); TZ^- = Total Anions (µeq/L); TDS = Total Dissolved Solids (mg/L); All cations and anions concentrations are in µeq/L.

Table 4.3 Hydro-chemical data of meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during ablation period of 2016

Parameter	**Site: Gomukh**							
	Time: 0830 hours				**Time: 1730 hours**			
	Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Water Temp.(ºC)	0.6	1.3	0.91	0.18	0.9	1.5	1.67	0.20
TSS (g/L)	0.399	3.501	1.333	0.919	0.425	5.703	2.034	1.622
pH	6.70	7.83	7.11	0.27	6.39	7.74	6.82	0.37
EC, µS/cm	66.4	119.2	101.7	13.4	49.0	82.9	69.8	7.8
Na^+, µeq/L	10.7	82.6	43.9	13.6	5.1	70.8	29.7	13.2
K^+, µeq/L	0.74	78.3	46.8	16.0	1.3	68.2	31.3	14.2
Ca^{2+}, µeq/L	330.1	744.2	556.5	101.5	226.0	651.1	413.3	115.1
Mg^{2+}, µeq/L	34.1	239.3	169.0	46.0	19.2	218.9	125.2	50.2
HCO_3^-, µeq/L	95.0	400.4	181.9	70.2	89.7	379.4	148.7	79.8
Cl^-, µeq/L	2.6	27.6	6.1	5.4	0.90	10.9	4.3	2.2
SO_4^{2-}, µeq/L	198.0	935.9	678.5	181.6	138.4	879.3	489.3	176.7
NO_3^-, µeq/L	0.0	6.2	3.3	1.6	0.3	5.7	2.0	1.1
TZ^+, µeq/L	419.9	1044.3	820.1	154.2	338.1	959.1	602.9	157.6
TZ^-, µeq/L	472.3	1133.4	887.7	165.2	377.7	1063.4	657.4	175.0
TDS, mg/L	33.9	75.9	60.6	10.8	26.2	71.0	44.9	11.4
C-ratio	0.10	0.57	0.22	0.11	0.10	0.71	0.24	0.14
Parameter	**Site: Bhojwasa**							
	Time: 0830 hours				**Time: 1730 hours**			
	Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Water Temp.(ºC)	1.1	2.0	1.39	0.13	1.1	2.1	1.71	0.18
TSS (g/L)	0.150	5.003	1.633	1.131	0.210	8.248	2.145	1.620
pH	5.66	7.65	6.88	0.38	5.42	7.86	6.72	0.45
EC, µS/cm	50.0	156.7	92.1	16.6	35.5	130.2	66.9	16.9
Na^+, µeq/L	4.5	105.8	47.9	18.3	5.3	141.9	37.3	22.7
K^+, µeq/L	0.69	131.6	50.8	20.9	0.74	93.8	38.6	20.3
Ca^{2+}, µeq/L	146.6	1060.3	495.6	130.9	131.2	922.2	374.2	124.9
Mg^{2+}, µeq/L	23.4	274.5	157.0	46.4	20.2	265.7	120.8	40.7
HCO_3^-, µeq/L	68.4	564.0	169.4	66.8	44.5	508.0	148.0	72.7
Cl^-, µeq/L	0.31	43.5	9.7	8.1	0.28	103.1	9.7	10.9
SO_4^{2-}, µeq/L	195.5	1203.0	609.2	180.2	117.0	973.1	450.2	146.4
NO_3^-, µeq/L	0.0	10.7	3.3	2.1	0.0	8.5	2.5	2.0
TZ^+, µeq/L	300.5	1499.3	759.3	187.0	216.0	1189.8	579.5	184.1
TZ^-, µeq/L	356.8	1585.0	809.6	196.6	241.8	1244.1	624.0	186.8
TDS, mg/L	24.6	109.8	55.6	13.3	16.4	87.4	43.0	13.1
C-ratio	0.06	0.47	0.23	0.08	0.07	0.57	0.25	0.09

Table 4.3 Contd.

Parameter	**Site: Gangotri**							
	Time: 0830 hours				**Time: 1730 hours**			
	Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Water Temp.(ºC)	2.1	4.8	3.64	0.56	2.9	5.0	4.13	0.63
TSS (g/L)	0.206	7.898	2.224	2.274	0.427	8.803	2.762	2.594
pH	6.71	7.90	7.06	0.29	6.51	7.20	6.75	0.15
EC, µS/cm	66.1	123.1	93.0	16.4	49.4	100.5	78.3	12.5
Na^+, µeq/L	0.74	122.3	44.5	23.1	26.4	66.4	37.11	10.1
K^+, µeq/L	1.3	86.8	44.0	22.8	25.6	74.0	45.2	11.7
Ca^{2+}, µeq/L	290.3	812.1	519.1	145.0	241.3	724.1	449.8	138.0
Mg^{2+}, µeq/L	43.7	301.3	174.2	63.6	80.3	210.2	151.5	34.4
HCO_3^-, µeq/L	125.3	418.4	187.5	74.3	94.6	286.3	172.5	61.8
Cl^-, µeq/L	1.6	33.9	6.3	7.0	1.9	9.7	5.0	2.2
SO_4^{2-}, µeq/L	276.4	1002.0	642.1	215.0	256.0	761.8	535.3	127.1
NO_3^-, µeq/L	0.0	6.9	2.9	2.1	0.0	6.2	2.7	2.3
TZ^+, µeq/L	374.9	1258.6	782.4	223.4	392.9	1022.8	684.5	172.1
TZ^-, µeq/L	410.2	1318.3	857.8	235.2	438.4	1077.8	733.4	166.5
TDS, mg/L	27.9	91.1	58.3	15.8	30.9	74.7	50.5	11.8
C-ratio	0.13	0.44	0.24	0.08	0.14	0.39	0.24	0.07

TSS = Total Suspended Sediment (g/L); EC = Electrical Conductivity (µS/cm); TZ^+ = Total Cations (µeq/L); TZ^- = Total Anions (µeq/L); TDS = Total Dissolved Solids (mg/L); All cations and anions concentrations are in µeq/L.

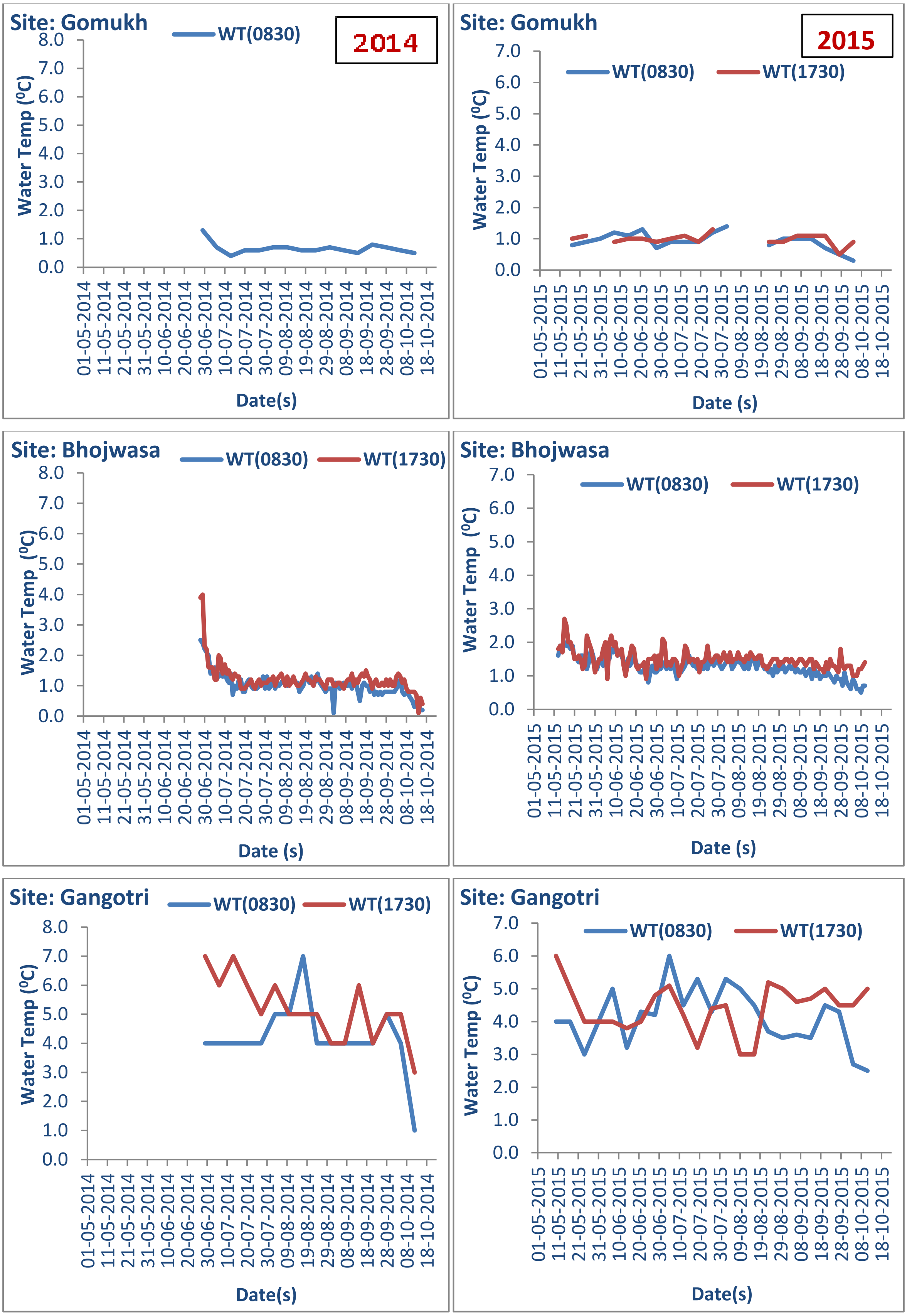


Fig. 4.1(a) Variation of water temperature (WT) in meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014 and 2015.

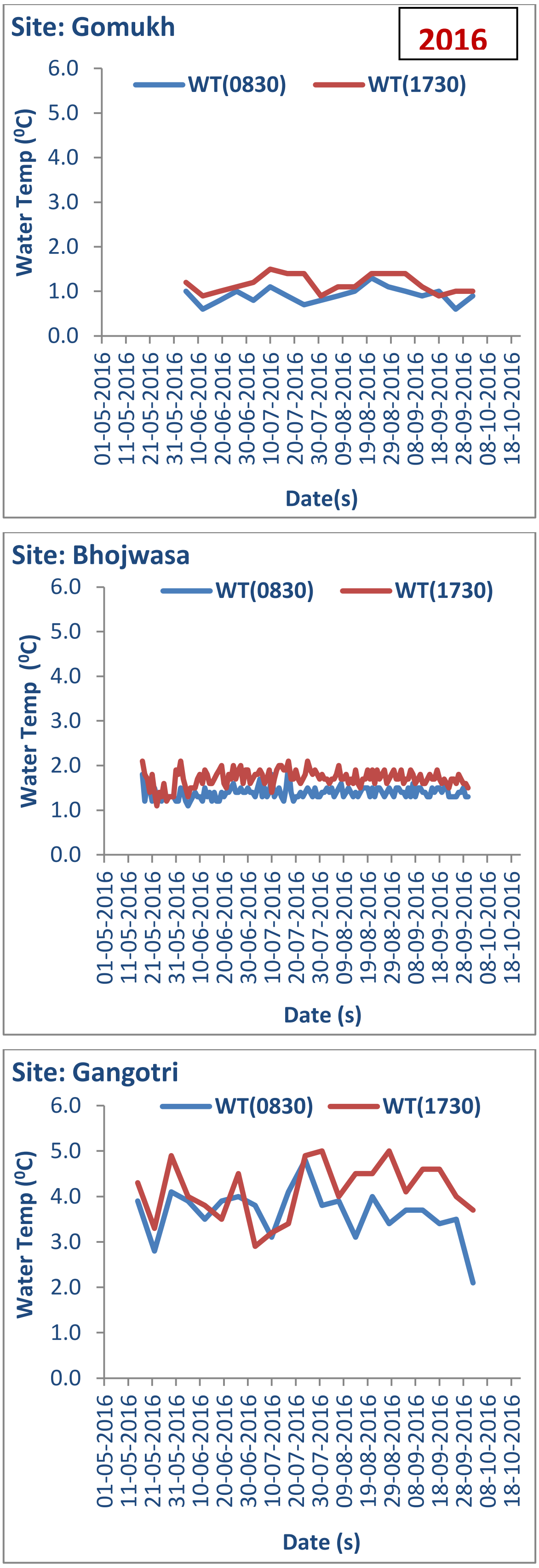


Fig. 4.1(b) Variation of water temperature (WT) in meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

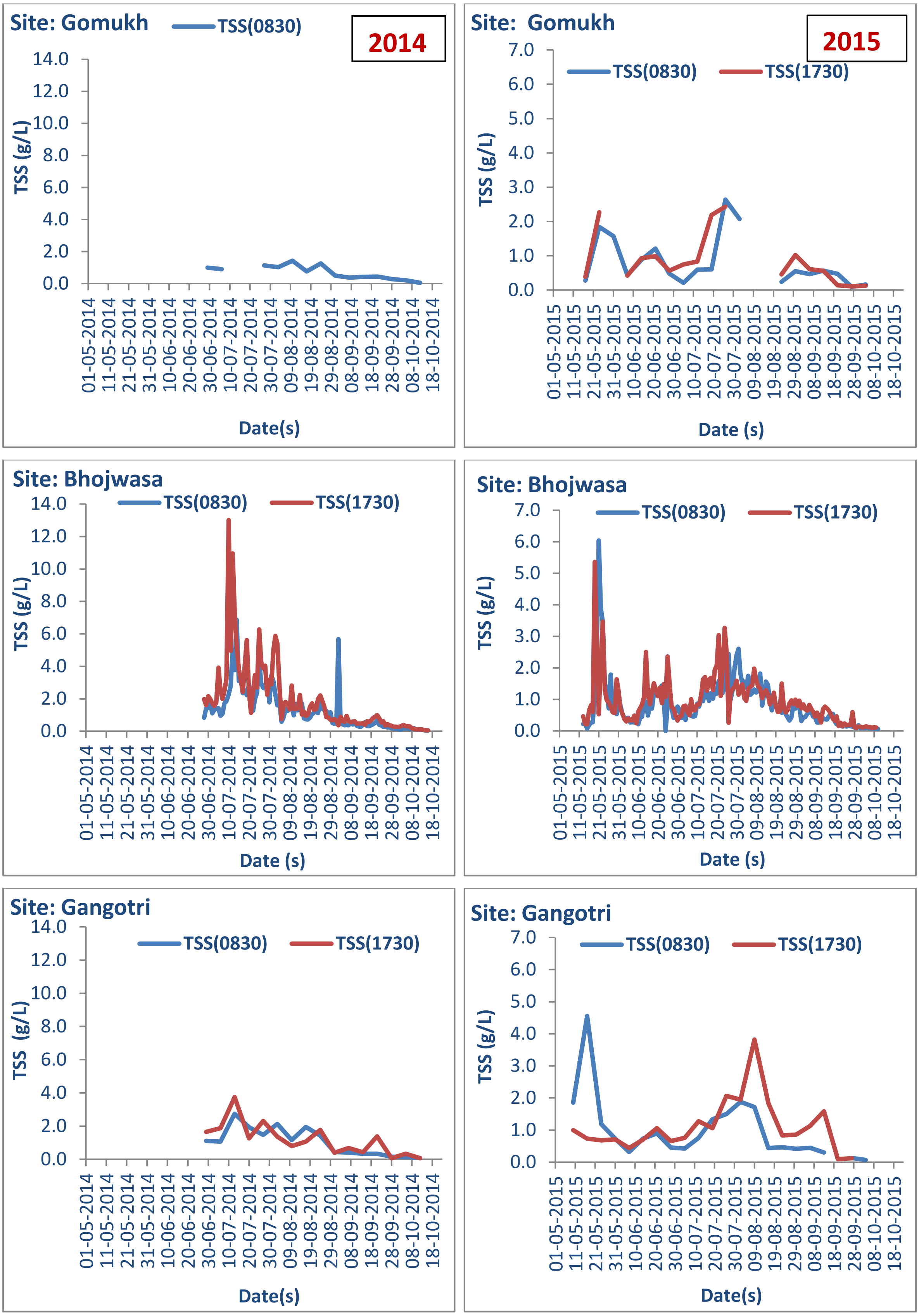


Fig. 4.2(a) Variation of Total Suspended Sediment (TSS) in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014 and 2015

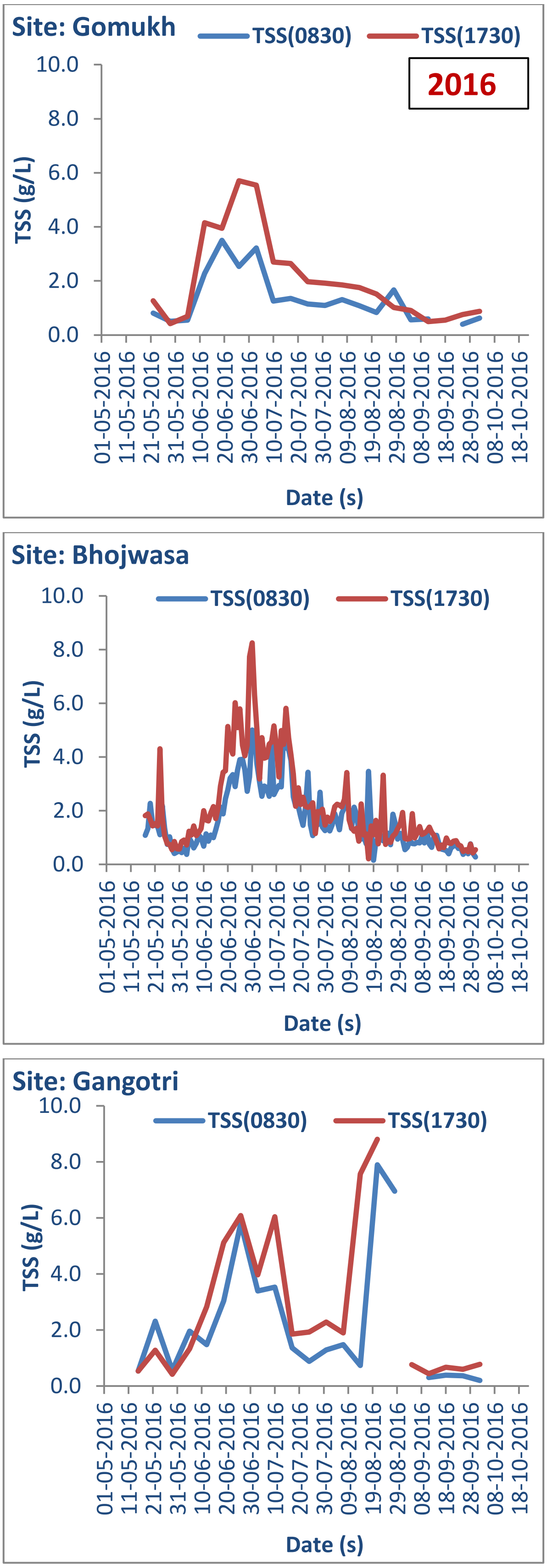


Fig. 4.2(b) Variation of Total Suspended Sediment (TSS) in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

4.1.3 Variation of pH at Gomukh, Bhojwasa and Gangotri

pH plays an important role in low temperature chemical process in controlling the solute acquisition during suspended sediment-meltwater interaction. Variation of pH in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri is shown in Fig. 4.3(a) & (b) during the period of investigation of 2014-2016. pH varies from 6.63 to 8.53 with average value 7.18 at 0830 hours and 6.13 to 7.80 with average value 6.93 at 1730 hours in the meltwater of River Bhagirathi at Gomukh, 5.66 to 8.90 with average value 7.10 at 0830 hours and 5.42 to 8.70 with average value 6.90 at 1730 hours in the meltwater of River Bhagirathi at Bhojwasa and 6.39 to 8.20 with average value 7.27 at 0830 hours and 6.17 to 8.33 with average value 7.15 at 1730 hours in the meltwater of River Bhagirathi at Gangotri respectively during the period of investigation of 2014-2016.

4.1.4 Variation of Electrical Conductivity (EC) at Gomukh, Bhojwasa and Gangotri

Electrical conductivity (EC) represents the ionic enrichment characteristics of the meltwater. Variation of EC in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri is shown in Fig. 4.4(a) & (b) during the period of investigation of 2014-2016. EC varies from 49.0 to 125.6 µS/cm with average value 90.3 µS/cm at 0830 hours and 39.6 to 95.6 µS/cm with average value 67.9 µS/cm at 1730 hours in the meltwater of River Bhagirathi at Gomukh, 31.0 to 156.7 µS/cm with average value 83.7 µS/cm at 0830 hours and 18.0 to 147.4 µS/cm with average value 63.7 µS/cm at 1730 hours in the meltwater of River Bhagirathi at Bhojwasa and 53.0 to 125.0 µS/cm with average value 85.4 µS/cm at 0830 hours and 41.7 to 117.4 µS/cm with average value 77.9 µS/cm at 1730 hours in the meltwater of River Bhagirathi at Gangotri respectively during the period of investigation of 2014-2016.

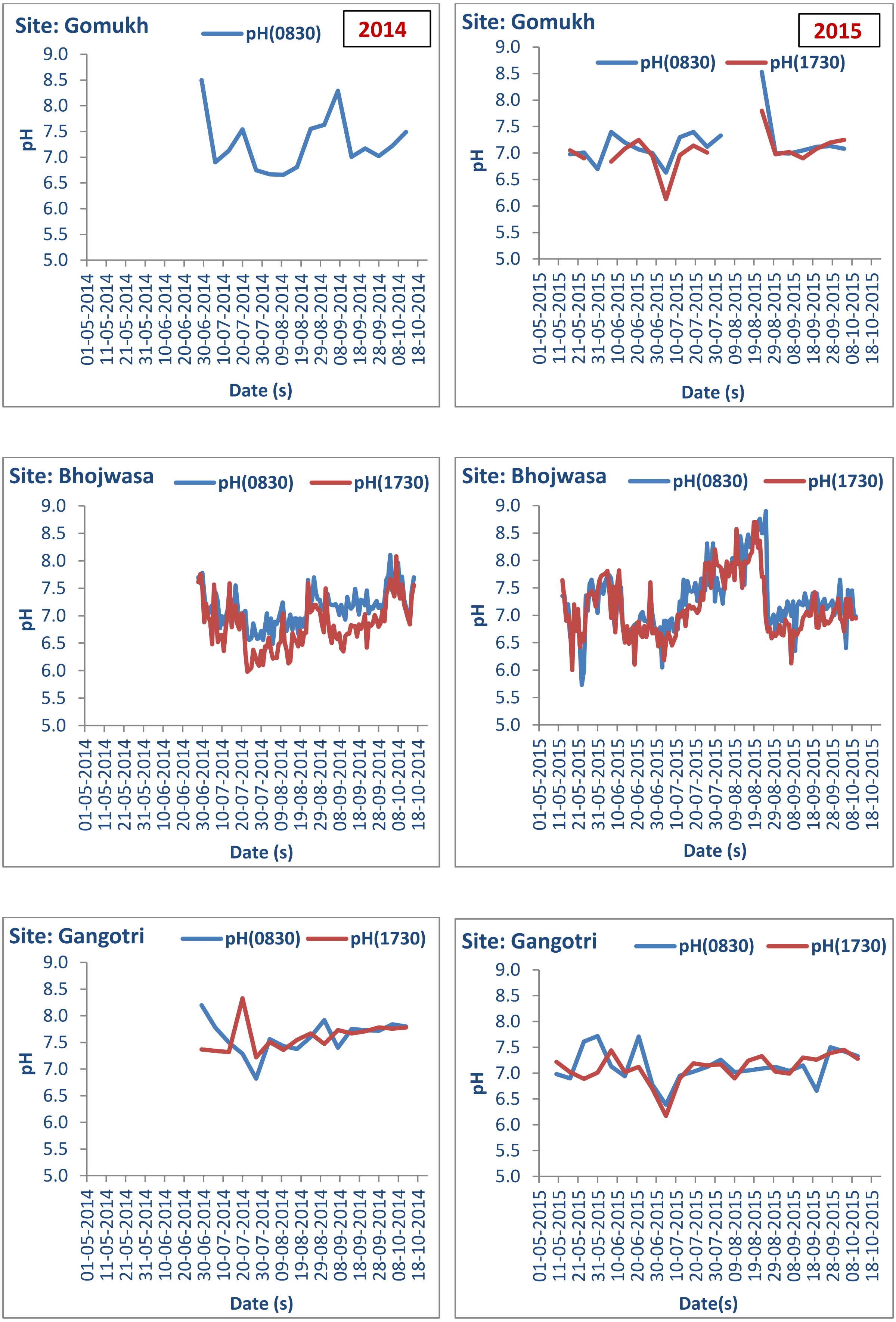


Fig. 4.3(a) Variation of pH in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014 and 2015

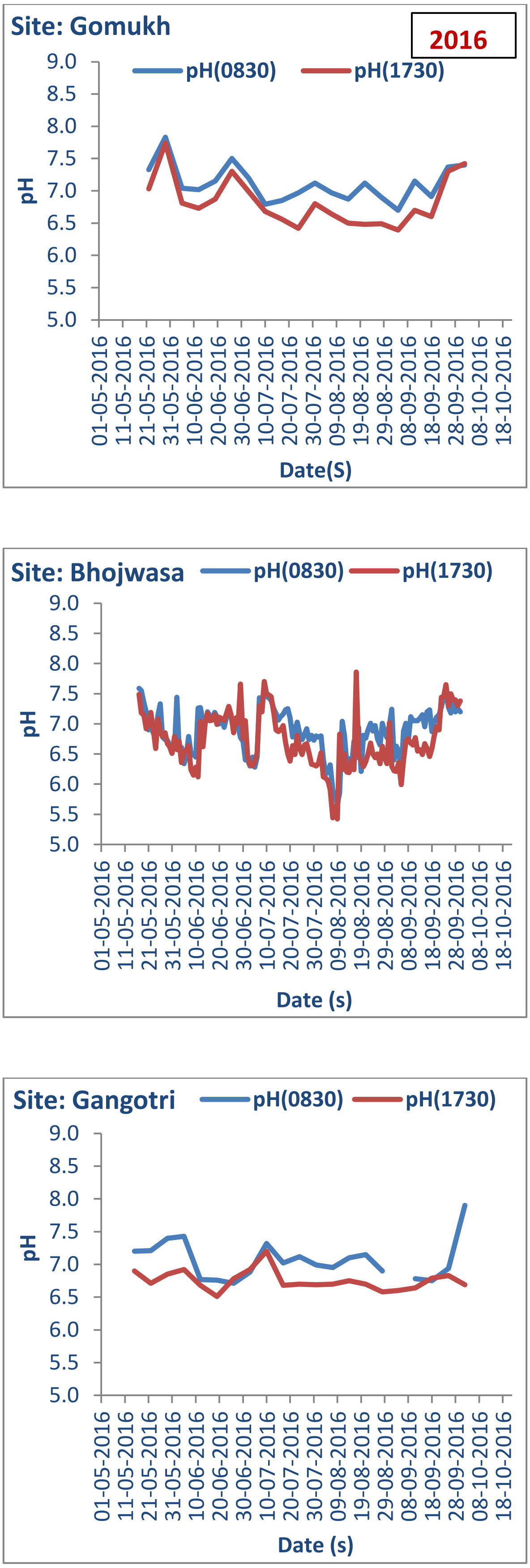


Fig. 4.3(b) Variation of pH in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

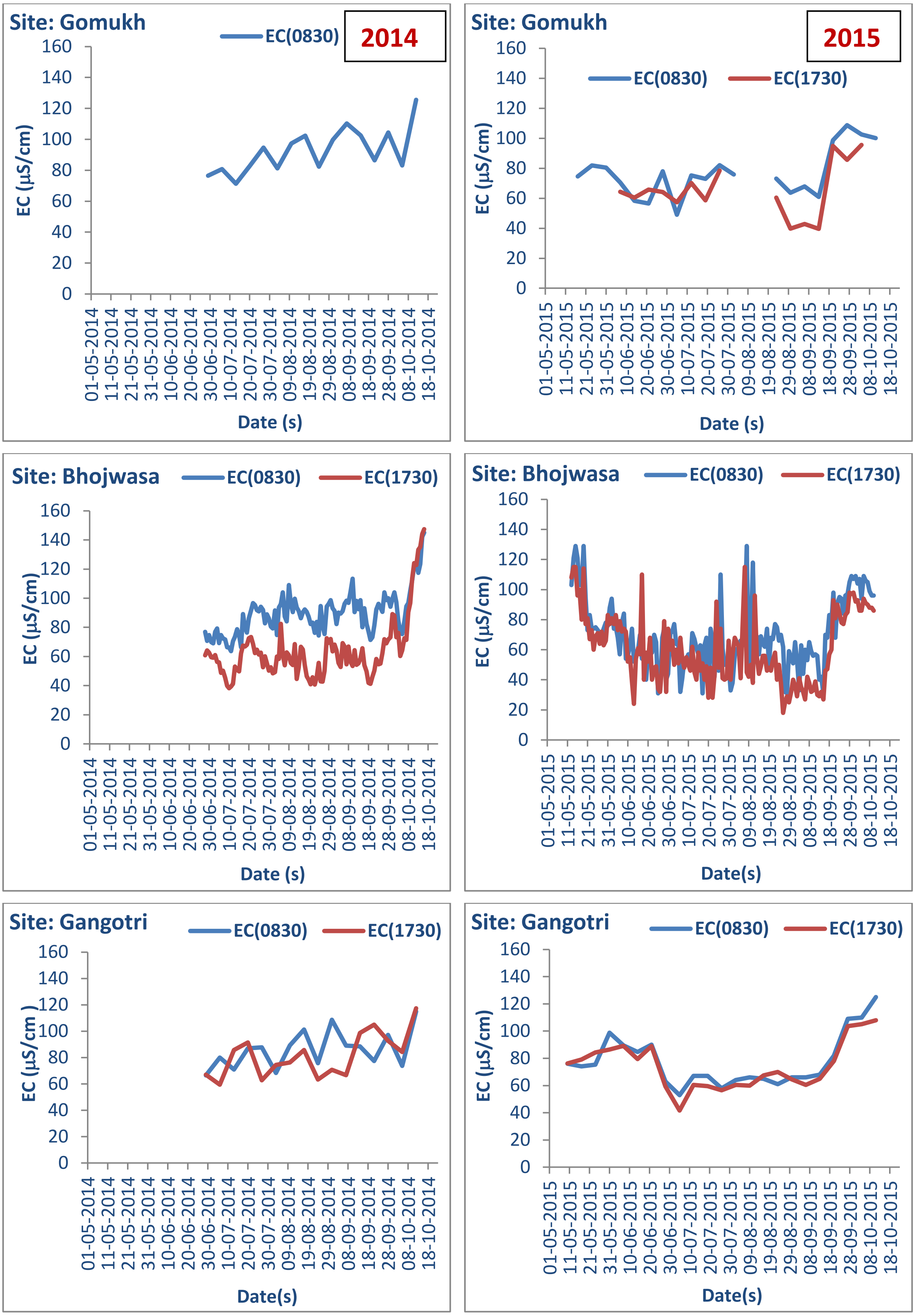


Fig. 4.4(a) Variation of EC in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014 and 2015

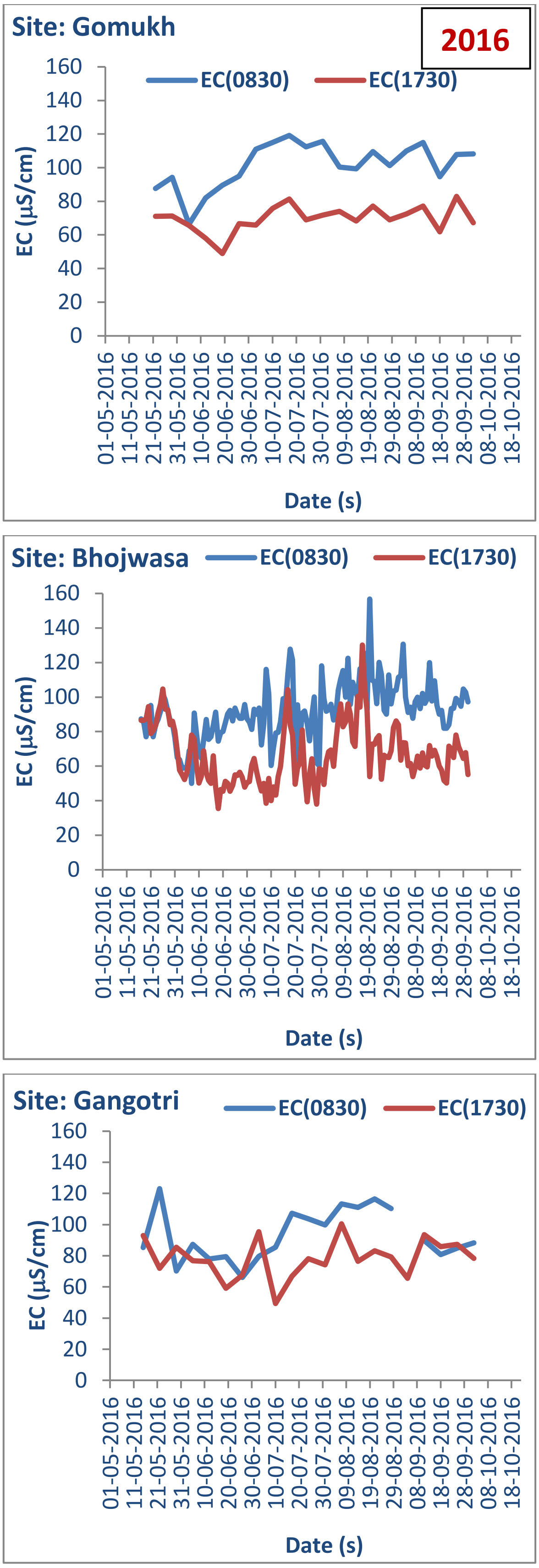


Fig. 4.4(b) Variation of EC in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

4.1.5 Variation of Total Dissolved Solid (TDS) at Gomukh, Bhojwasa and Gangotri

Total dissolved solid (TDS) was calculated by summation of the masses of all the major dissolved constituents i.e. major cations and major anions. Variations in the concentration of different ions with time are possibly due to different weathering intensities generating meltwater at different discharge values (Kumar et al., 2009). There has been a marked temporal variation in the TDS of the meltwater draining from Gangotri Glacier. Variation of TDS in the meltwaters of river Bhagirathi at Gomukh, Bhojwasa and Gangotri is shown in Fig. 4.5(a) & (b) during the period of investigation of 2014-2016. TDS varies from 34 to 78 mg/L with average value 60 mg/L at 0830 hours and 26 to 73 mg/L with average value 49 mg/L at 1730 hours in the meltwater of River Bhagirathi at Gomukh, 8.8 to 127 mg/L with average value 52 mg/L at 0830 hours and 8.6 to 111 mg/L with average value 42 mg/L at 1730 hours in the meltwater of River Bhagirathi at Bhojwasa and 28 to 91 mg/L with average value 59 mg/L at 0830 hours and 31 to 98 mg/L with average value 54 mg/L at 1730 hours in the meltwater of River Bhagirathi at Gangotri during the period of investigation of 2014-2016.

TDS was high in the mornings and reduced towards evenings [Fig. 4.5(a) & (b)]. The model of Rainwater and Guy (1961), Collins (1983), Kumar et al. (2009), was used to explain the observed temporal variation in the TDS. In the morning, low supply of solar energy reduced the melting and dilution of subglacial water. The subglacial water produced at pressure melting point, has high ionic chemical enrichment as a result of high residence time and longer contact with the solute rich base. In the afternoon with an increase in insolation, englacial channels become active and large amount of supraglacial meltwaters become available for transportation so that discharge is maximum in the evening, resulting in increased dilution of TDS.

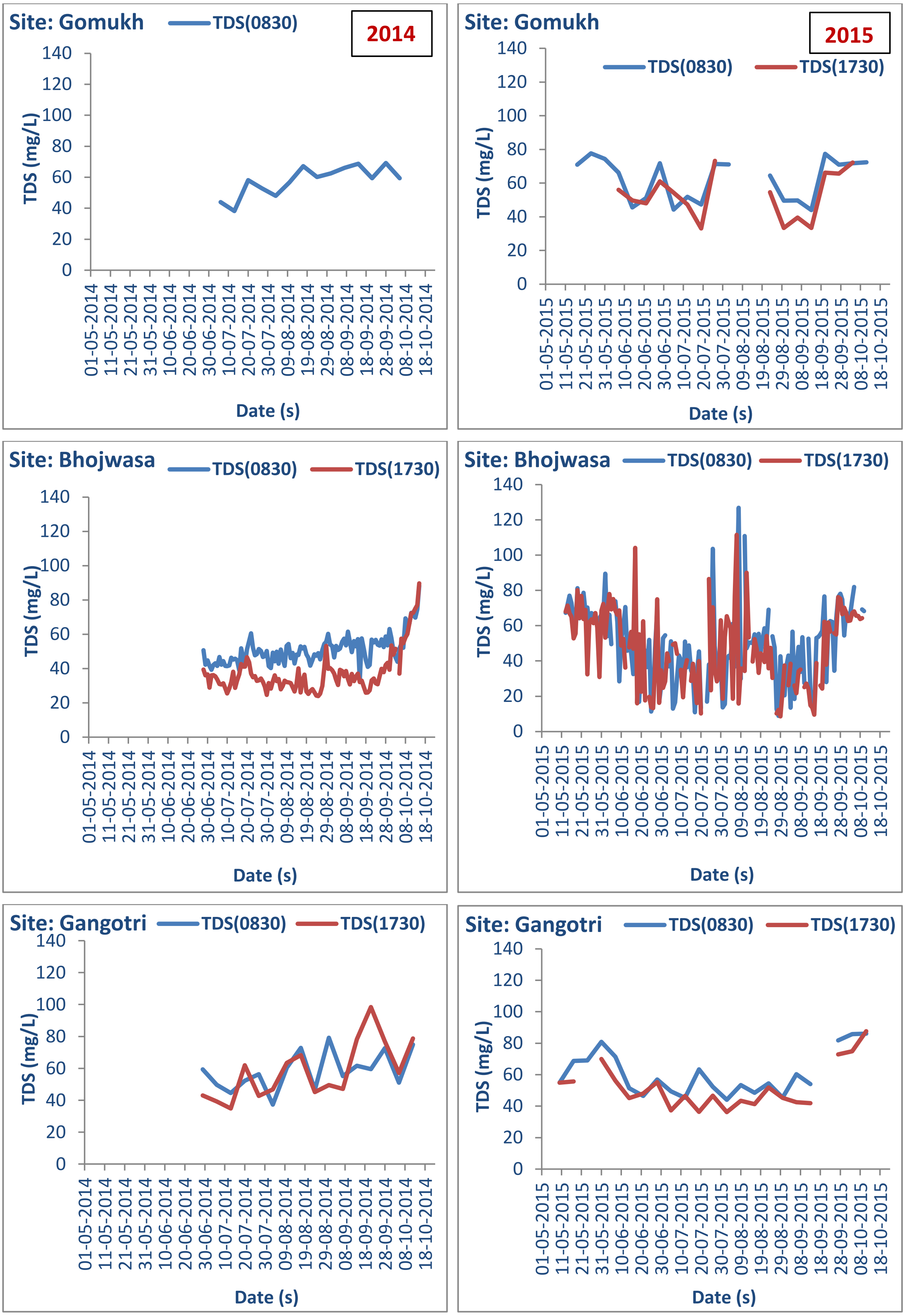


Fig. 4.5(a) Variation of TDS in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014 and 2015

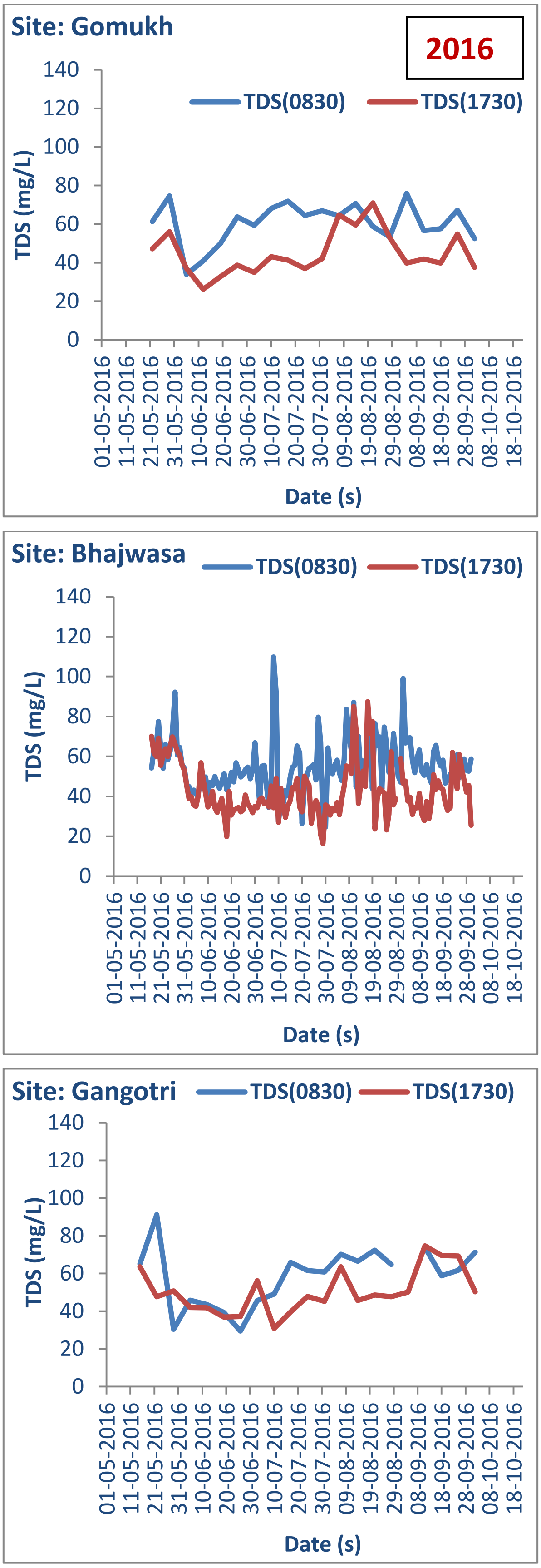


Fig. 4.5(b) Variation of TDS in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

4.1.6 Variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) at Gomukh, Bhojwasa and Gangotri

Variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the meltwaters of river Bhagirathi at Gomukh, Bhojwasa and Gangotri during the period of investigation of the year 2014, 2015 and 2016 is shown in Fig. 4.6(a-b), 4.7(a-b) and 4.8(a-b) respectively. The average concentration of Na^+, K^+, Ca^{2+} and Mg^{2+} was observed to be 46 µeq/L (11-102 µeq/L), 49 µeq/L (0.7-133 µeq/L), 551 µeq/L (330-807 µeq/L) and 172 µeq/L (34-251 µeq/L) at 0830 hours and 35 µeq/L (5.1-71 µeq/L), 34 µeq/L (1.3-68 µeq/L), 448 µeq/L (226-677 µeq/L) and 139 µeq/L (19-231 µeq/L) at 1730 hours respectively in meltwater of River Bhagirathi at Gomukh, 45 µeq/L (2.1-116 µeq/L), 43 µeq/L (0.01-132 µeq/L), 468 µeq/L (61-1225 µeq/L) and 141 µeq/L (1.6-339 µeq/L) at 0830 hours and 36 µeq/L (0.4-142 µeq/L), 34 µeq/L (0.0-148 µeq/L), 384 µeq/L (48-1456 µeq/L) and 121 µeq/L (4.8-368 µeq/L) at 1730 hours respectively in meltwater of River Bhagirathi at Bhojwasa and 47 µeq/L (0.7-136 µeq/L), 46 µeq/L (1.3-96 µeq/L), 530 µeq/L (290-847 µeq/L) and 166 µeq/L (44-301 µeq/L) at 0830 hours and 53 µeq/L (17-675 µeq/L), 42 µeq/L (19-74 µeq/L), 468 µeq/L (241-789 µeq/L) and 153 µeq/L (77-238 µeq/L) at 1730 hours respectively in meltwater of River Bhagirathi at Gangotri during the period of investigation of 2014-2016. The average Ca^{2+} concentration was followed by Mg^{2+}, Na^+ and K^+.

Further, the cation chemistry implies that Ca^{2+} and Mg^{2+} were the dominant cations, on an average constituting 67.6% and 21.2% of the total cations respectively, followed by K^+ (5.8%) and Na^+ (5.3%) in meltwater of River Bhagirathi at Gomukh, Ca^{2+} and Mg^{2+} were the dominant cations, on an average constituting 67.6% and 20.1% of the total cations respectively, followed Na^+ (6.3%) and K^+ (6.0%) in meltwater of River Bhagirathi at Bhojwasa and again Ca^{2+} and Mg^{2+} were the dominant cations, on an average constituting 66.3% and 21.3% of the total cations respectively, followed by Na^+ (6.5%) and K^+ (6.0%) in meltwater of River Bhagirathi at Gangotri during the period of investigation of 2014-2016.

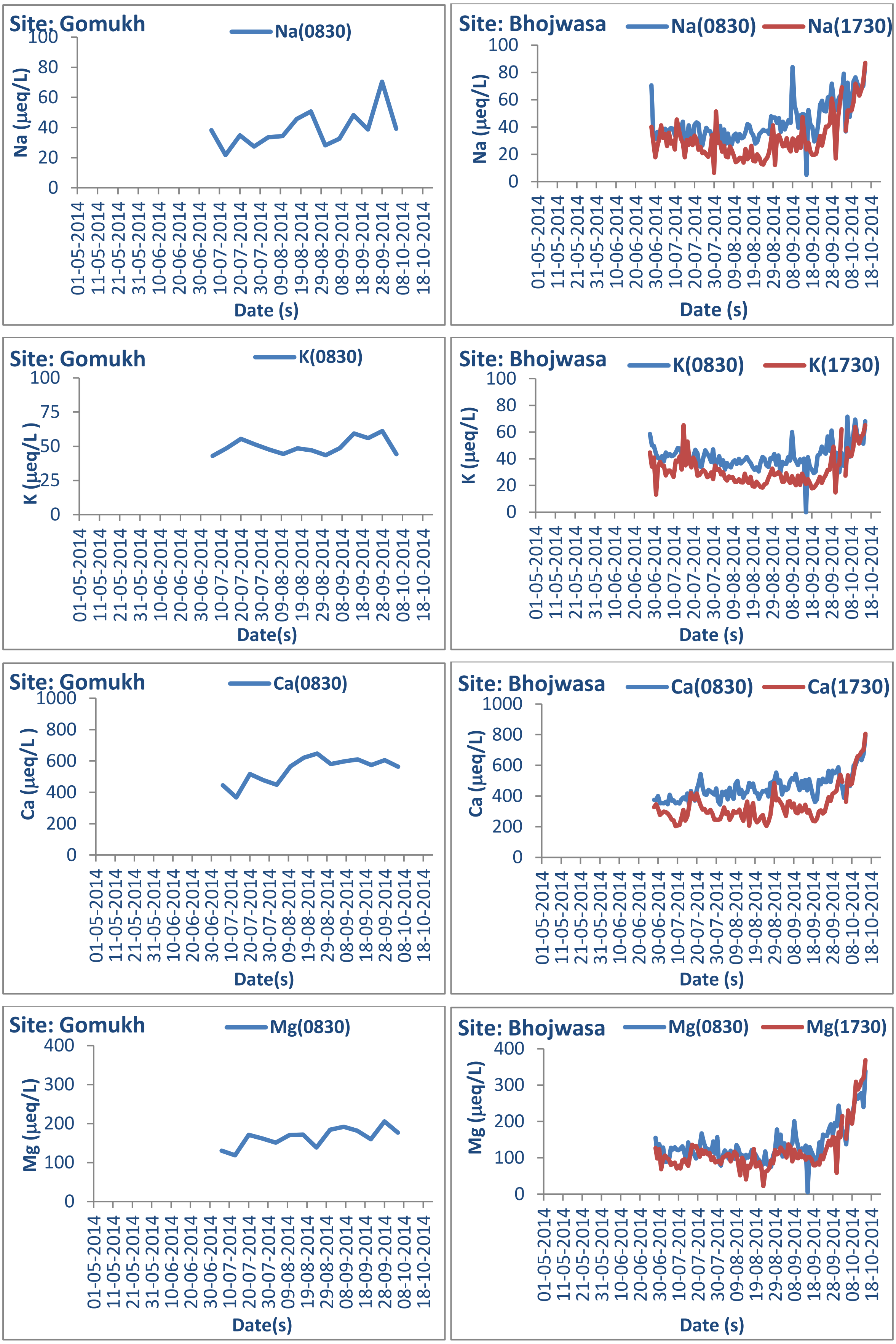


Fig. 4.6(a) Variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the meltwater of River Bhagirathi at Gomukh and Bhojwasa during the year 2014

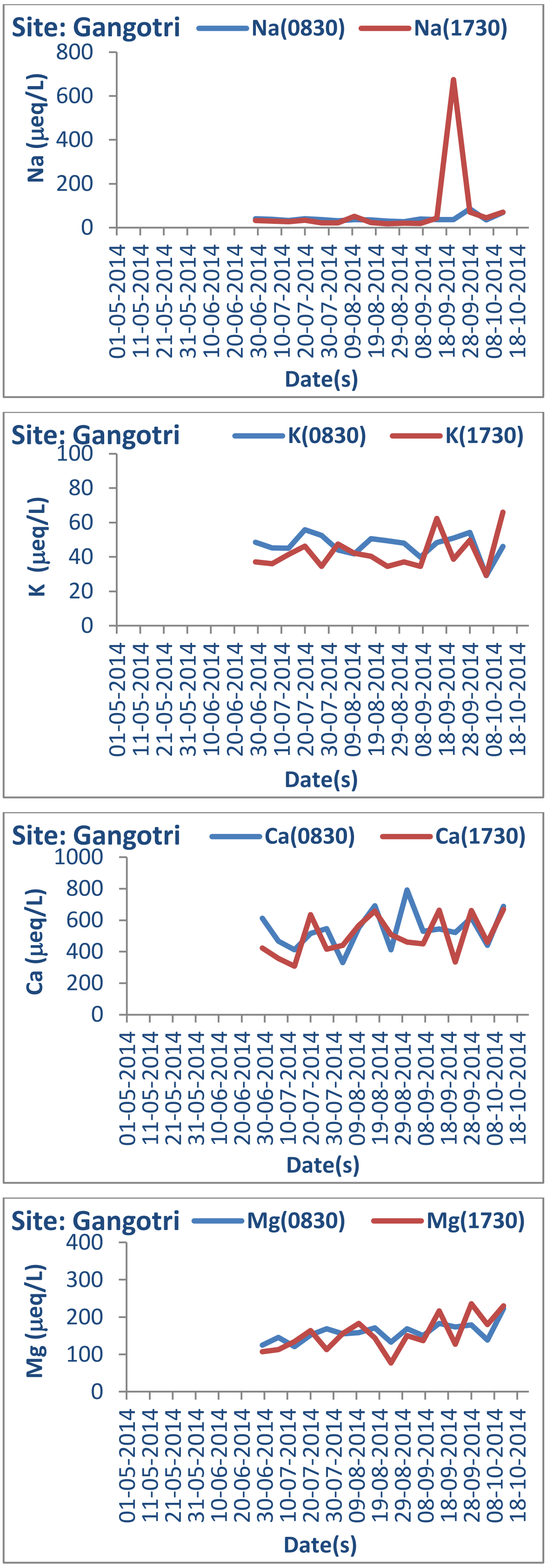


Fig. 4.6(b) Variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the meltwater of River Bhagirathi at Gangotri during the year 2014

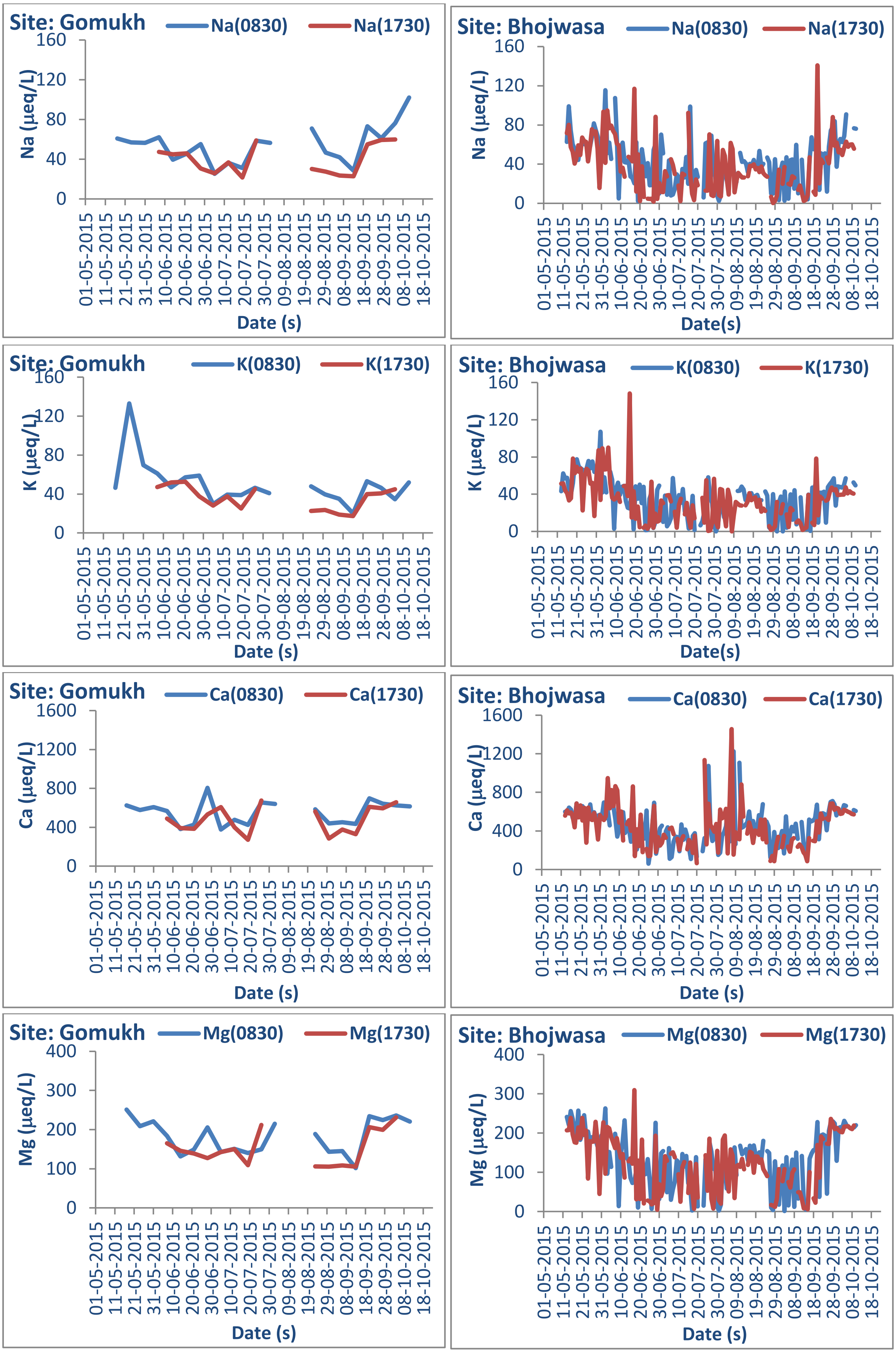


Fig. 4.7(a) Variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the meltwater of River Bhagirathi at Gomukh and Bhojwasa during the year 2015

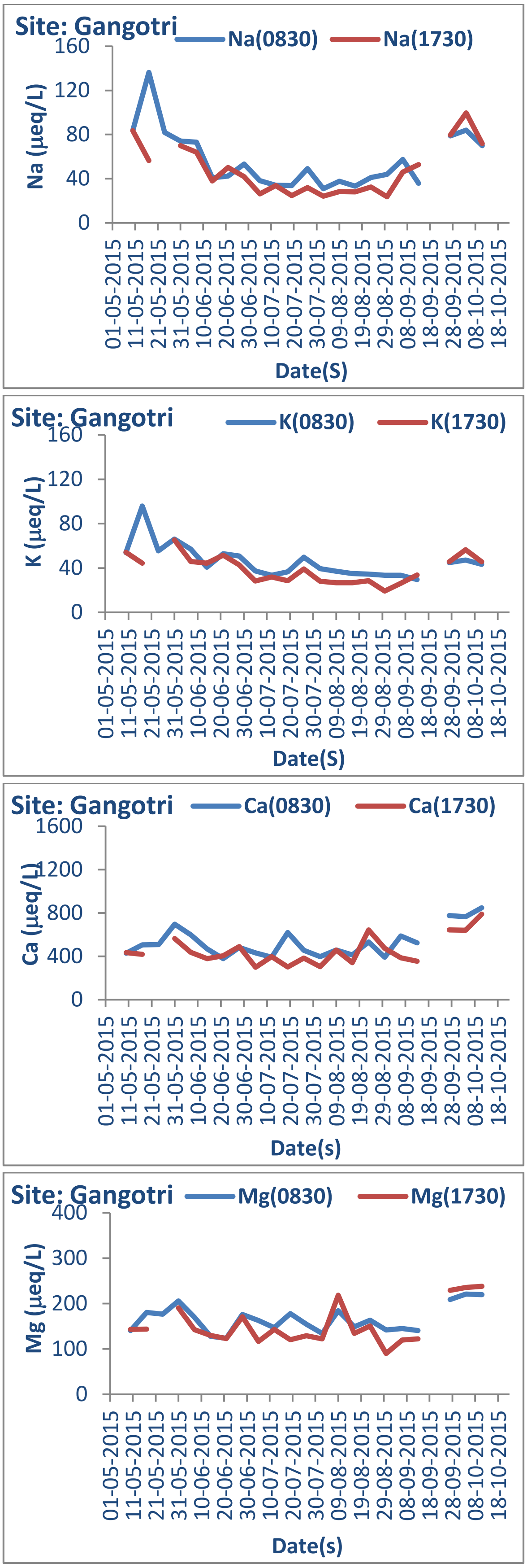


Fig. 4.7(b) Variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the meltwater of River Bhagirathi at Gangotri during the year 2015

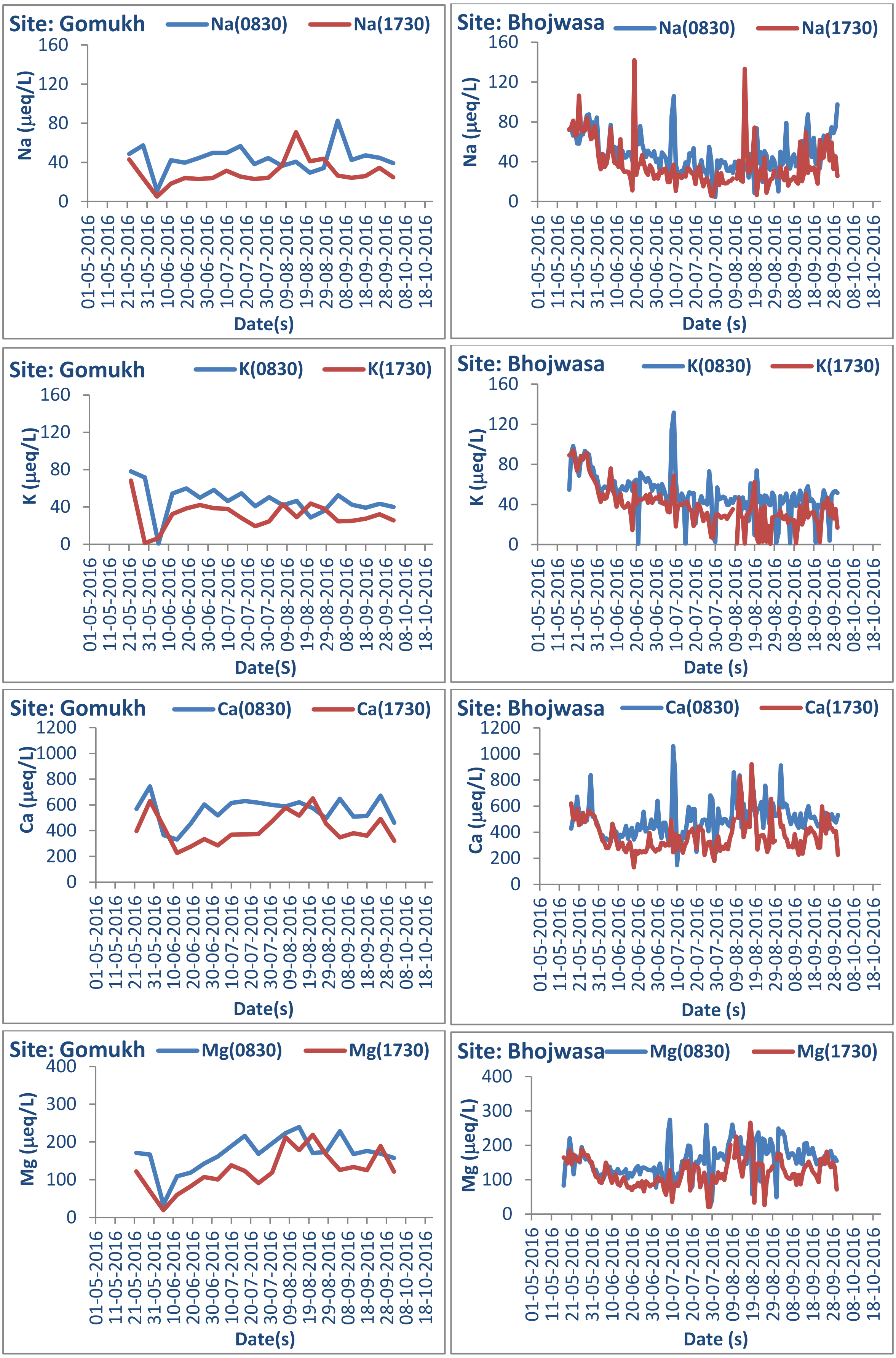


Fig. 4.8(a) Variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the meltwater of River Bhagirathi at Gomukh and Bhojwasa during the year 2016

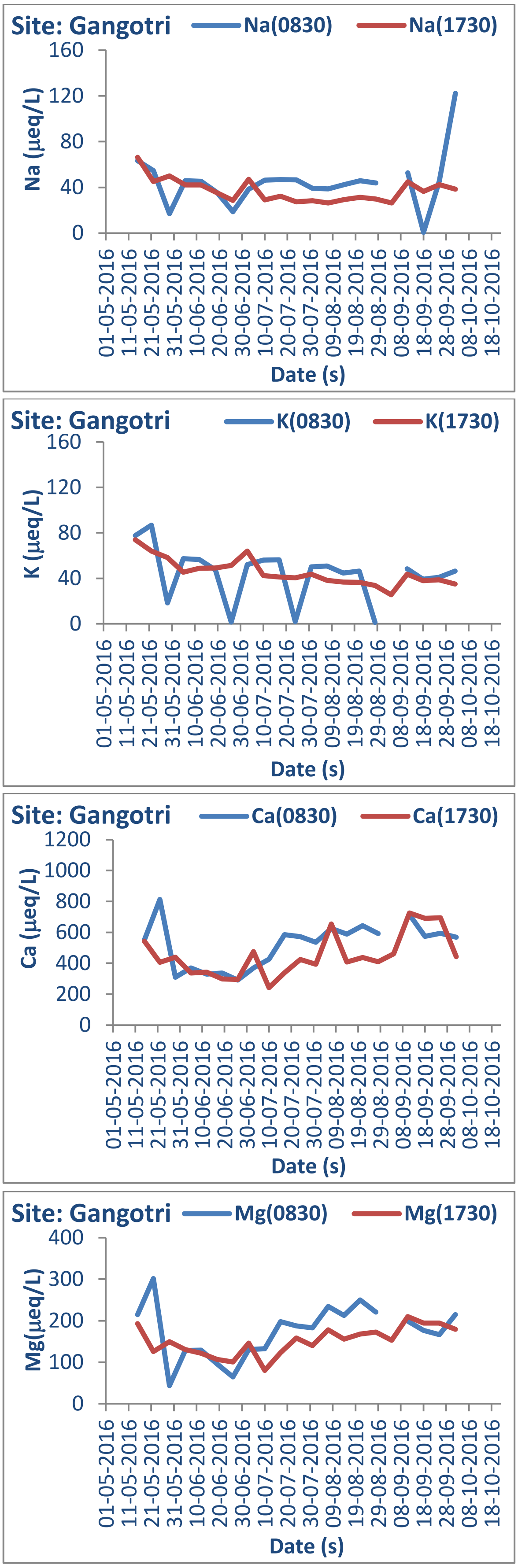


Fig. 4.8(b) Variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) in the meltwater of River Bhagirathi at Gangotri during the year 2016

4.1.7 Variation of major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) at Gomukh, Bhojwasa and Gangotri

Variation of major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3) in the meltwaters of river Bhagirathi at Gomukh, Bhojwasa and Gangotri during the period of investigation of the year 2014, 2015 and 2016 is shown in Fig. 4.9(a-b), 4.10(a-b) and 4.11(a-b) respectively. The average concentration of HCO_3^-, Cl^-, SO_4^{2-} and NO_3^- was observed to be 138 µeq/L (12-400 µeq/L), 15 µeq/L (2.6-67 µeq/L), 712 µeq/L (198-982 µeq/L) and 9.7 µeq/L (0-26 µeq/L) at 0830 hours and 147 µeq/L (72-379 µeq/L), 9.5 µeq/L (0.9-23 µeq/L), 544 µeq/L (138-879 µeq/L) and 6.4 µeq/L (0.3-17 µeq/L) at 1730 hours respectively in meltwater of River Bhagirathi at Gomukh, 152 µeq/L (50-1199 µeq/L), 17 µeq/L (0.1-188 µeq/L), 573 µeq/L (32-1203 µeq/L) and 6.2 µeq/L (0-29 µeq/L) at 0830 hours and 130 µeq/L (12-920 µeq/L), 12 µeq/L (0.1-103 µeq/L), 458 µeq/L (46-1240 µeq/L) and 4.0 µeq/L (0-45 µeq/L) at 1730 hours respectively in meltwater of River Bhagirathi at Bhojwasa and 180 µeq/L (55-418 µeq/L), 14 µeq/L (1.6-77 µeq/L), 644 µeq/L (276-1002 µeq/L) and 17 µeq/L (0-23 µeq/L) at 0830 hours and 177 µeq/L (64-833 µeq/L), 13 µeq/L (1.9-39 µeq/L), 566 µeq/L (256-986 µeq/L) and 5.2 µeq/L (0-19 µeq/L) at 1730 hours respectively in meltwater of River Bhagirathi at Gangotri during the period of investigation of 2014-2016. The average SO_4^{2-} concentration was followed by HCO_3^-, Cl^- and NO_3^-.

Further, the anion chemistry indicates that SO_4^{2-} and HCO_3^- were the dominant anions, on an average constituting 80.7% and 16.4% of the total anions respectively, followed by Cl^- (1.6%) and NO_3^- (0.8%) in meltwater of River Bhagirathi at Gomukh, SO_4^{2-} and HCO_3^- were the dominant anions, on an average constituting 75.5% and 21.6% of the total anions respectively, followed by Cl^- (2.1%) and NO_3^- (0.8%) in meltwater of River Bhagirathi at Bhojwasa and again SO_4^{2-} and HCO_3^- were the dominant anions, on an average constituting 75.3% and 22.4% of the total anions respectively, followed by Cl^- (1.7%) and NO_3^- (0.7%) in meltwater of River Bhagirathi at Gangotri during the period of investigation of 2014-2016.

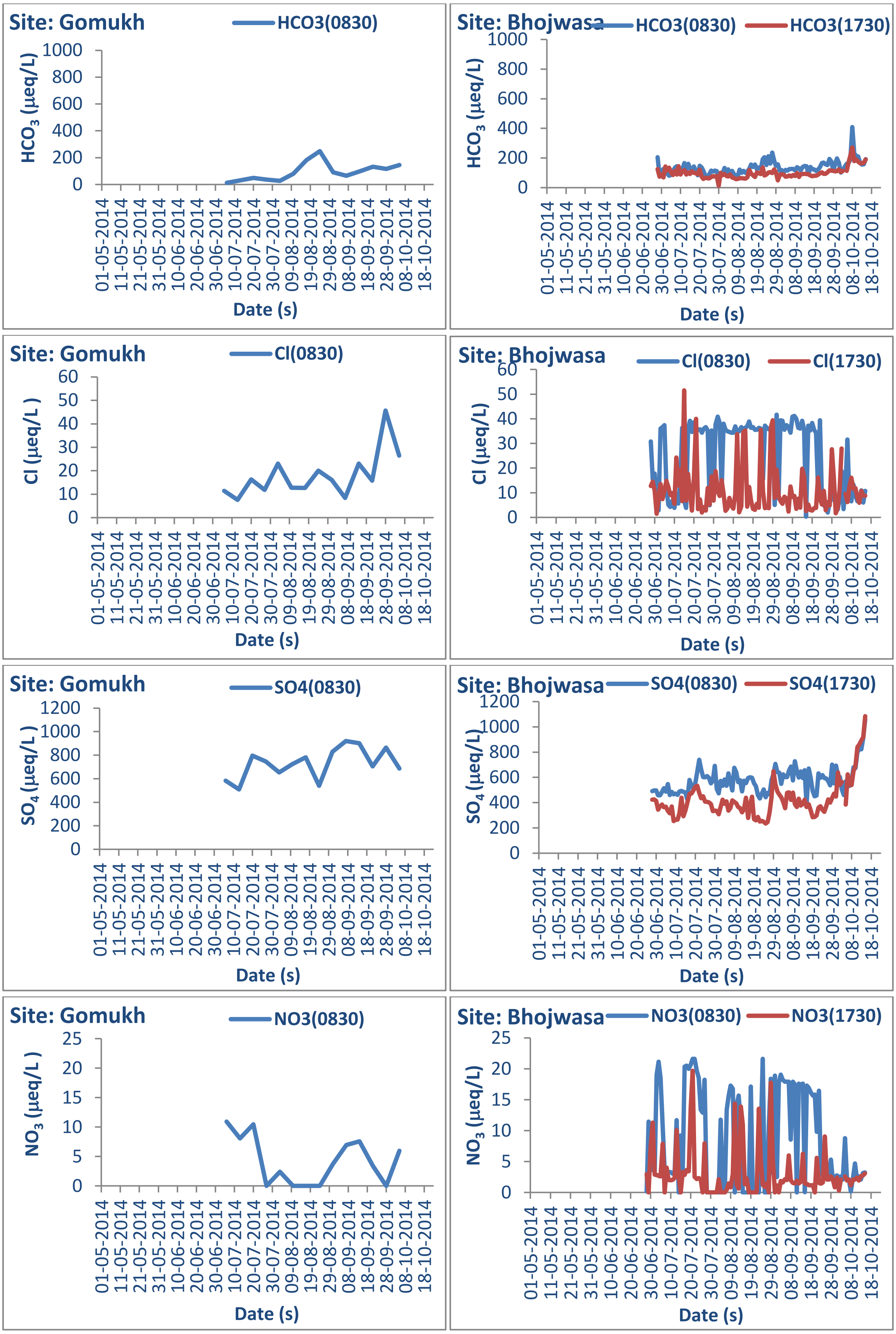


Fig. 4.9(a) Variation of major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Gomukh and Bhojwasa during the year 2014

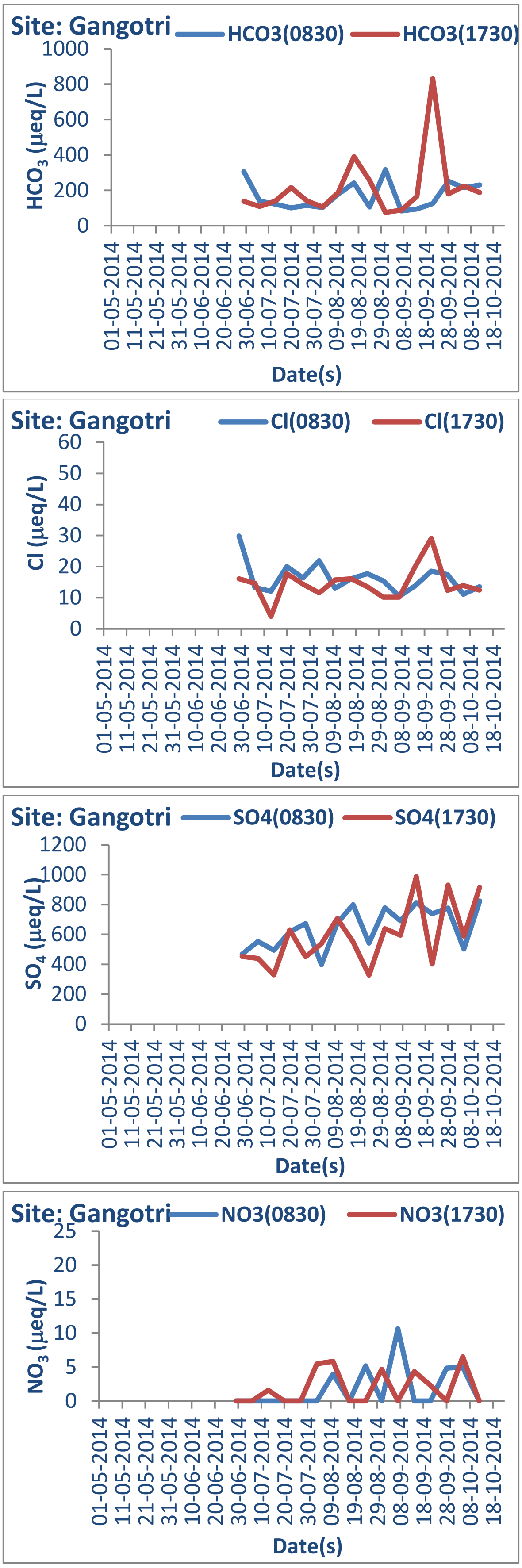


Fig. 4.9(b) Variation of major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Gangotri during the year 2014

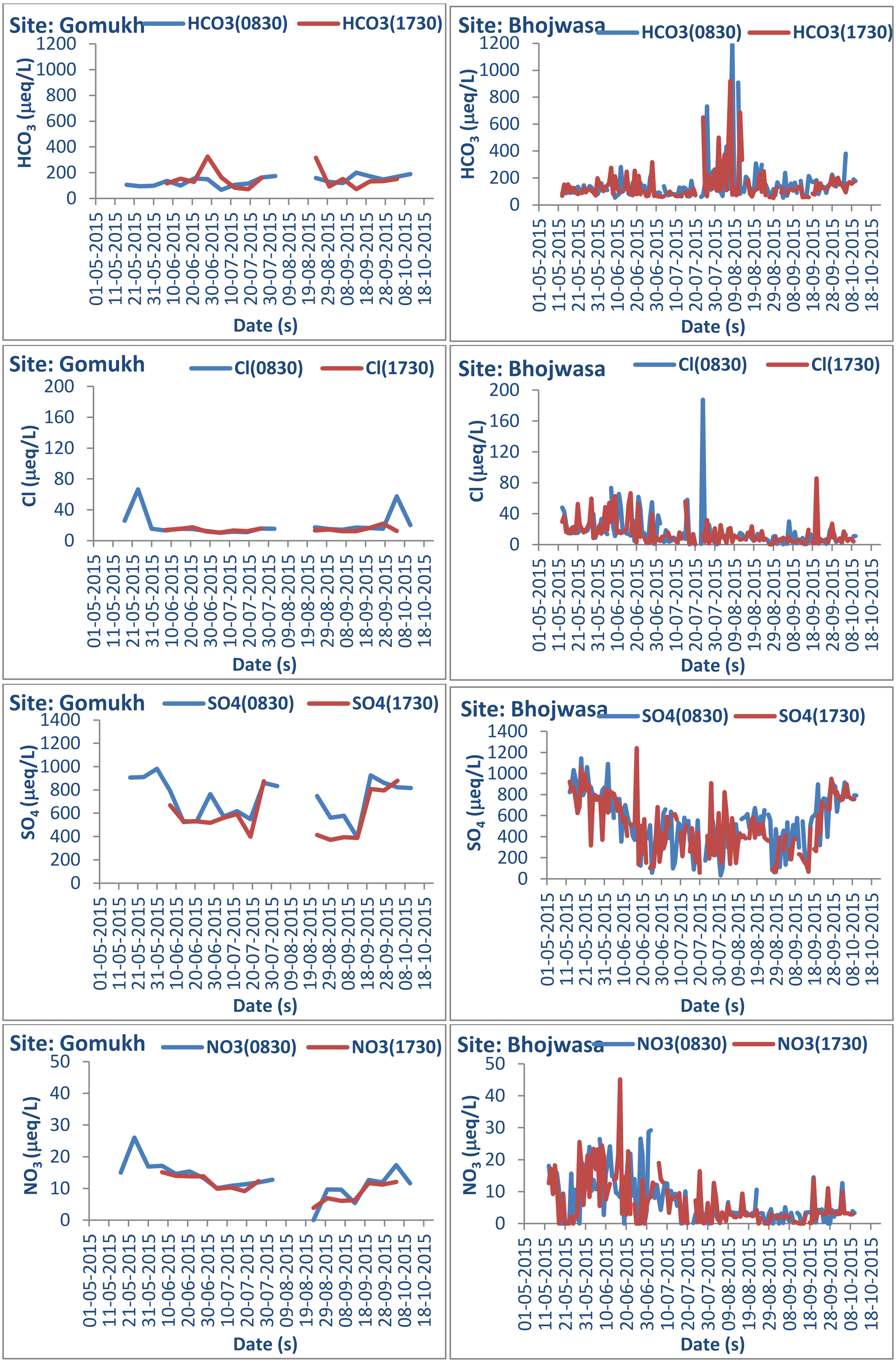


Fig. 4.10(a) Variation of major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Gomukh and Bhojwasa during the year 2015

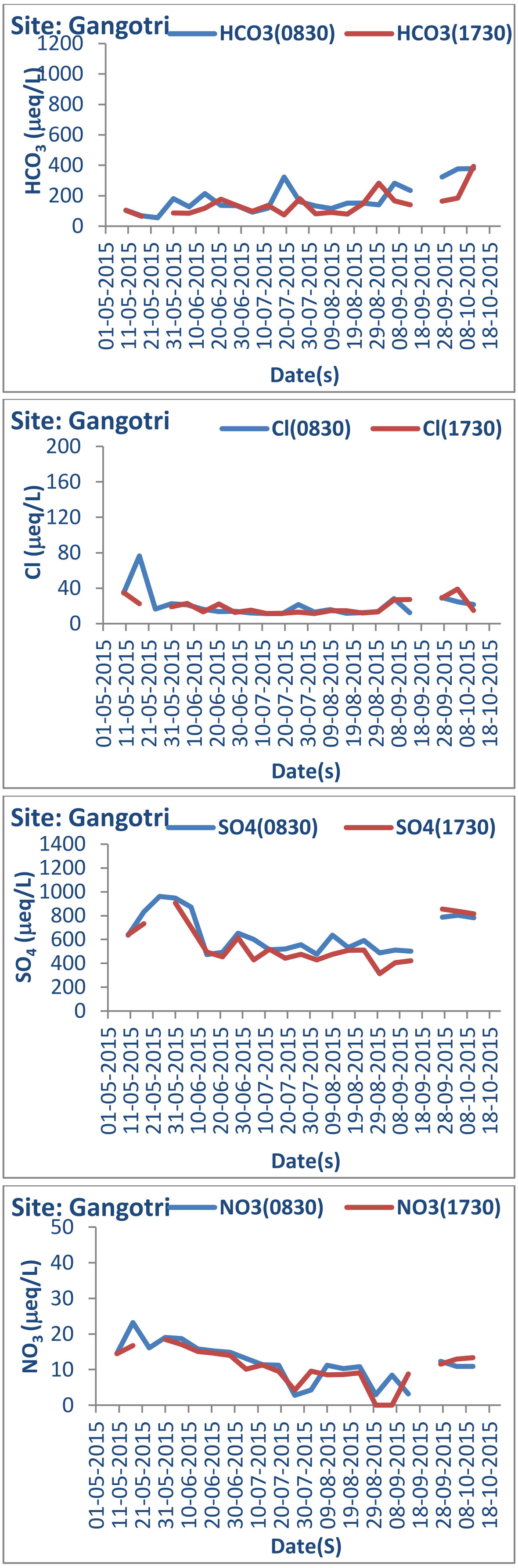


Fig. 4.10(b) Variation of major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Gangotri during the year 2015

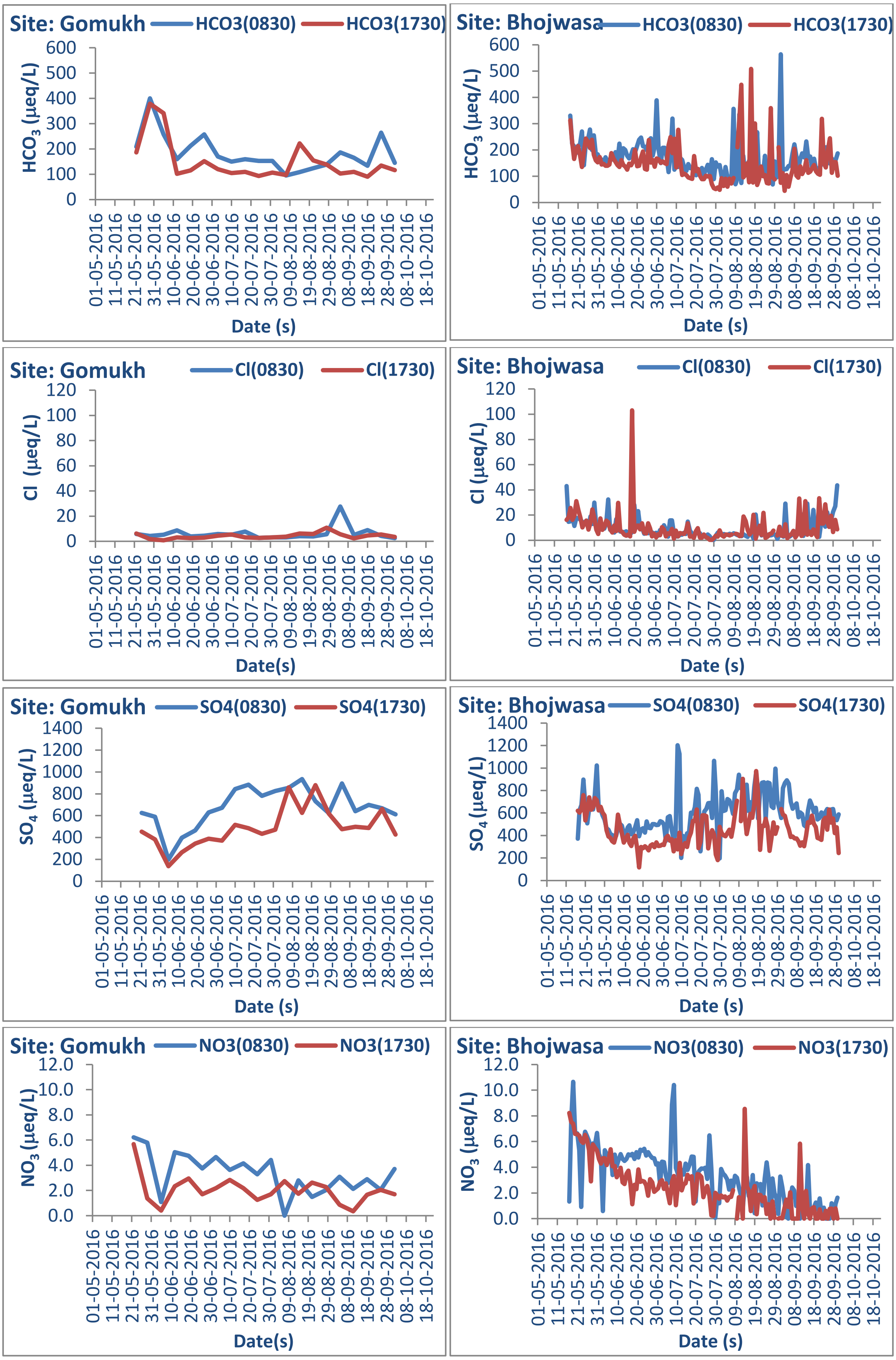


Fig. 4.11(a) Variation of major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Gomukh and Bhojwasa during the year 2016

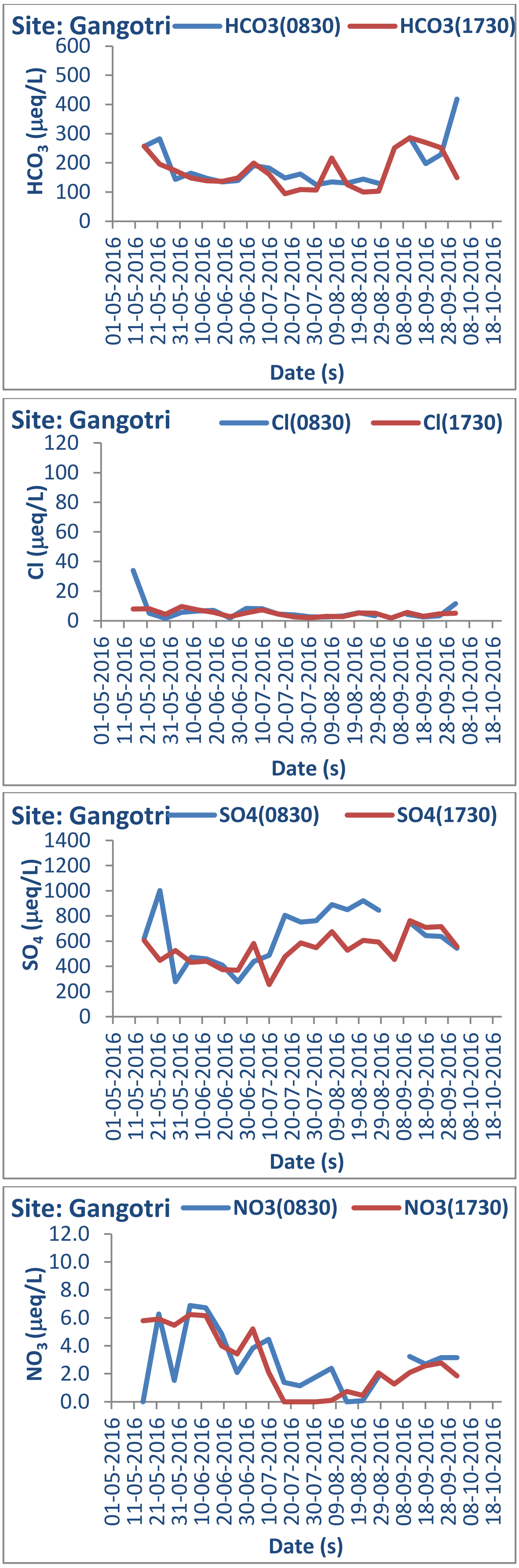


Fig. 4.11(b) Variation of major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Gangotri during the year 2016

4.1.8 Variation of metal concentrations at Gomukh, Bhojwasa and Gangotri

Metal concentrations of Fe, Zn, Cu, Cd and Pb were analysed in the meltwater of River Bhagirathi collected from Gomukh, Bhojwasa and Gangotri weekly during the ablation period of investigation of the year 2016. The results are given in Table 4.4 and variation of metal concentrations at 0830 hours and 1730 hours is shown in Fig. 4.12(a) & (b) respectively.

Table 4.4 Metal concentrations in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during ablation period of 2016

Metal	**Site: Gomukh**							
	Time: 0830 hours				**Time: 1730 hours**			
	Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Fe, µg/L	10	340	41.5	82.8	10	400	35	86.1
Zn, µg/L	2.6	226.8	41.7	52.9	1.6	87.1	33	29
Cu, µg/L	0.0	11.5	1.2	2.5	0.0	1.3	0.5	0.4
Cd, µg/L	0.1	12.8	1.0	2.8	0.0	0.9	0.4	0.2
Pb, µg/L	0.0	1.3	0.2	0.3	0.0	0.3	0.1	0.1
Metal	**Site: Bhojwasa**							
	Time: 0830 hours				**Time: 1730 hours**			
	Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Fe, µg/L	0.0	140	17.8	30.8	0.0	250	27.4	54.5
Zn, µg/L	2.3	85.3	33.3	30.9	2.0	96.9	37.7	31.8
Cu, µg/L	0.0	3.0	0.8	0.9	0.0	5.4	0.6	1.2
Cd, µg/L	0.0	0.9	0.3	0.3	0.0	2.8	0.4	0.6
Pb, µg/L	0.0	7.0	0.4	1.6	0.0	3.8	0.2	0.9
Metal	**Site: Gangotri**							
	Time: 0830 hours				**Time: 1730 hours**			
	Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
Fe, µg/L	0.0	60	14.5	14.7	0.0	90	16.5	19.5
Zn, µg/L	1.0	75.9	27	24.8	0.9	71.8	22.2	22.5
Cu, µg/L	0.0	2.4	0.5	0.6	0.0	43.7	2.7	9.7
Cd, µg/L	0.1	59.8	3.3	13.3	0.1	0.7	0.3	0.2
Pb, µg/L	0.0	0.9	0.3	0.3	0.0	0.9	0.3	0.3

During the period of investigation, the average concentration of Fe, Zn, Cu, Cd and Pb was observed to be 41.5 µg/L (10-340 µg/L), 41.7 µg/L (2.6-226.8 µg/L), 1.2 µg/L (0-11.5 µg/L), 1.0 µg/L (0.1-12.8 µg/L) and 0.2 µg/L (0-1.3 µg/L) at 0830 hours and 35 µg/L (10-400 µg/L), 33 µg/L (1.6-87.1 µg/L), 0.5 µg/L (0-1.3 µg/L),0.4 µg/L (0-0.9 µg/L) and 0.1 µg/L (0-0.3 µg/L) at 1730 hours respectively in meltwater of River Bhagirathi at Gomukh, 17.8 µg/L (0-140 µg/L), 33.3 µg/L (2.3-85.3 µg/L), 0.8 µg/L (0-3.0 µg/L), 0.3 µg/L (0-0.9 µg/L) and 0.4 µg/L (0-7.0 µg/L) at 0830 hours and 27.4 µg/L (0-250 µg/L), 37.7 µg/L (2-96.9 µg/L), 0.6 µg/L (0-5.4 µg/L), 0.4 µg/L (0-2.8 µg/L) and 0.2 µg/L (0-3.8 µg/L) at 1730 hours respectively in meltwater of River Bhagirathi at Bhojwasa and 14.5 µg/L (0-60 µg/L), 27 µg/L (1.0-75.9 µg/L), 0.5 µg/L (0-2.4 µg/L), 3.3 µg/L (0.1-59.8 µg/L) and 0.3 µg/L (0-0.9 µg/L) at 0830 hours and 16.5 µg/L (0-90 µg/L), 22.2 µg/L (0.9-71.8 µg/L), 2.7 µg/L (0-43.7 µg/L), 0.3 µg/L (0.1-0.7 µg/L) and 0.3 µg/L (0-0.9 µg/L) at 1730 hours respectively in meltwater of River Bhagirathi at Gangotri.

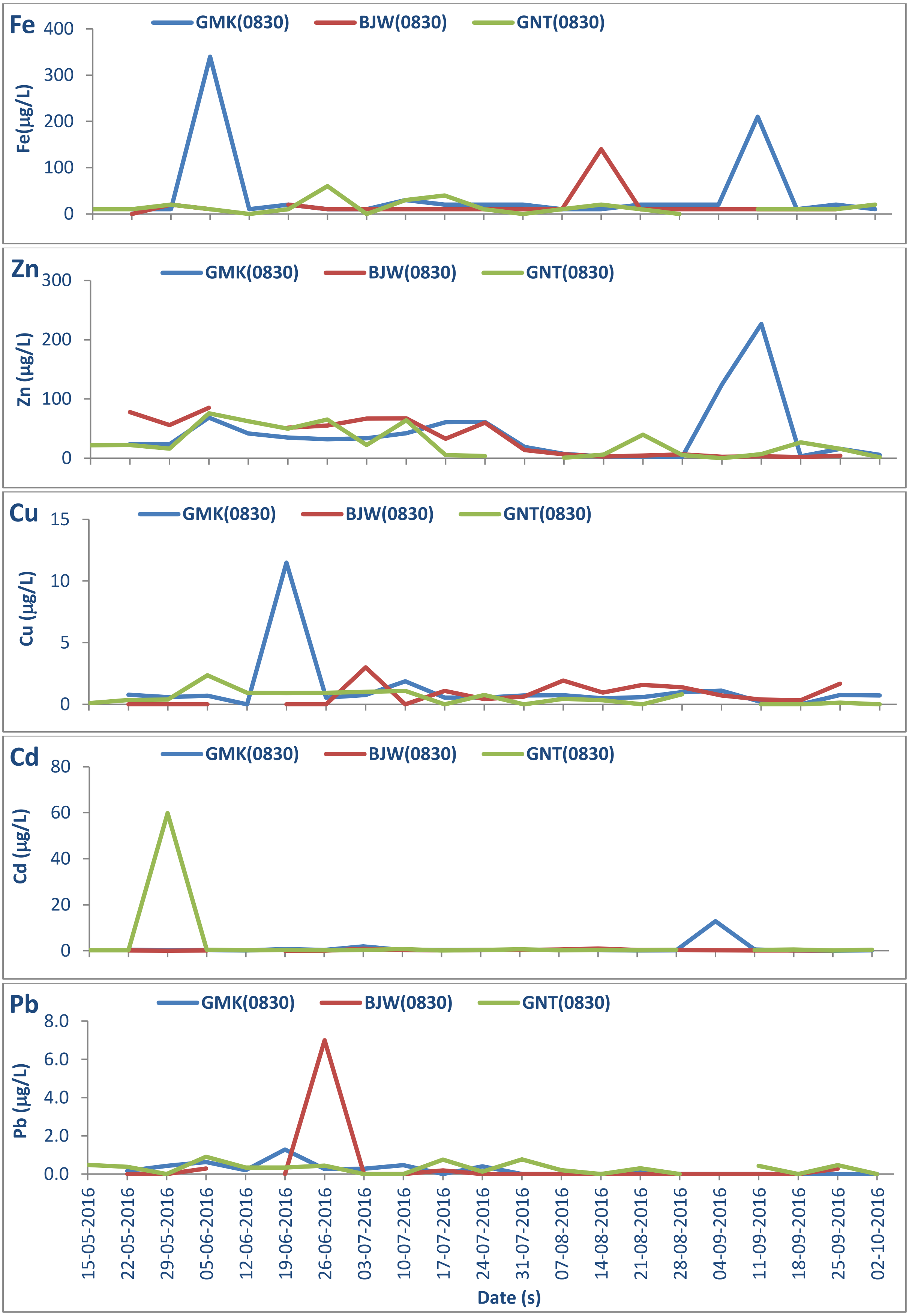


Fig. 4.12(a) Variation of metal (Fe, Zn, Cu, Cd and Pb) at 0830 hours in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

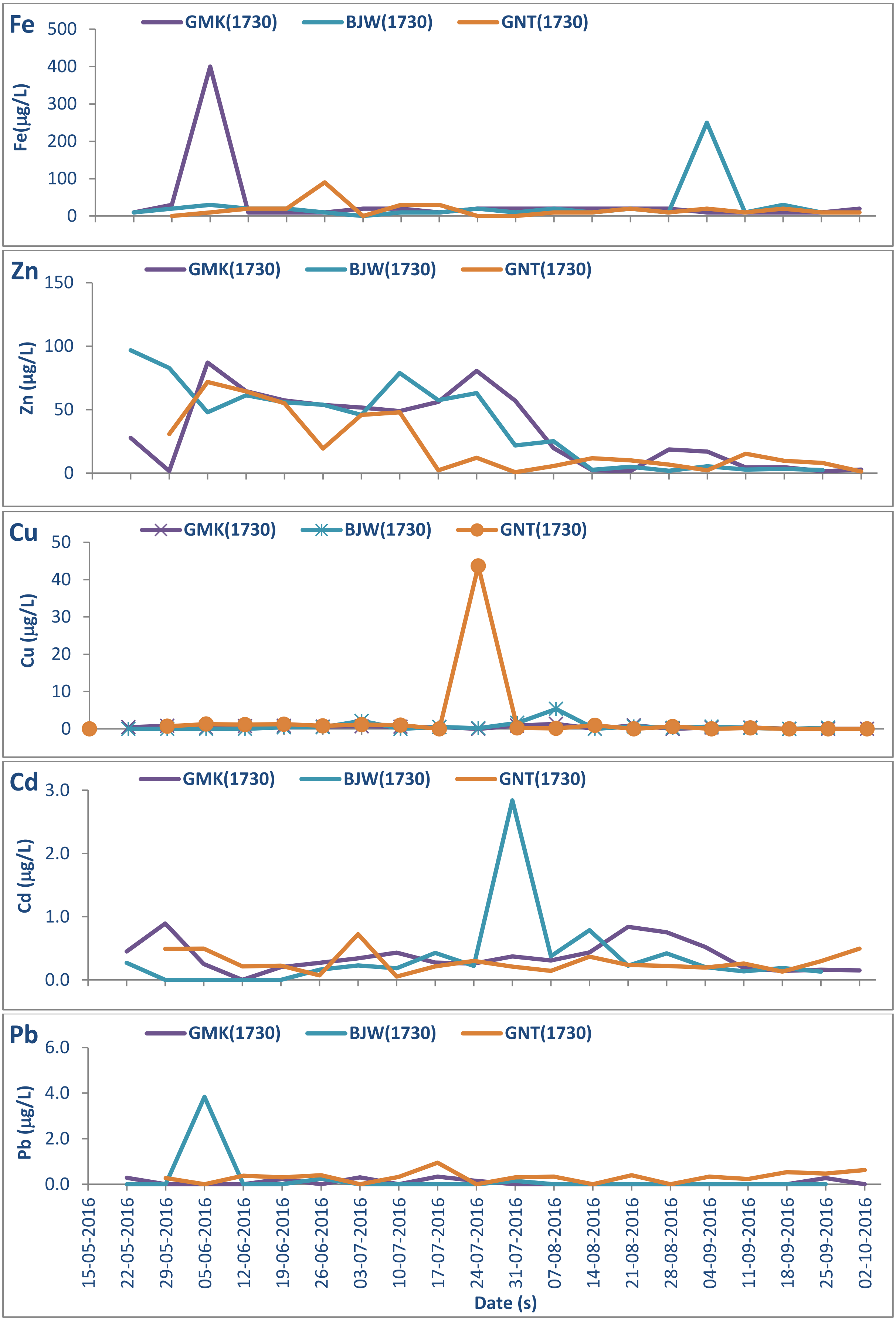


Fig. 4.12(b) Variation of metal (Fe, Zn, Cu, Cd and Pb) at 1730 hours in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

Almost all analyzed metal concentrations were found within the acceptable limits for drinking purpose prescribed by BIS (BIS, 2012). Average metal concentration of Fe, Zn and Cu was observed higher in meltwater of River Bhagirathi at Gomukh as compared to Bhojwasa and Gangotri because of evolution of Gangotri glacier from Gomukh.

4.2 Comparative Study of Hydro-chemistry of Meltwater at 3 sites of River Bhagirathi (Gomukh, Bhojwasa and Gangotri)

4.2.1 Total Suspended Sediment (TSS)

The main sources of production of sediment from the glacier fed channels are bedrock system (glacier bottom ice and bed rock), glacier system (sedimentation from different part of glacier such as snout, ablation zone, accumulation zone and lateral moraines) and channel system. High suspended sediment concentration in melt season was observed in the meltwater of River Bhagirathi at Bhojwasa followed by Gangotri and Gomukh (Fig. 4.13) which may be attributed to intensive melting (high discharge), increased stream area cross section and higher availability of glacier debris. The reduced suspended sediment concentration in the meltwater of River Bhagirathi at Gangotri during peak ablation/monsoon period suggests less sediment inflow vis a vis with discharge.

4.2.2 pH

pH plays an important role in low temperature chemical process in controlling the solute acquisition during suspended sediment-meltwater interaction. Lowest pH value in the meltwater of River Bhagirathi was observed at Gomukh followed by Bhojwasa and Gangotri (Fig. 4.14) which may be attributed to dominance of oxidation of sulphide at Gomukh followed by Bhojwasa and Gangotri, which contributes large number of protons (H^+) during oxidation in the meltwater of River Bhagirathi at Gomukh and thereby reducing the pH.

4.2.3 Electrical conductivity (EC)

Electrical conductivity (EC) represents the ionic enrichment characteristics of the meltwater. High value of EC in the meltwater of River Bhagirathi was observed at Gomukh followed by Bhojwasa and Gangotri (Fig. 4.15) which may be attributed to interaction of meltwater with freshly grinded sediment at Gomukh resulting high solute acquisition of meltwater of River Bhagirathi at Gomukh.

4.2.4 HCO_3 and SO_4

Two major anions, HCO_3 and SO_4, in glacial meltwaters are mainly derived from the dissolution of atmospheric carbon dioxide and carbonates and the oxidation of sulphides (Souchez and Lemmens, 1987). Higher value of HCO_3 concentration was observed in the meltwater of River Bhagirathi at Bhojwasa followed by Gangotri and Gomukh (Fig. 4.16), which may be attributed to the enhanced dominance of carbonate dissolution at Bhojwasa as compared to Gangotri and Gomukh while higher value of SO_4 concentration was observed in the meltwater of River Bhagirathi at Gomukh followed by Gangotri and Bhojwasa (Fig. 4.17), which may be attributed to the dominance of oxidation of sulphide at Gomukh followed by Gangotri and Bhojwasa.

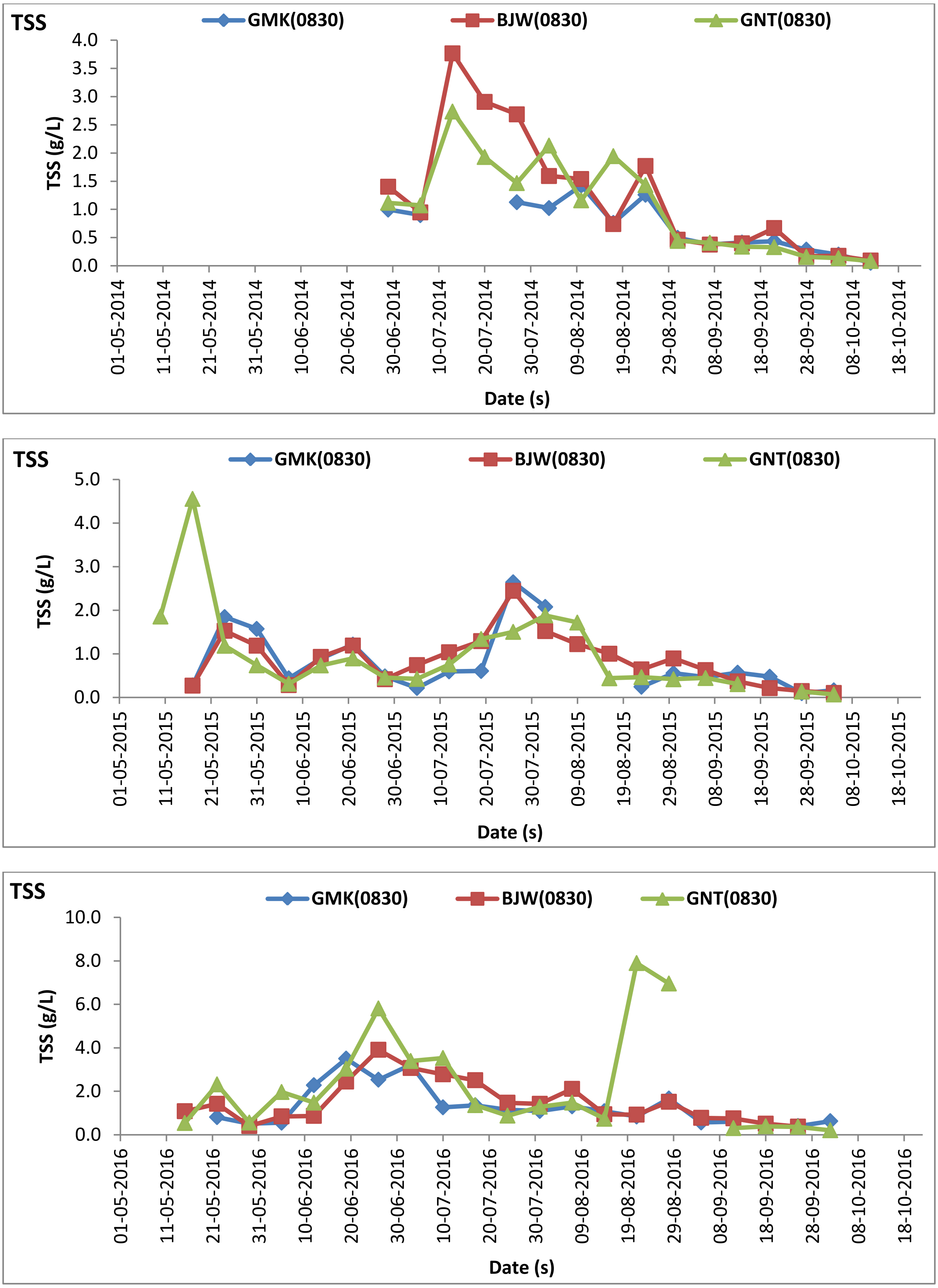


Fig. 4.13 Comparative study of Total Suspended Sediment (TSS) in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016

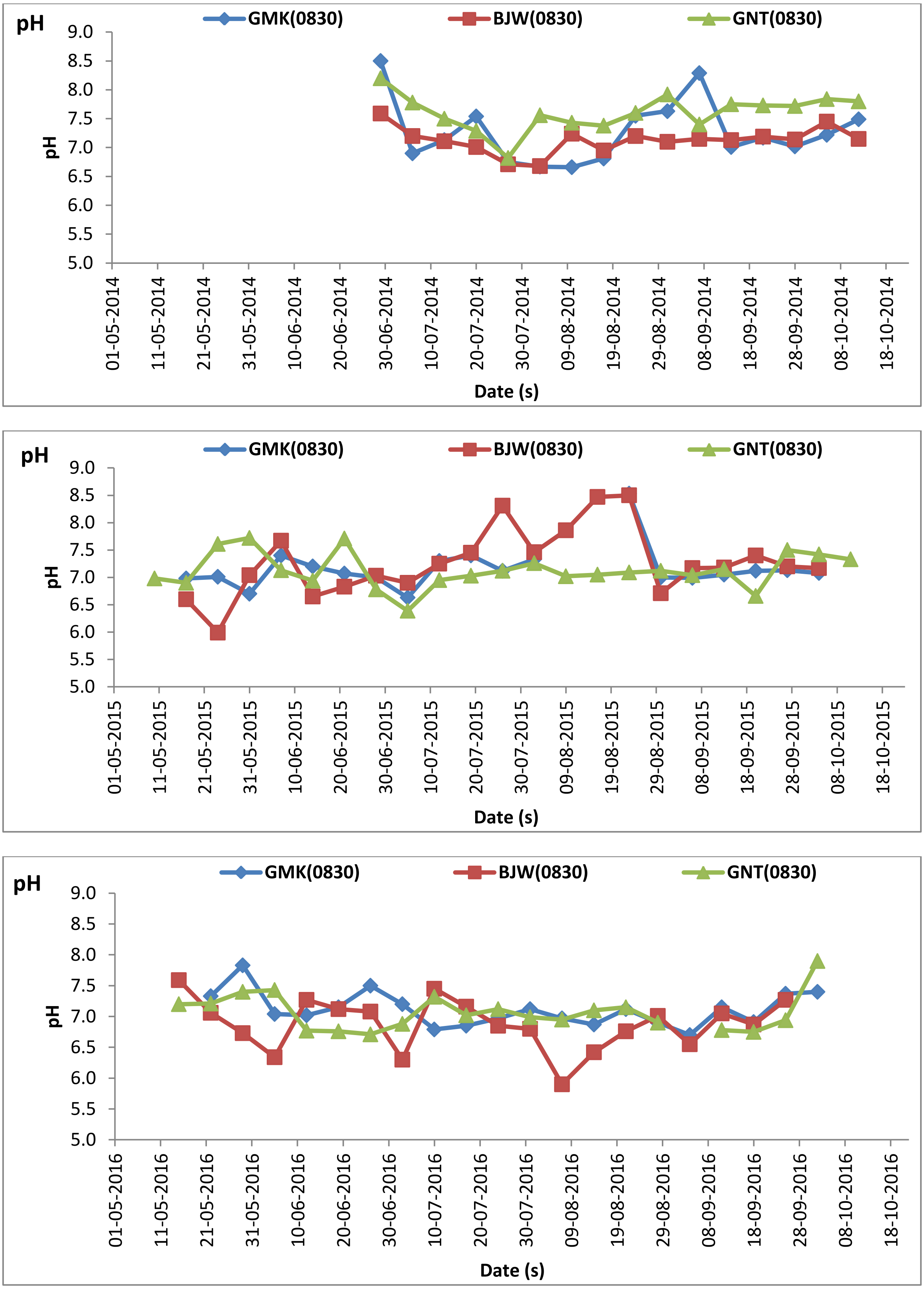


Fig. 4.14 Comparative study of pH in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016

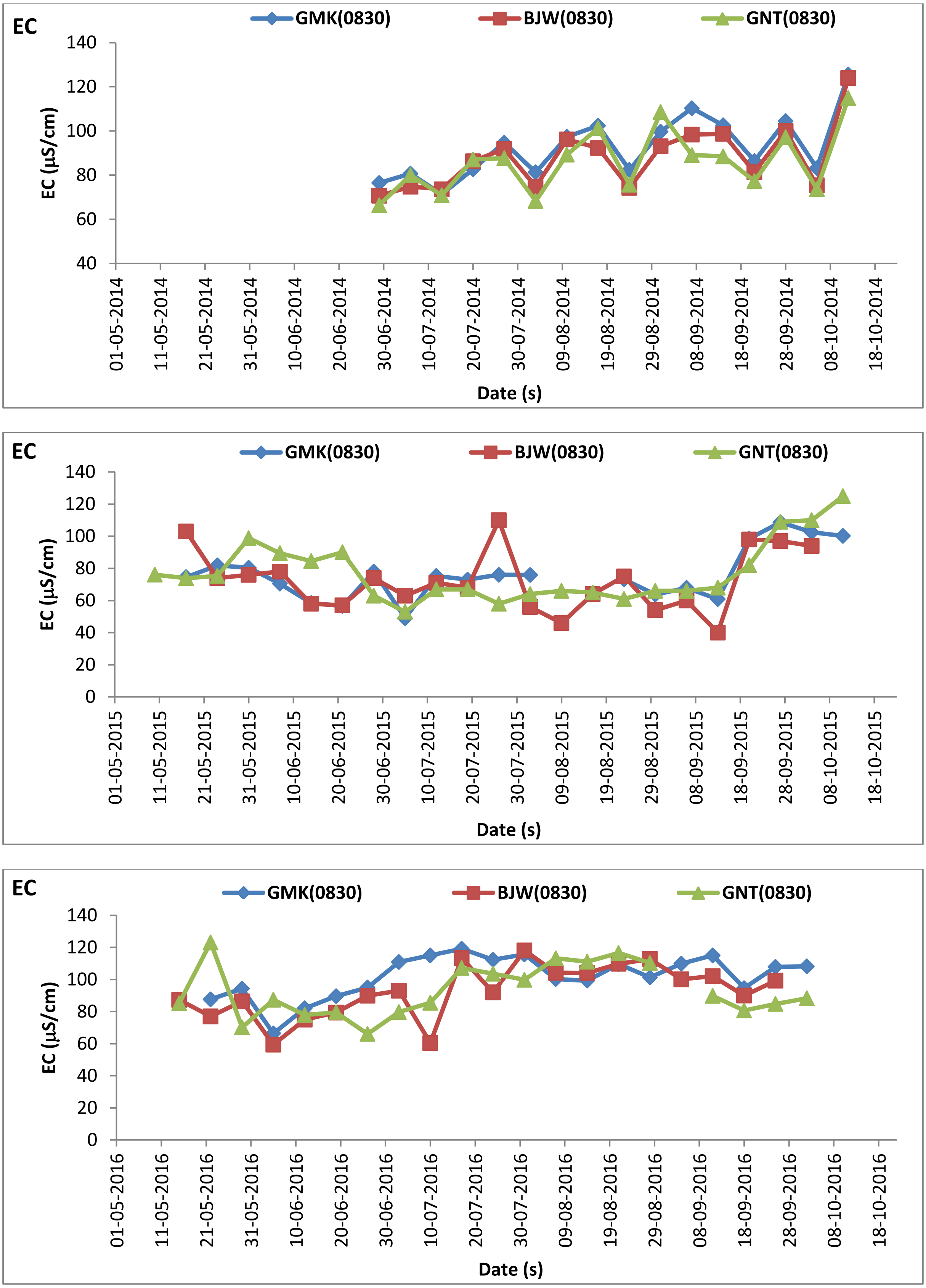
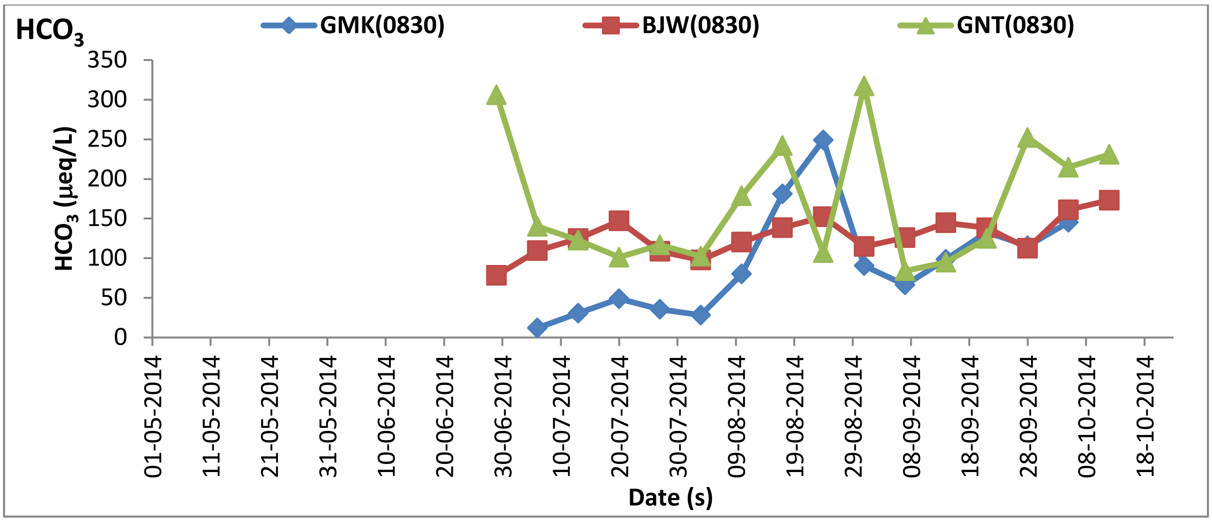
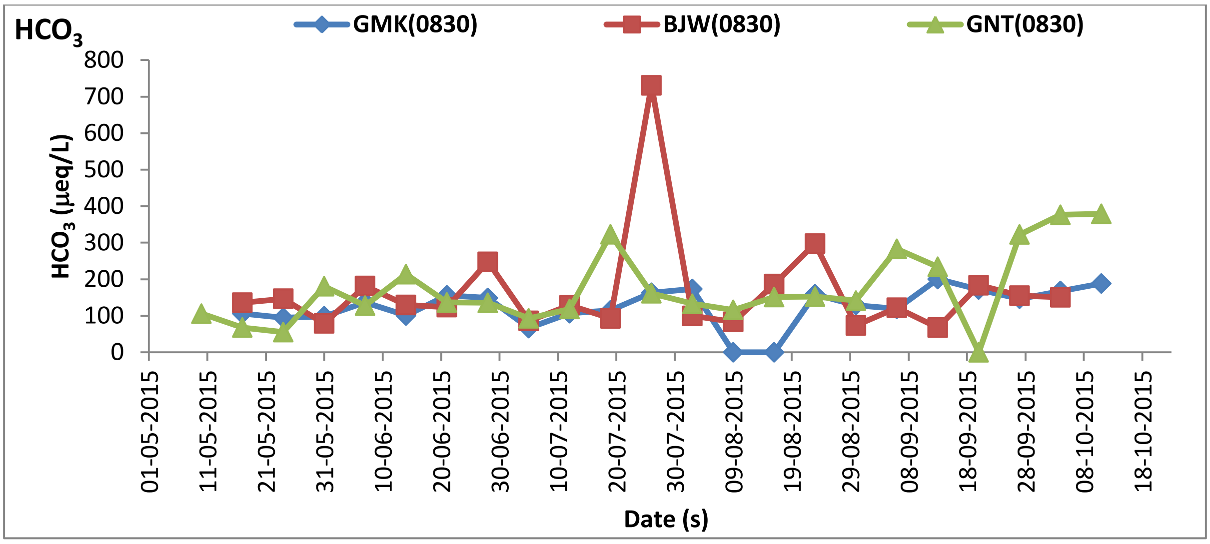


Fig. 4.15 Comparative study of Electrical Conductivity (EC) in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016





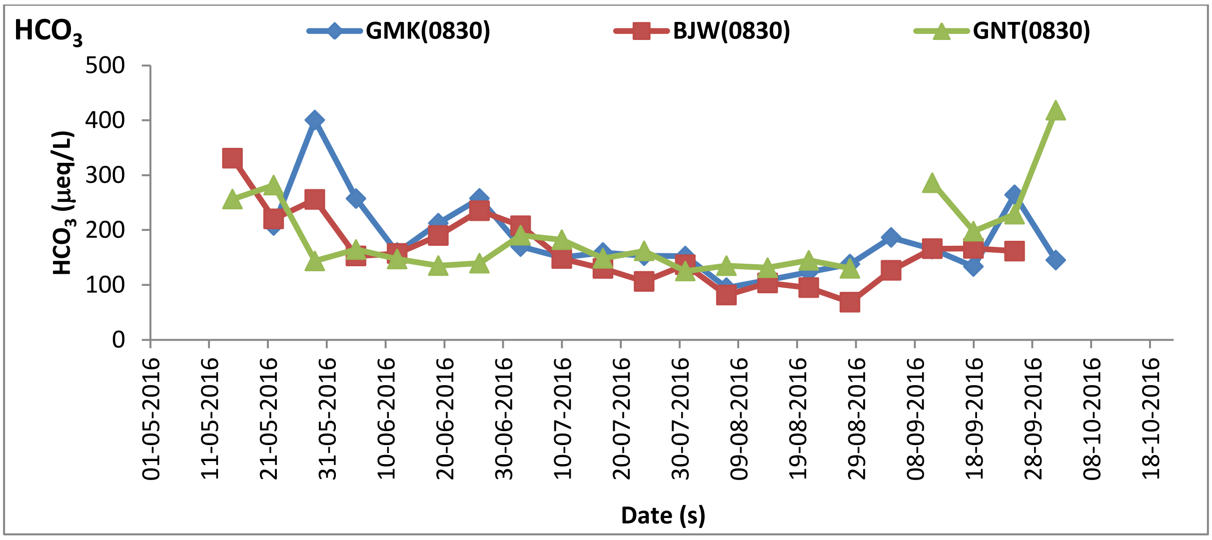
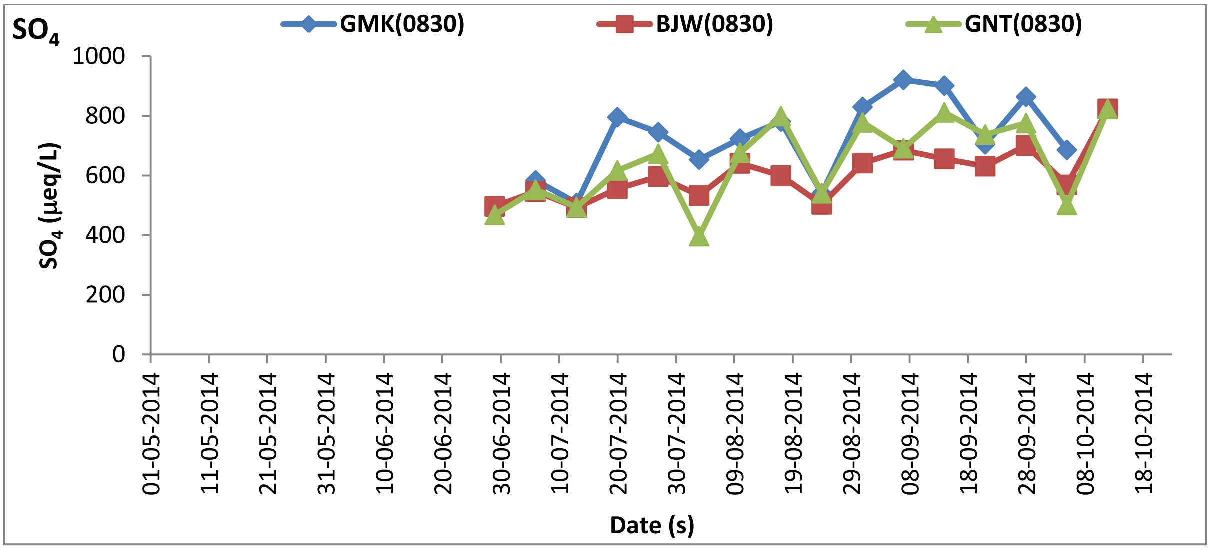
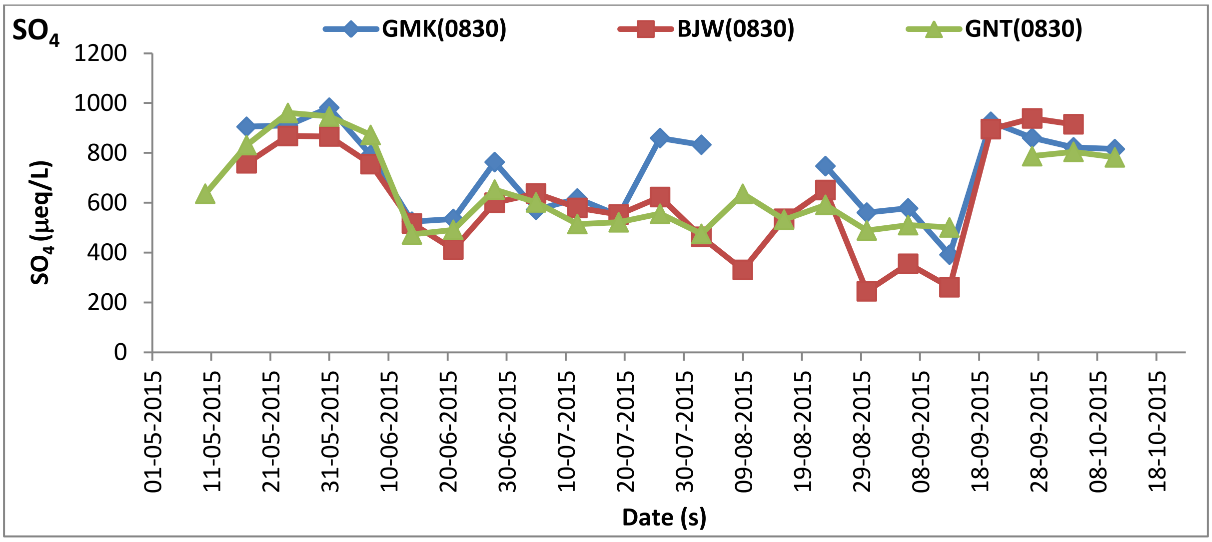


Fig. 4.16 Comparative study of HCO_3 in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016





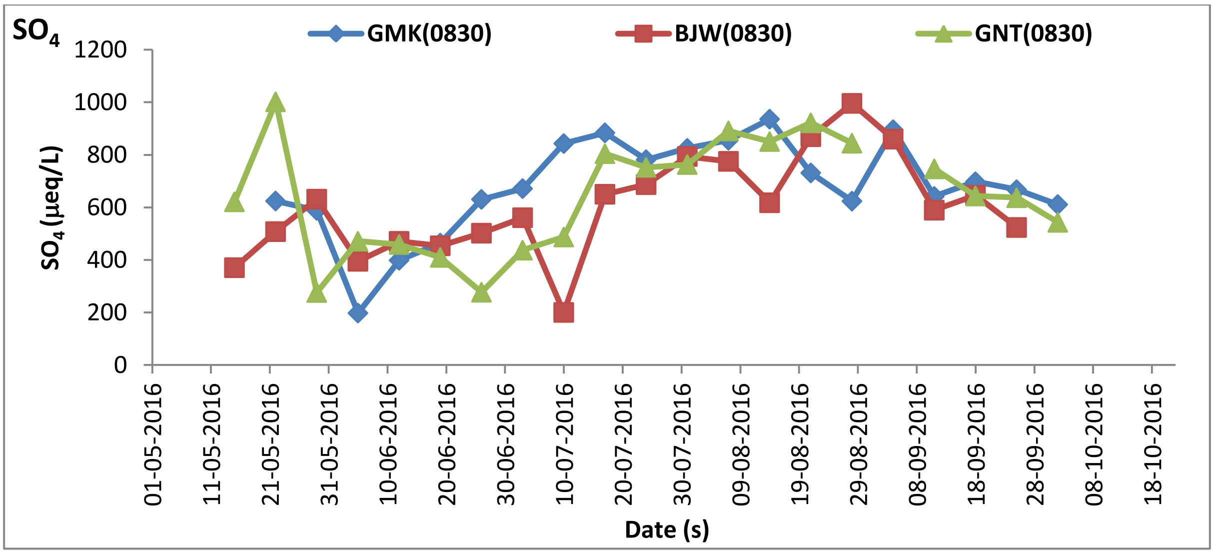


Fig. 4.17 Comparative study of SO_4 in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016

Chapter 5

VARIABILITY OF THE MAJOR-ION CHEMISTRY OF GLACIAL MELTWATER

5.1 Inter-annual Variations of Major Ion Chemistry and Solute Fluxes of Meltwater of River Bhagirathi

Inter-annual variations of solute and sediment fluxes in a glacial system are closely linked to the discharge variations. On a year to year basis, these variations could be linked to the variations in the atmospheric temperature or winter and summer precipitation. Snow cover variations play a crucial role in glacial systems as it is widely accepted that the development of subglacial drainage system closely follows that of snow cover in upper elevations (Nienow et al., 1998), which in turn is responsible for chemical and sediment flux in these rivers. Snow melt water routed through the glacier surface and from surrounding non- glacier area play a significant role in diluting the base flow and the contributions through subglacial distributed system leading to the diurnal inverse relationship between discharge and chemical constituents. Similar dilution occur seasonally also when higher melt occur during July and August months. Sediment concentration in glacial meltwaters is closely linked to the discharge variation and further influences the chemical characteristics of melt water. Here we summarise the inter-annual, seasonal and diurnal variations in discharge, suspended sediment and other chemical parameters in the meltwater of River Bhagirathi at Bhojwasa during three years of observations i.e. 2014, 2015 and 2016 in the following sections.

5.1.1 Inter-annual variation of discharge

In the present investigation, daily discharge of River Bhagirathi was measured at Bhojwasa, 4 km downstream from the snout at Gomukh. Daily discharge at Bhojwasa varies from 3.9 to 199.2, 14.5 to 183.3 and 19.9 to 131.3 m^3/s during the ablation period of the year 2014, 2015 and 2016 respectively. Fig.5.1 shows the seasonal discharge variations during the three observation years. Discharge hydrograph of the year 2014 shows sharp rising and falling limb and persistent high flow period covering entire month of July. Year 2015 shows a prolonged rising limb with delayed peak flows occurring in the months of August (7th August). This suggests that the snow cover in the catchment persisted for longer duration in 2015. Peak discharge was subdued with discharge peaking on 15th July in the year 2016. The delay in peak discharge in the year 2015 may attributed to the delayed snowmelt from higher elevations of the Gangotri catchment as revealed from the assessment of snow cover variations during these three years (Fig. 5.1).

5.1.2 Inter-annual variation of suspended sediment

Suspended sediment concentration (TSS) in glacial meltwaters is directly linked with the discharge variations. TSS concentration is also linked with the development and progression of subglacial channel network (Thayyen et al., 1999) as subglacial zone is the major source area of glacial sediments. Generally, in glacial systems, TSS concentration peaks just before the discharge peak and seasonal hysteresis between discharge and TSS concentration is often reported. The sediments, which get deposited throughout the winter period gets evacuated during the early stages of subglacial channel development. In 2014 and 2016, this early evacuation of sediment is clearly visible in the data (Fig. 5.1). During these two years of 2014 and 2016, TSS concentration varies from 0.054 to 7.988 g/L, and 0.413 to 6.625 g/L. However, the year 2015 did not experience any significant sediment evacuation neither during the initial stage nor later. TSS concentration during the year 2015 ablation months varied between 0.031 to 3.469 g/L. This is remarkably low values as compared to 2014 and 2016. We think that the under development of subglacial drainage system could be the reason for such a low sediment flux during 2015. Study of snow cover persistence over the glacier vindicated this assessment as the year 2015 experienced prolonged snow cover at higher elevations of the basin. During the observation years TSS flux varies from 78.6 to 112,603 tons/day, 172 to 24,821 tons/day 915 to 56,120 tons/day during the ablation period of the year 2014, 2015 and 2016 respectively. Comparatively low TSS concentration and also TSS flux was observed in the year 2015, which may be attributed to low discharge during the year as TSS follow the trend of discharge (Fig. 5.1& 5.2).

5.1.3 Inter-annual variation of major ion chemistry

The potential of solute acquisition by melt waters in the subglacial environment is several times higher than in other glacial environments, due to (i) the slow transit time of water within the subglacial system (Tranter and Raiswell, 1991; Tranter et al., 1993; Brown et al., 1994a; 1996b; Collins, 1995), (ii) the availability of large amounts of freshly comminuted rock flour, (iii) the availability of reactive minerals, such as carbonates and sulphide in the rock flour, and (iv) the relatively rapid oxidation of sulphide in the fresh rock flour, providing additional protons for chemical weathering (Tranter et al., 1993; Brown et al., 1994b, 1996b).

pH varies from 6.29 to 7.89, 6.20 to 8.62 and 5.54 to 7.68 during the ablation period of the year 2014, 2015 and 2016 respectively. Comparatively high pH (>7.0) was observed in the year 2015, especially during the seasonal high flow period which may be attributed to the higher surface melt contribution from prolonged snow cover in the basin and also associated with under development of subglacial zone during the year, limiting the pyrite oxidation which results in less production of proton (H^+) ions and thereby increasing the pH (Fig. 5.1). Electrical conductivity (EC) of meltwater varies from 51.6 to 143.2 µS/cm, 28.5 to 122.0 µS/cm and 50.0 to 119.4 µS/cm during the ablation period of the year 2014, 2015 and 2016 respectively. Comparatively large fluctuations in EC values were observed in the year 2015, which could be attributed to the higher snow melt during the peak melt period as described earlier (Fig. 5.1).

HCO_3 concentration varies from 31 to 339 µeq/L, 29 to 726 µeq/L and 35 to 325 µeq/L during the ablation period of the year 2014, 2015 and 2016 respectively while HCO_3 flux varies from 5.0 to 121 tons/day, 5.8 to 701 tons/day and 17.1 to 152 tons/day during the ablation period of the year 2014, 2015 and 2016 respectively (Fig. 5.1 & 5.2). SO_4 concentration varies from 230 to 1072 µeq/L, 23 to 1095 µeq/L and 218 to 969 µeq/L during the ablation period of the year 2014, 2015 and 2016 respectively while SO_4 flux varies from 12.7 to 429 tons/day, 11.6 to 393 tons/day and 42.7 to 333 tons/day during the ablation period of the year 2014, 2015 and 2016 respectively (Fig. 5.1 & 5.2). HCO_3 concentration follows the trend of discharge during peak discharge while SO_4 concentration does not follow the discharge trend during the year 2015 implying that no contribution of subglacial system which involve pyrite oxidation, domination of contribution from supraglacial system (Fig. 5.1). But in case of fluxes, both HCO_3 and SO_4 follow the same trend as that of discharge (Fig. 5.2).

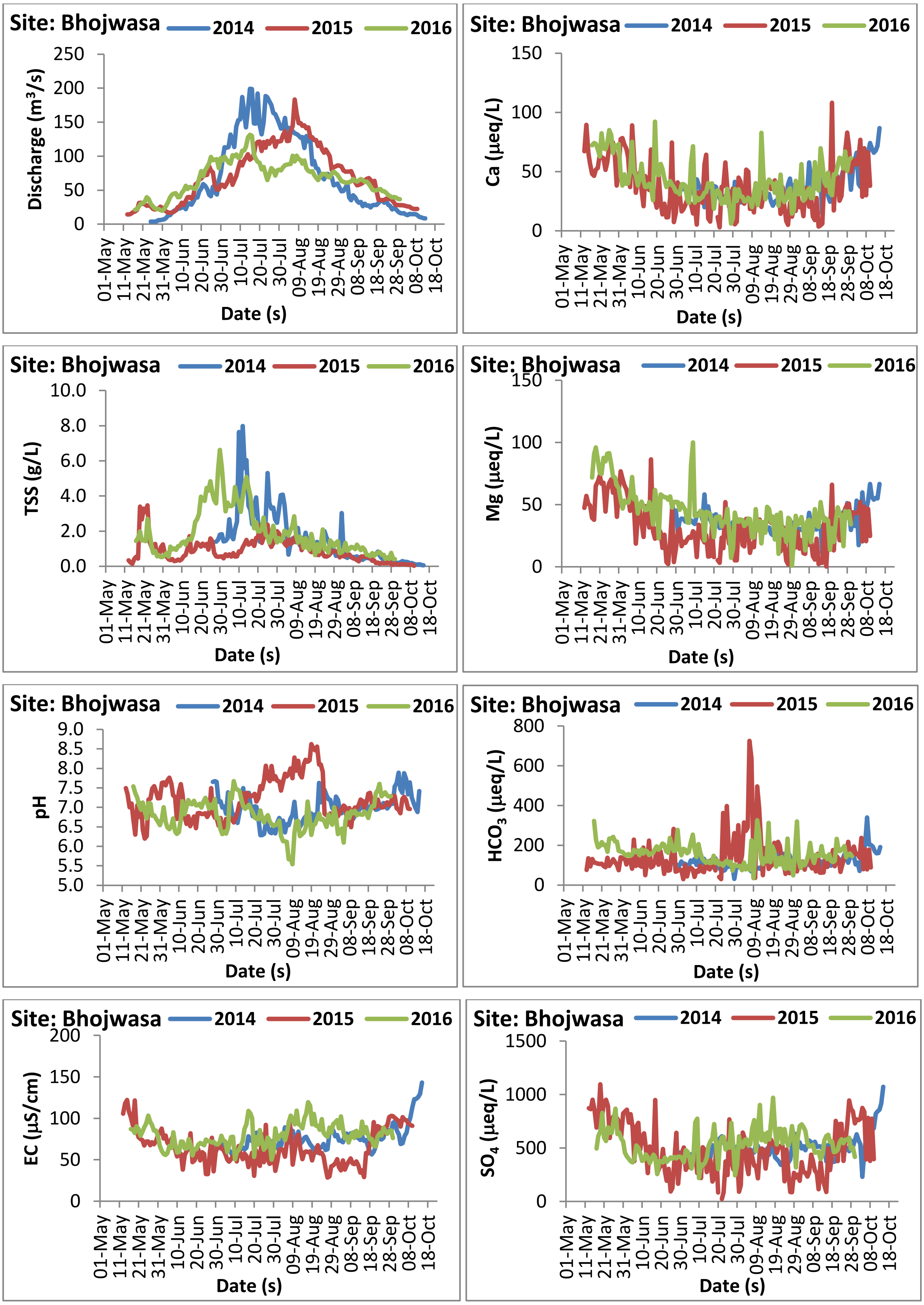


Fig. 5.1 Variations of daily mean discharge, TSS, pH, EC, Ca, Mg, HCO$_3$ and SO$_4$ in the meltwater of River Bhagirathi at Bhojwasa during the year 2014, 2015 and 2016

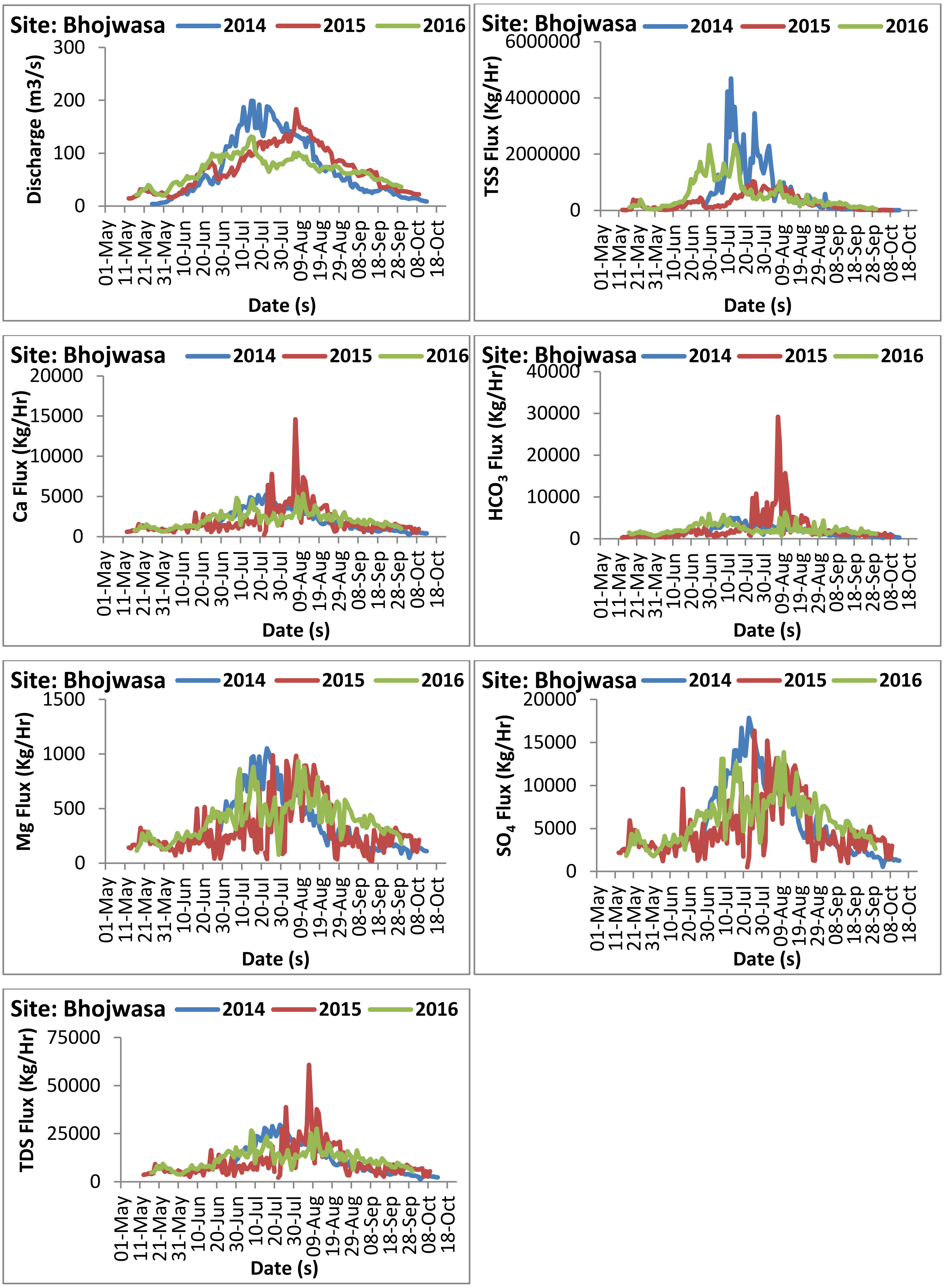


Fig. 5.2 Variations of daily mean discharge, Fluxes of TSS, Ca, Mg, HCO_3, SO_4 and TDS in meltwater at Bhojwasa during the period 2014-2016

5.2 Seasonal Variations of Major Ion Chemistry and Solute Fluxes of Meltwater of River Bhagirathi

The stream runoff in the Uttarakhand Himalaya have significant seasonal variations forced by melting of the winter snow preceded by the summer monsoon rains and intervening dry periods forcing lean flows.The runoff from the glacierized valleys of the Ganga river basin is first fed by snowmelt as the transient snowline recedes, which results in discharge from snow melt peaks by the end of June. Further, the southwest monsoon between July and August over the Garhwal Himalaya facilitate the annual discharge peaks in these months. Of particular importance is the monsoon which bursts over the eastern part of the Himalaya in the first week of June and contributes a large proportion of the annual runoff in a few months (Sharma, 1993). The monsoon is deflected by mountains and moves westward, extending throughout the region by the end of July, where it persists till mid-September (Mani, 1981). The percentage of the monsoon runoff component varies across the elevations in the basin as higher elevations receive relatively lower precipitation than lower elevations. The form of precipitation is also critical for glacier melt component with rainfall over glacier enhances the melting and snow decelerates. As glacier also melt fast during the same time of monsoon leading to a complex system at work.

Daily average meltwater discharge of River Bhagirathi at Bhojwasa for rising limb of hydrograph (May-June), peak flow (July-August) and falling limb of hydrograph (September-mid October) during the year 2014, 2015 and 2016 was observed to be 43.4, 107.7 and 42.2 m^3/s respectively. The pH of was slightly acidic to alkaline during rising limb of hydrograph (6.26–7.65), peak flow (6.05–7.97) and falling limb of hydrograph (6.43–7.62). The EC varied from 43.8 to 113 µS/cm with an average value of 72.3 ± 16.5 µS/cm during rising limb of hydrograph, from 43.4 to 102 µS/cm with an average value of 69.7 ± 12.8 µS/cm during peak flow and from 50.5 to 116 µS/cm with an average value of 79.1 ± 17.5 µS/cm during falling limb of hydrograph. TDS of meltwater samples varied from 22.1 to 80.0 mg/L with an average value of 51.5 ± 14.7 mg/L during rising limb of hydrograph, from 20.1 to 77.5 mg/L with an average value of 42.2 ± 11.6 mg/L during peak flow and from 24.1 to 79.5 mg/L with an average value of 47.6 ± 13.4 mg/L during falling limb of hydrograph during year 2014, 2015 and 2016. Same trend was observed by Singh et al. (2014).

The anions for all sampling seasons in decreasing order were observed to be SO_4^{-2}> $HCO3^-$> Cl^-> NO_3^-. Sulphate was the dominant anion accounting for 75.4% during rising limb of hydrograph, 75.2% during peak flow and 77.9% during falling limb of hydrograph of total anions (TZ^-). Bicarbonate was the next dominant anion after sulphate accounting for 21% during rising limb of hydrograph, 22% during peak flow and 20% during falling limb of hydrograph of total anions. First possibility of acquiring SO_4^{-2} content in the Gangotri glacier meltwater is dissolution of sulphate minerals (gypsum and anhydrite), whereas second possibility is the sulphide oxidation (Srivastava et al., 2004). Gangotri glacier is a tourist spot. Due to trekking and its religious importance, many tourists and pilgrims arrived during the study period. Relatively very low concentration of NO_3^- was reported from Gangotri glacier meltwater, indicating palatability of meltwater. The possible source of NO_3^- may be anthropogenic activities taking place in the study area. Whereas other possible source of NO_3^- may be the influence of atmospheric deposition associated with the acidic NO_3^- aerosol (Tranter et al., 1993).

The cations for all sampling seasons in decreasing order were observed to be Ca^{2+}>Mg^{2+}> K^+> Na^+. Calcium was the dominant cation accounting for 64.9% during rising limb of hydrograph, 69.1% during peak flow and 59.8% during falling limb of hydrograph of total cations (TZ^+). Magnesium was the next dominant cation after calcium accounting for 19.8% during both rising limb of hydrograph and peak flow and 22% during falling limb of hydrograph of total cations.

The seasonal variation of the dissolved ions in the Gangotri glacier meltwater is given in Fig. 5.3, which indicates that generally dissolved ions concentration was low during peak flow period and high during rising and falling limb period of hydrograph. Such dissolved ion concentration variations are indicative of a climatic control on the intensity of different processes operating in the study area (Singh and Hasnain, 1998). Due to availability of high incoming solar radiation and larger extent of the exposed glacierice during peak flow season (July–August) intense melting takes place in the study area (Singh et al., 2006). This is responsible for increasing discharge and dilution of the dissolved ions, resulting in depressed dissolved ion concentration. Whereas during rising and falling limb of hydrograph season, due to reduced incoming solar radiation, the melting is also low, which decreases discharge in falling limb of hydrograph period (Singh et al., 2006; Singh and Hasnain, 1998), resulting in enhanced dissolved ion concentration in meltwater draining from Gangotri glacier.

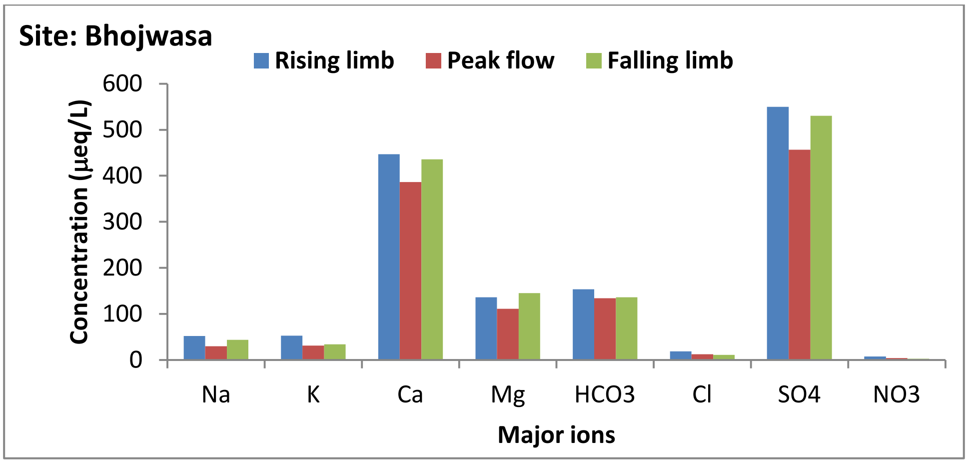


Fig. 5.3 Seasonal variations of dissolved ions at Bhojwasa

The relative importance of two major proton producing reactions – sulphide oxidation and carbonation can be calculated on the basis of the ($HCO_3/HCO_3 + SO_4$) ratio, called the C-ratio (Brown et al., 1996b). A ratio of 1 would signify weathering by carbonation reactions (Reynolds and Johnson, 1972); and dissolution and dissociation of the atmospheric CO_2 are exclusively deriving protons. Conversely if the C-ratio is 0.5, it signifies a coupled reaction involving carbonate dissolution and sulphide oxidation and protons derived from the pyrite oxidation. The average C-ratio for meltwater of River Bhagirathi at Bhojwasa is 0.24 ± 0.08 during rising limb period of hydrograph, 0.22 ± 0.09 during peak flow and 0.20 ± 0.05 during falling limb period of hydrograph, which indicates that the major proton producing reaction is oxidation of sulphide (Fig. 5.4). The coupled reaction involving carbonate and CO_2 dissolution and oxidation of sulphide minerals derived protons largely control the chemistry of meltwater draining from Gangotri glacier (Ahmad and Hasnain, 2001).

Solute fluxes in glacial meltwaters usually increase with discharge in an aquatic system. The largest solute fluxes are transported by the most dilute meltwater as solute concentration is usually inversely related to discharge (Sharp et al., 1995a). Daily variation of discharge, fluxes of TSS, Ca, Mg, HCO_3, SO_4 and TDS in meltwater of River Bhagirathi at Bhojwasa during the period 2014-2016 is shown in Fig. 5.2. Fluxes of all major dominating cations (Ca^{+2} and Mg^{+2}) and major dominating anions (HCO_3^- and SO_4^{-2}) follow the same trend as that of discharge. Daily average meltwater discharge for rising limb of annual hydrograph (May and June), crest (July and August) and falling limb of annual hydrograph (September to Mid-October) from 2014 to 2016 was observed to be 43.4, 107.7 and 42.2 m^3/s respectively.

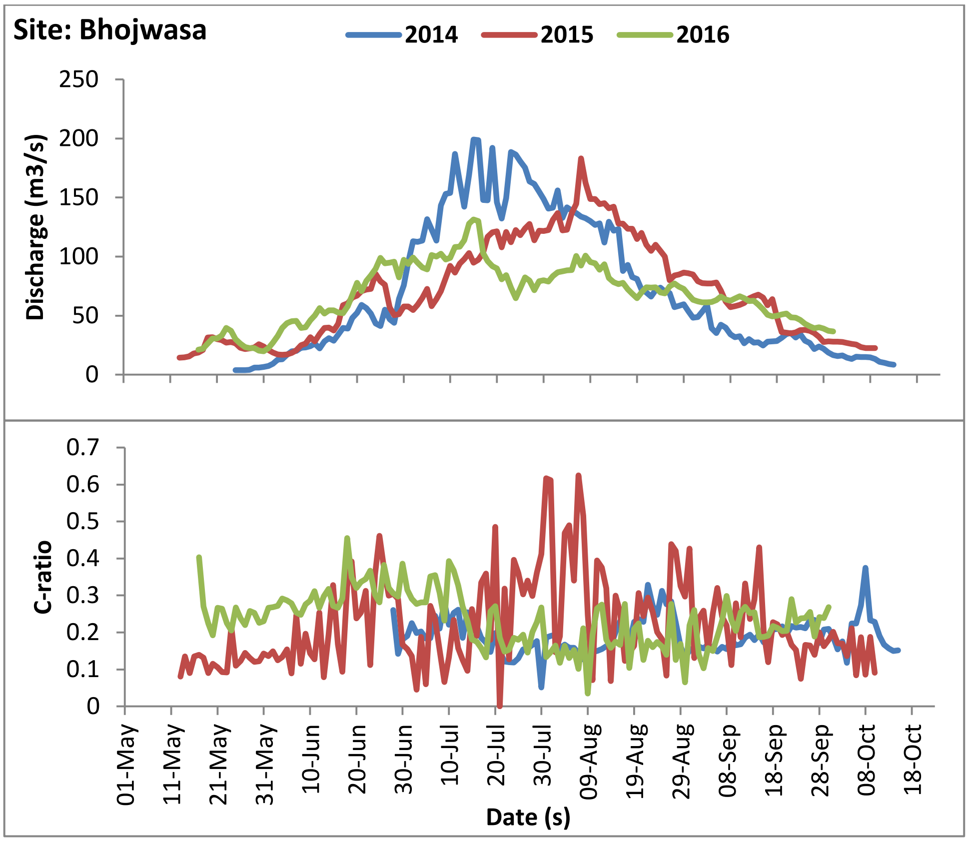


Fig. 5.4 Variation of C-ratio with discharge in the meltwater of River Bhagirathi at Bhojwasa

Bedrock system (glacier bottom ice and bed rock), glacier system (sedimentation from different parts of the glacier such as snout, ablation zone, accumulation zone and lateral moraines) and channel system are the main sources of production of sediment from the glacier fed channels (Singh et al., 2003). Daily mean suspended sediment concentrations were observed to be 1.569, 1.932 and 0.514 g/L during rising limb of annual hydrograph, peak flow and falling limb of hydrograph respectively showing highest suspended sediment concentration during peak flow period, which coincides with the period of high glacial melt in the "Himalayan catchments" (Thayyen and Gergan, 2010). This is followed by rising and falling limb period respectively. Daily mean suspended sediment load was calculated to be 5885, 17982 and 1874 t/day for rising limb, peak flow and falling limb of hydrograph period respectively during the study period. Suspended sediment concentration and load are low during the low discharge period (falling limb) and high during the high discharge period (monsoon + Glacier melt). These seasonal variations in suspended sediment concentration during the study period may be attributed to the progression of subglacial drainage network development. The distributed channel system in the subglacial zone is dormant during winter season with less water availability and high overburden pressure of glacier ice. As melt season progresses, more and more snow and glacier melt routed to the subglacial zone and the distributed channel spread to the higher elevations of the glacier. Higher sediment flux from glacier is also indicative of good integration of distributed system

(Thayyen et al., 1999, 2003). These processes are also linked with the solute acquisition in the meltwater, which could be distinctly different for Alpine and Himalayan glacier systems (Hasnain and Thayyen, 1999). Along with the subglacial channel development, intensive melting (high discharge), increased stream area cross section and higher availability of glacier debris are the factors responsible for high suspended sediment concentration and load in the seasonal high flow period (Singh and Hasnain, 1998; Haritashya et al., 2006) whereas in the recession limb of the glacial hydrograph, suspended sediment concentration is reduced significantly. This trend may be attributed to flush out of sediment by the meltwater in the preceding months (Ostrem, 1975; Collins, 1990). The average ratio of TSS/TDS was observed to be 30.9 in rising limb of the hydrograph, 46.2 during peak flow and 10.9 in recession limb of the annual hydrograph indicating varying degrees of dominance of physical weathering over chemical weathering with increasing discharge in the Gangotri glacier basin. The summary of daily mean suspended sediment load draining from Gangotri glacier and its comparison with other selected Himalayan glacier meltwaters are given in Table 5.1. Suspended sediment load of Gangotri glacier meltwater is much higher than that of other Himalayan glaciers, which may be due to high discharge, large quantity of rock debris and geology of the study area.

Daily mean HCO_3 flux for rising limb, peak flow and recession limb of the annual hydrograph was calculated to be 35.1, 76.0 and 30.4 t/day respectively whereas daily mean SO_4 flux for rising limb, peak flow and recession limb of the annual hydrograph was calculated to be 99.0, 204.0 and 92.9 t/day respectively. Although the concentrations of HCO_3 and SO_4 of meltwater of River Bhagirathi at Bhojwasa draining from Gangotri glacier were minimum but the fluxes of HCO_3 and SO_4 were maximum due to high discharge during peak flow period. This supports our contention that the weathering of supraglacial moraines initiated by monsoonal rainfall enhances the sulphate concentration at high discharges.

TDS flux is calculated with the help of discharge and TDS of meltwater. TDS was calculated by summation of the masses of all the major dissolved constituents (HCO_3^- , Cl^-, SO_4^{-2}, NO_3^-, Na^+,K^+, Ca^{+2} and Mg^{+2}). Daily mean TDS flux for rising limb, peak flow and recession limb of the annual hydrograph was calculated to be 190.3, 389.1 and 172.2 t/day respectively. Although TDS of meltwater of river Bhagirathi at Bhojwasa draining from Gangotri glacier was minimum during peak flow period but TDS flux was maximum due to high discharge during the same period.

Table 5.1 Daily mean suspended sediment load of Gangotri glacier meltwater and comparison with other Himalayan glaciers meltwater

Glacier	Region	Basin area (km^2)	Suspended sediment load (t/day)	References
Chhota Shigri	Himachal Pradesh, India	45	135	Vohra (1991)
Dokriani	Uttarakhand, India	16.1	447	Singh and Ramasastri (1999)
Dunagiri	Uttarakhand, India	17.9	47	Srivastava et al. (1999)
Changme Khangpu	Sikkim	4.5	18	Puri (1999)
Gangotri	Uttarakhand, India	556	11,673	Singh et al. (2014)
Gangotri	Uttarakhand, India	556	8,580	Present Study

5.3 Relationship between Discharge and Major Ion Flux

To study the relationship between discharge and fluxes, plots are drawn between discharge and fluxes of TSS, Na, K, Ca, Mg, HCO_3, Cl, SO_4, $NO_3$and TDS in meltwater of River Bhagirathi at Bhojwasa during the period 2014-2016 and are given in Fig. 5.5 and 5.6. It can be inferred from these plots that TSS flux and TDS flux are highly correlated with discharge with r^2=0.563 and 0.693 respectively. SO_4 flux is highly correlated with discharge with r^2=0.682 while HCO_3 flux with low value of r^2=0.340. Ca flux and Mg flux are significantly correlated with discharge with r^2=0.625 and 0.628 respectively while Na flux and K flux are correlated with discharge comparatively with less r^2=0.540 and 0.577 respectively.

5.4 Chemical and Physical Weathering Rates

Chemical and physical denudation rates play important role in solute acquisition studies. These rates are high in high altitude Himalayan drainage system (Singh and Hasnain, 1998). The cation (chemical) and physical denudation rates of Gangotri glacier are calculated using the concentration of major cations (Na^+, K^+, Ca^{+2} and Mg^{+2}) in meltwater, TSS values, meltwater runoff and catchment area. The cation denudation rates of Gangotri glacier meltwater at Bhojwasa were evaluated to be 34.1, 67.3 and 30.7 t km^{-2} y^{-1} for rising limb, peak flow and falling limb of the annual hydrograph respectively. This is higher than the recorded value at Chhota Shigri glacier (western Himalaya, India) and Glacier No – 1(Eastern Tianshan, Northwest China) (Hasnain et al., 1989; Feng et al., 2012). The summary of cation denudation rates of Gangotri glacier and other selected glaciers of the world are given in Table 5.2.

The physical weathering rate of the Gangotri glacier catchment was evaluated to be 3864, 11805 and 1230 t km^{-2} y^{-1} for rising limb, peak flow and falling limb of the annual hydrograph respectively. This is much higher than the average erosion rate of Indian sub-continent (327 t km^{-2} y^{-1}) and world (150 t km^{-2} y^{-1}) (Singh and Hasnain, 1998). The presence of large and active glaciers and relatively younger age of the Himalayan mountains with their high seismicity and steep valleys with frequent avalanching are responsible for high rates of erosion in the Himalayan region (Hasnain and Chauhan,1993).

Table 5.2 Cation denudation rates of Gangotri Glacier meltwater at Bhojwasa and comparison with other selected Glacier basins

Glacier	Study Period	Catchment area (km^2)	Glacierised area (%)	Cation denudation rates (t km^{-2} y^{-1})	References
Chhota Shigri	1987	40	25	17.4	Husnain et al. (1989)
Dokriani	1992	23	45	9.7	Husnain and Thayyen (1996)
Glacier No. 1	2006/2007	3.34	54	11.46/13.90	Feng et al. (2012)
Haut	1990	11.7	54	13.7	Sharp et al. (1995a)
South Cascade	1992	6.1	34	14.1	Anderson et al. (1997)
Kuannersuit	2001	258	65	15.9	Yde et at. (2005)
Gangotri	2008	556	51.4	34.9	Singh et al. (2014)
Gangotri	2016	556	51.4	44.03	Present Study

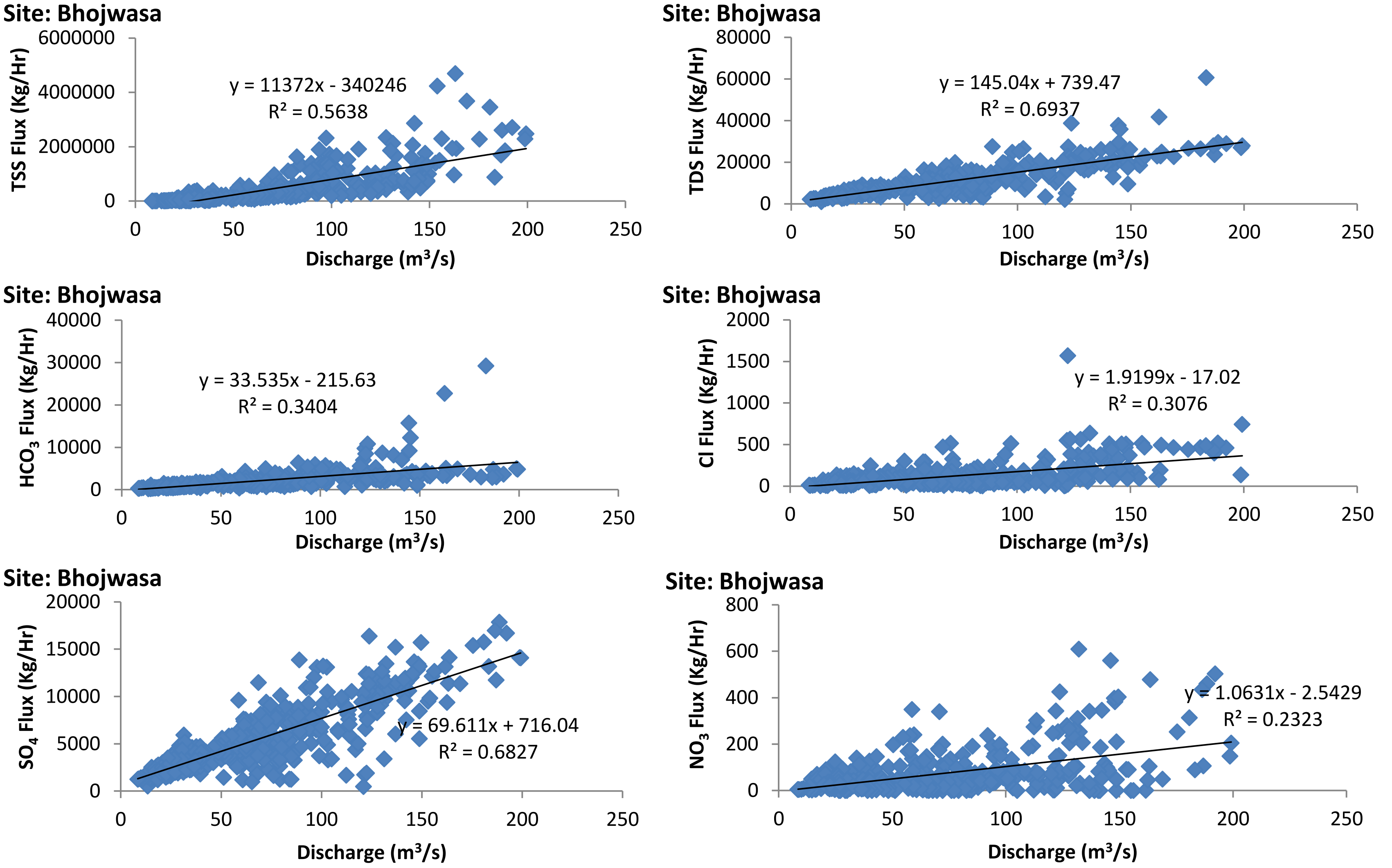


Fig. 5.5 Relationship between the fluxes of anions with meltwater discharge at Bhojwasa during the period of investigation (2014-2016)

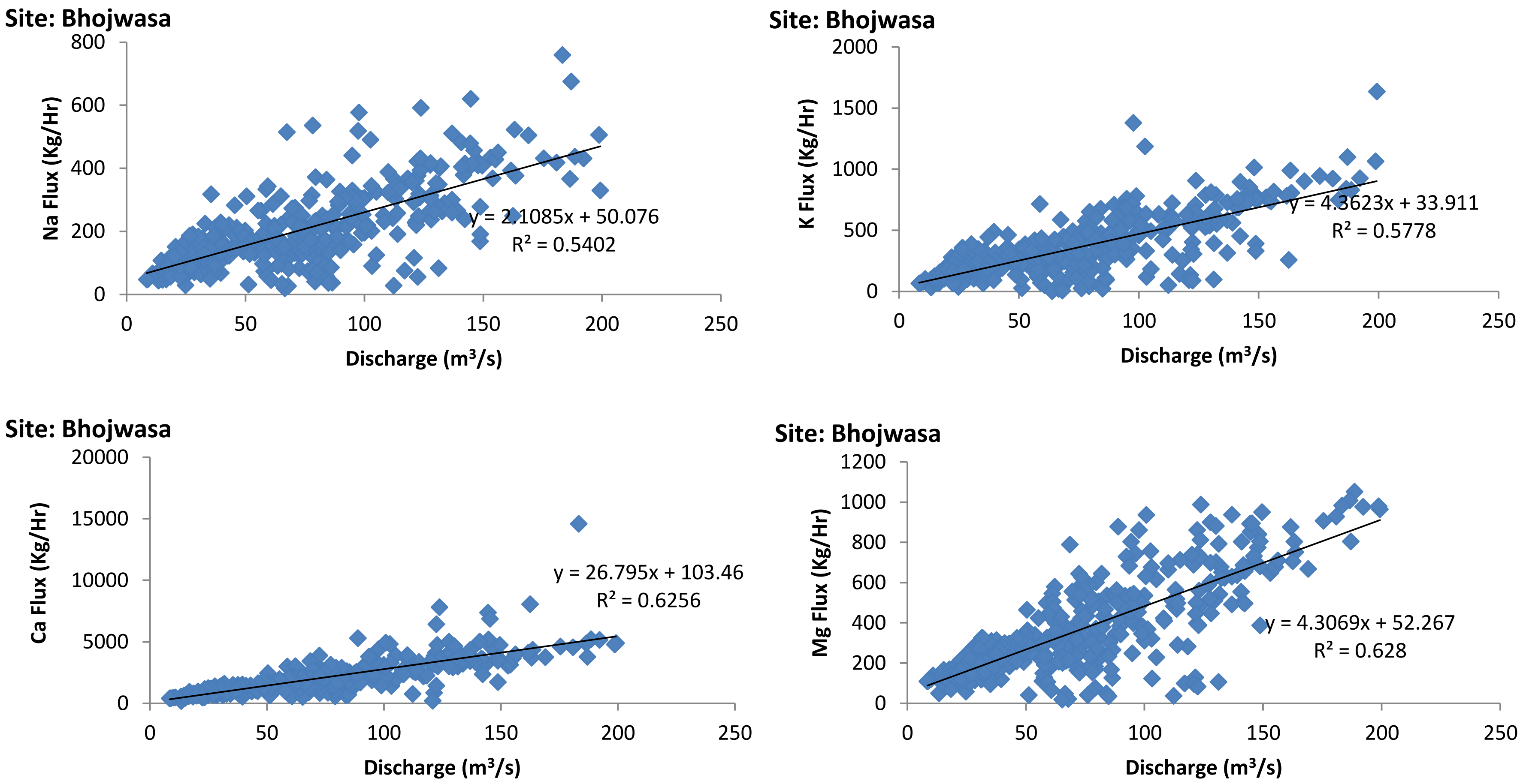


Fig. 5.6 Relationship between the fluxes of cations with meltwater discharge during the period of investigation (2014-2016)

5.5 Diurnal Variations of Different Hydrological and Hydro-chemical Parameters

In non-glacierised catchments, it is often assumed that precipitation events are of minor significance when compared to the effect of seasonal changes in stream discharge between peak and baseflow conditions (Horton et al., 1999). However, in glacierised catchments, large ablation-driven diurnal discharge variations affects glacier meltwater chemistry. Thus, the time of sample collection and the number of samples analysed needs careful consideration and more frequent sampling may be necessary for understanding hydo-chemical behaviour of a glacierised catchment. Considering this aspect, hourly meltwater samples were collected from River Bhagirathi at Bhojwasa on 30thor 31stof every month during the period of investigation of the year 2014, 2015 and 2016 and diurnal variation of different hydrological and hydro-chemical parameters is shown in Fig. 5.7(a-b), 5.8(a-b) and 5.9(a-b) respectively. It can be seen from these figures that there is a sharp change (decrease) in the electrical conductivity of meltwater between 1200 hours to 1500 hours which may be attributed to dilution effect due to higher rate melting because of higher air temperature during this period. Almost same trend are observed for major cations and anions. Variability in the dilution of solute rich subglacial flow with respect to the ground environment by dilute surface glacier meltwater causes variation in the dissolved ion concentration of meltwater draining from the glacier (Rainwater and Guy, 1961). A marked diurnal variation in the TDS of meltwater of River Bhagirathi emerging from Gangotri glacier was observed. TDS shows higher concentration in the morning and decrease in the evening and again follow increasing trend at night [Fig. 5.7(a), 5.8(a) & 5.9(a)]. Distribution of hourly discharge from Gangotri glacier shows that minimum runoff is observed in the morning (0700–1000 h) whereas in evening (1700–1900 h) maximum runoff occurs (Singh et al., 2011). This shows that TDS concentrations are inversely correlated with discharge. It means generally TDS value is higher during low discharge and low during the high discharge. Such a trend is explained by the model of Rainwater and Guy (1961), Collins (1983), Kumar et al. (2009). Due to increase in insolation in the afternoon, englacial channels become active hence transportation of huge amount of supraglacial meltwater takes place from the glacier and at certain lag of time, in evening discharge is maximum causing dilution of TDS. Whereas due to low supply of solar energy in the morning, melting and dilution of subglacial meltwater draining from Gangotri glacier is reduced. Due to longer contact with the solute rich base and high residence time, the subglacial water has high dissolved ion enrichment producedat pressure melting point.

Further, higher TSS was observed during afternoon hours, which may also be attributed to high discharge in the river because of higher melting contribution to flow during this period.

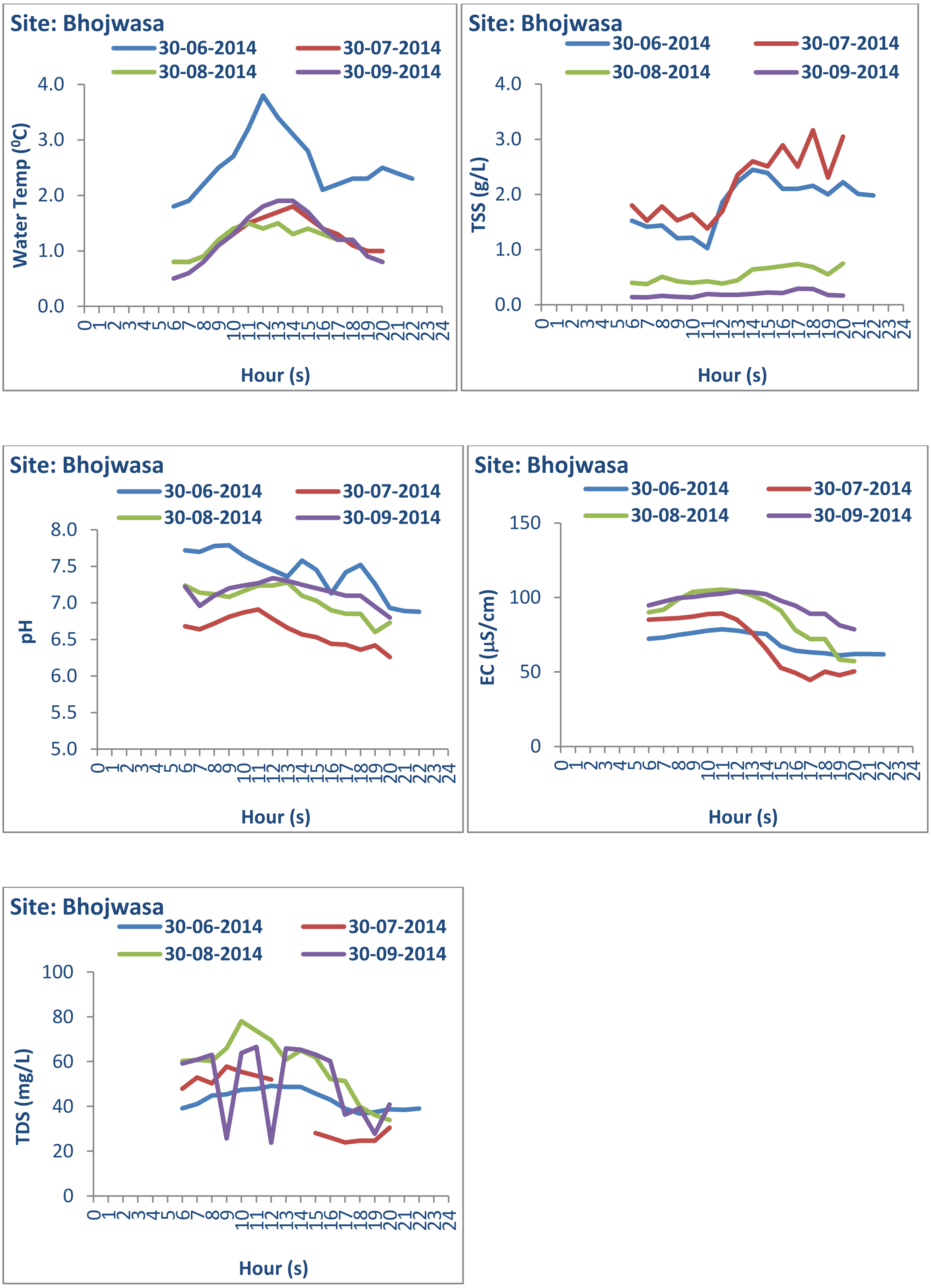


Fig. 5.7(a) Diurnal variation of water temperature, TSS, pH, EC and TDS in the meltwater of River Bhagirathi at Bhojwasa during the year 2014

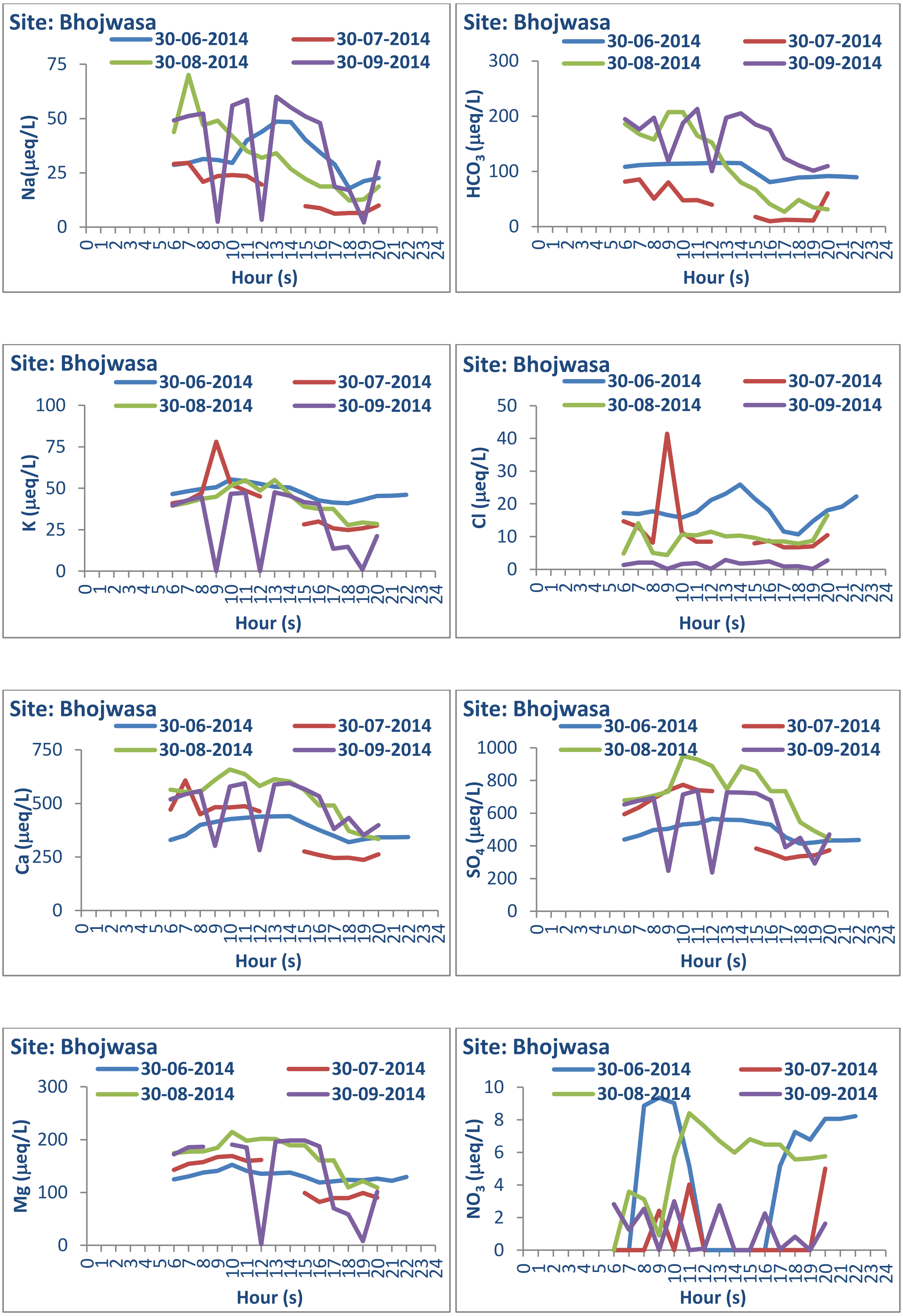


Fig. 5.7(b) Diurnal variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Bhojwasa during the year 2014

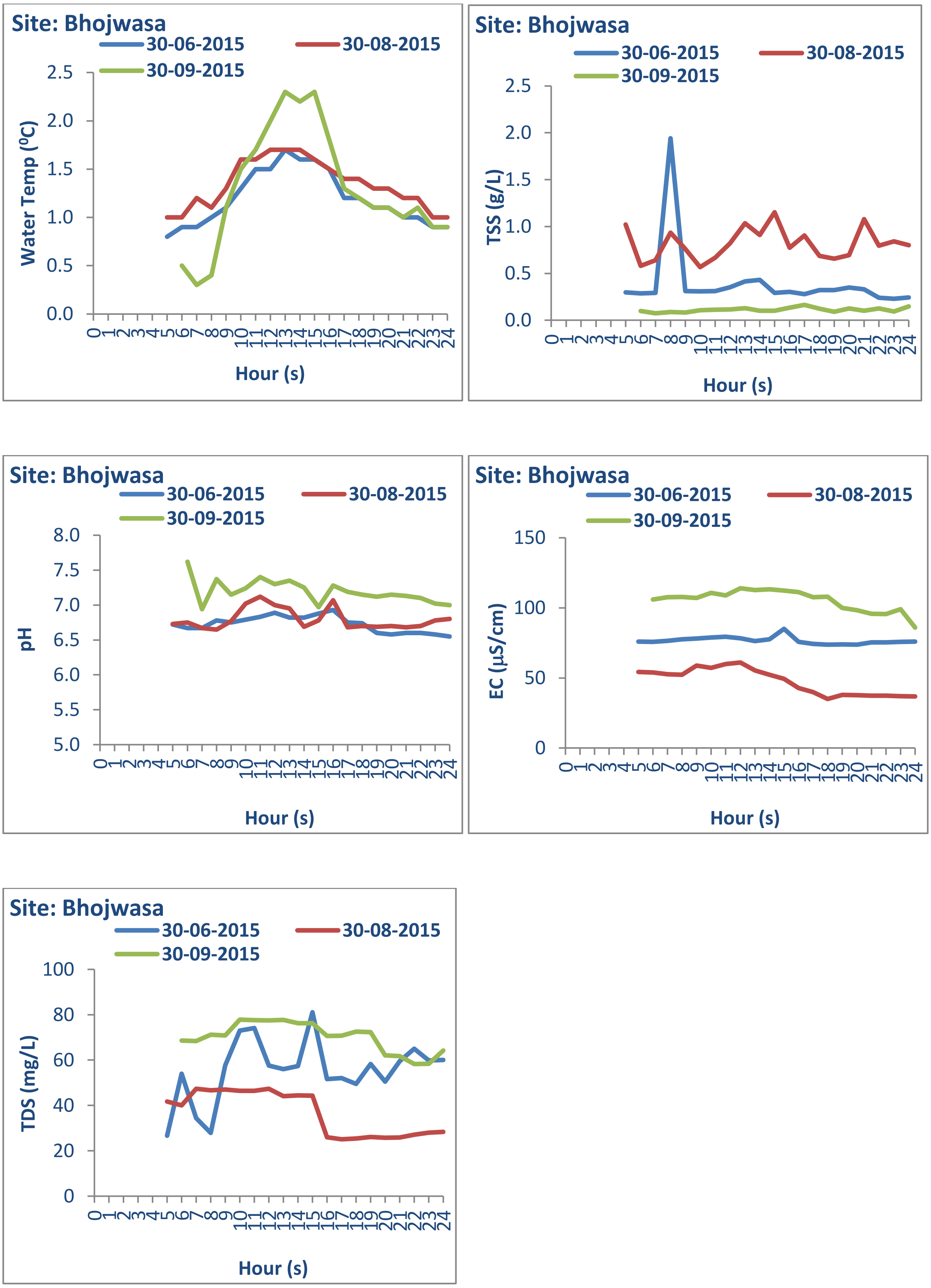


Fig. 5.8(a) Diurnal variation of water temperature, TSS, pH, EC and TDS in the meltwater of River Bhagirathi at Bhojwasa during the year 2015

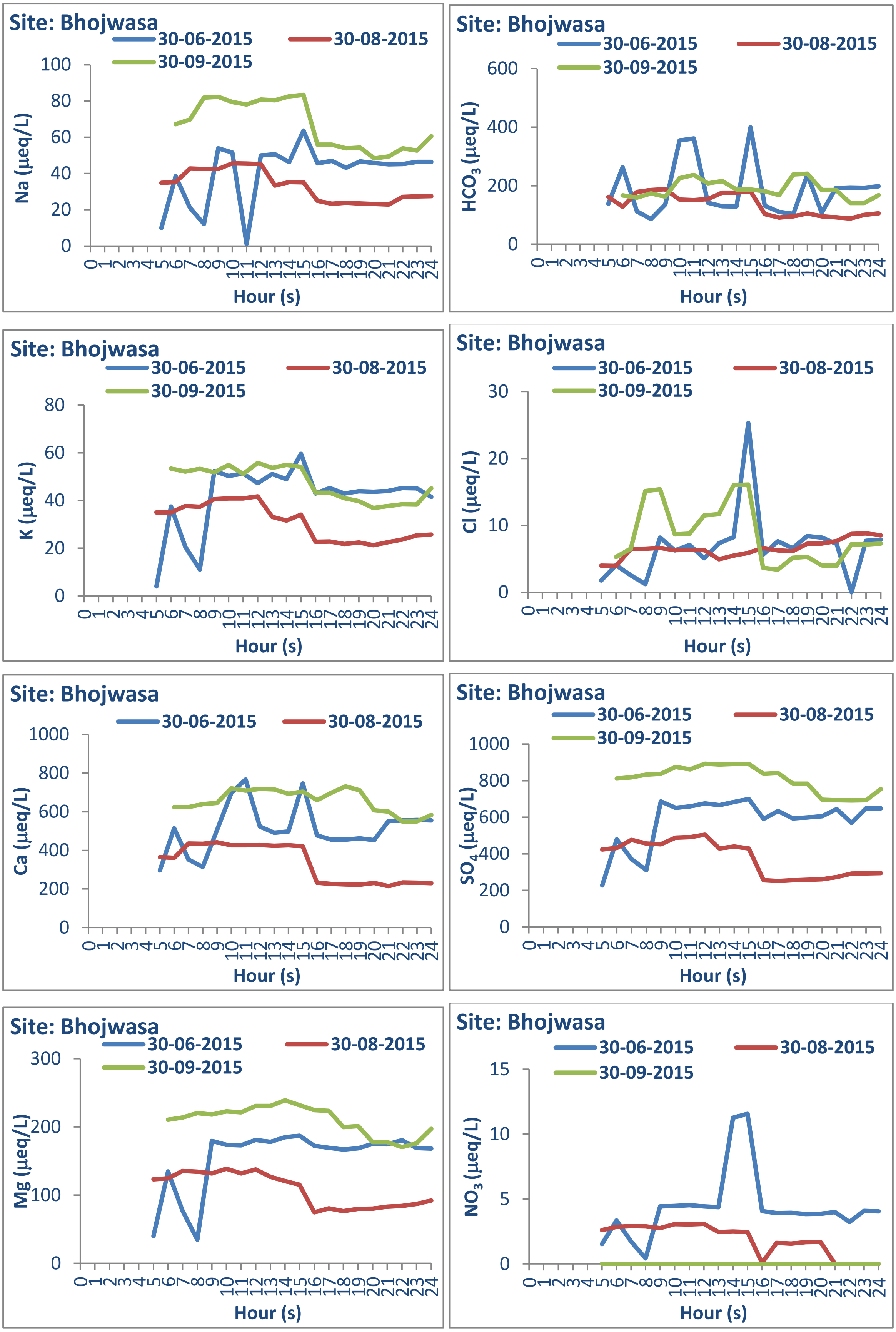


Fig. 5.8(b) Diurnal variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Bhojwasa during the year 2015

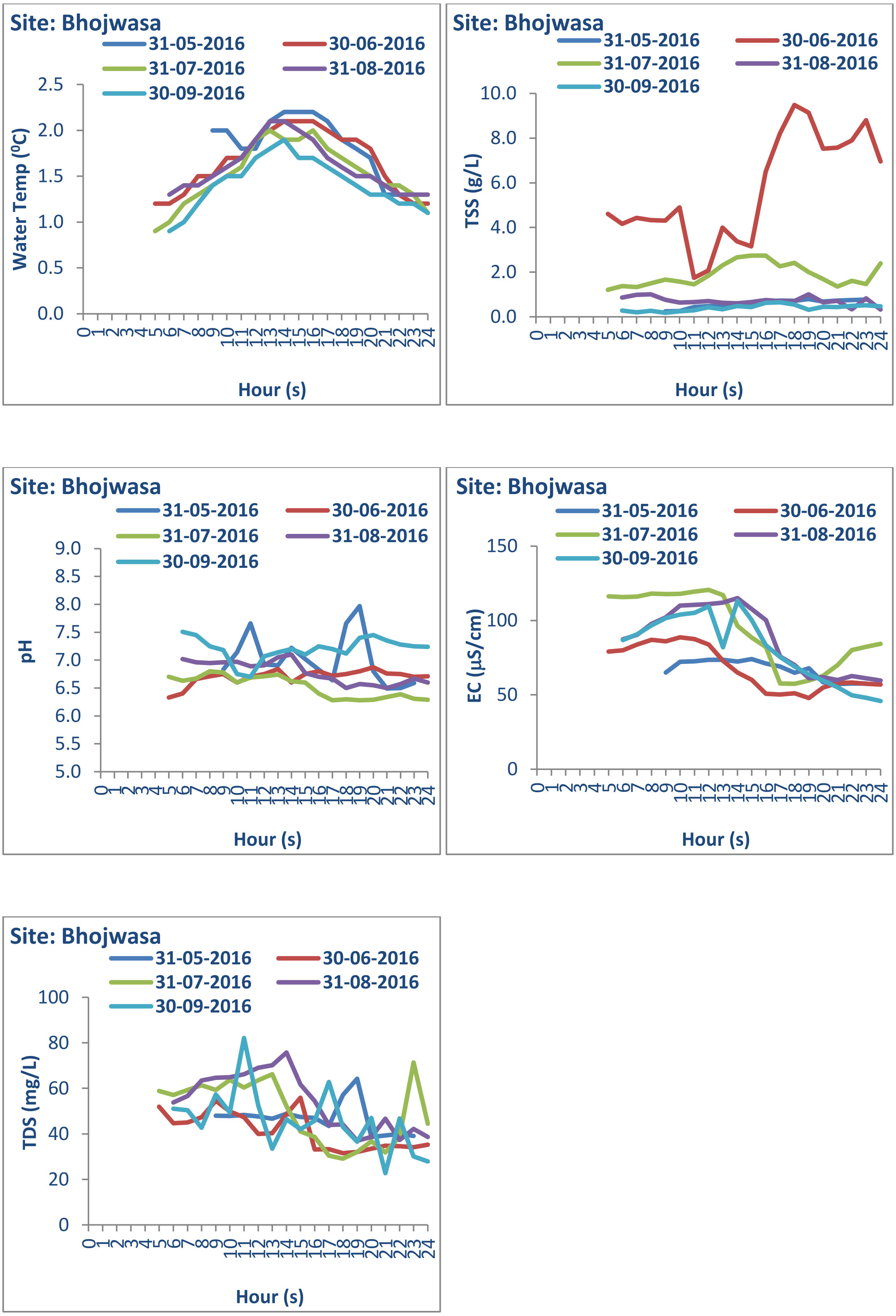


Fig. 5.9(a) Diurnal variation ofwater temperature, TSS, pH, EC and TDS in the meltwater of River Bhagirathi at Bhojwasa during the year 2016

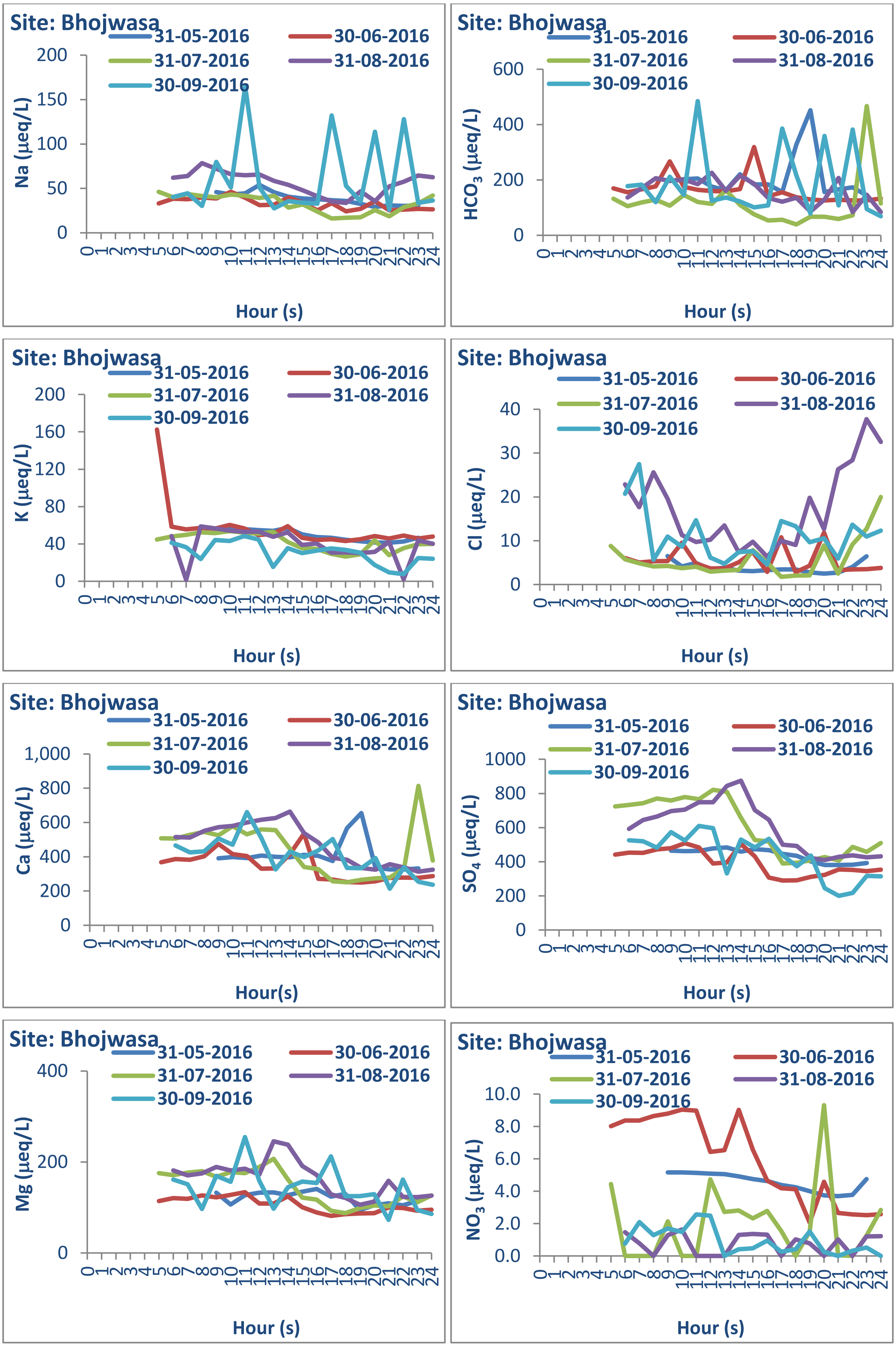


Fig. 5.9(b) Diurnal variation of major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) and major anions (HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-) in the meltwater of River Bhagirathi at Bhojwasa during the year 2016

Chapter 6

CHEMICAL CHARACTERIZATION OF SUSPENDED AND BED SEDIMENTS

6.1 Surface Characterization of Sediments

Surface characteristics of sediments play an important role in solute acquisition during freshly grinded sediment-meltwater interaction. In the present investigation, the surface characteristics of suspended and bed sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri were studied using SEM analysis. The images of suspended and bed sediments were magnified upto 10,000X for study.

6.1.1 Surface characterization of suspended sediments

The proglacial meltwater stream always carries a huge amount of suspended sediments. Our sampling site around Gangotri glacier is no exception. The sediments derived are mineral grains and not rock fragments and it is also evident from the scale of the SEM images. SEM images of suspended sediments collected from River Bhagirathi at Gomukh, Bhojwasa and Gangotri are given in Fig. 6.1. It can be inferred from these images that the sediments are argillaceous (clay size) sediment. The grains are in-equigranular and sub-rounded. A few platy minerals can also be seen.

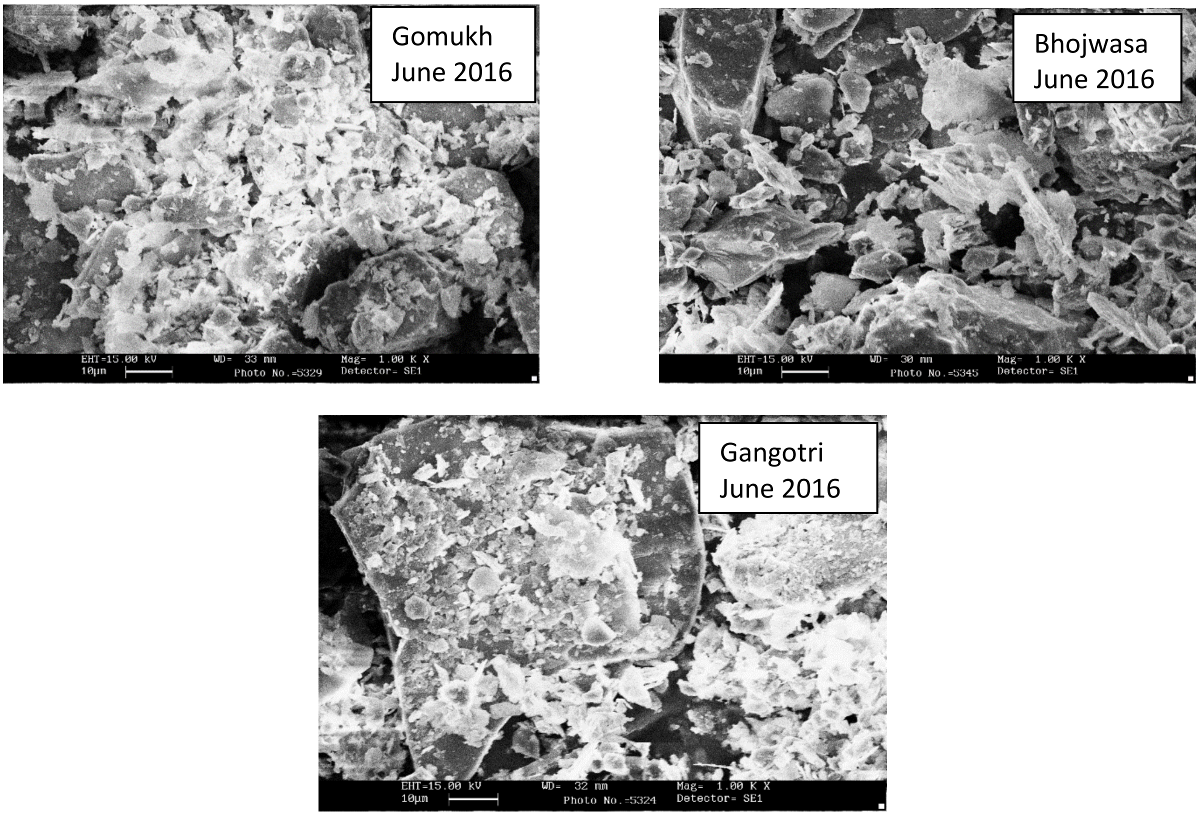


Fig. 6.1 SEM images of suspended sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri collected during the month of June 2016

SEM images of suspended sediments collected from River Bhagirathi at Bhojwasa in the month of May, June, July, August and September 2016 are given in Fig. 6.2. These images show highly heterogeneous, clay size loose materials indicating extensive weathering by the glacier upstream and presence of rocks prone to chemical weathering.

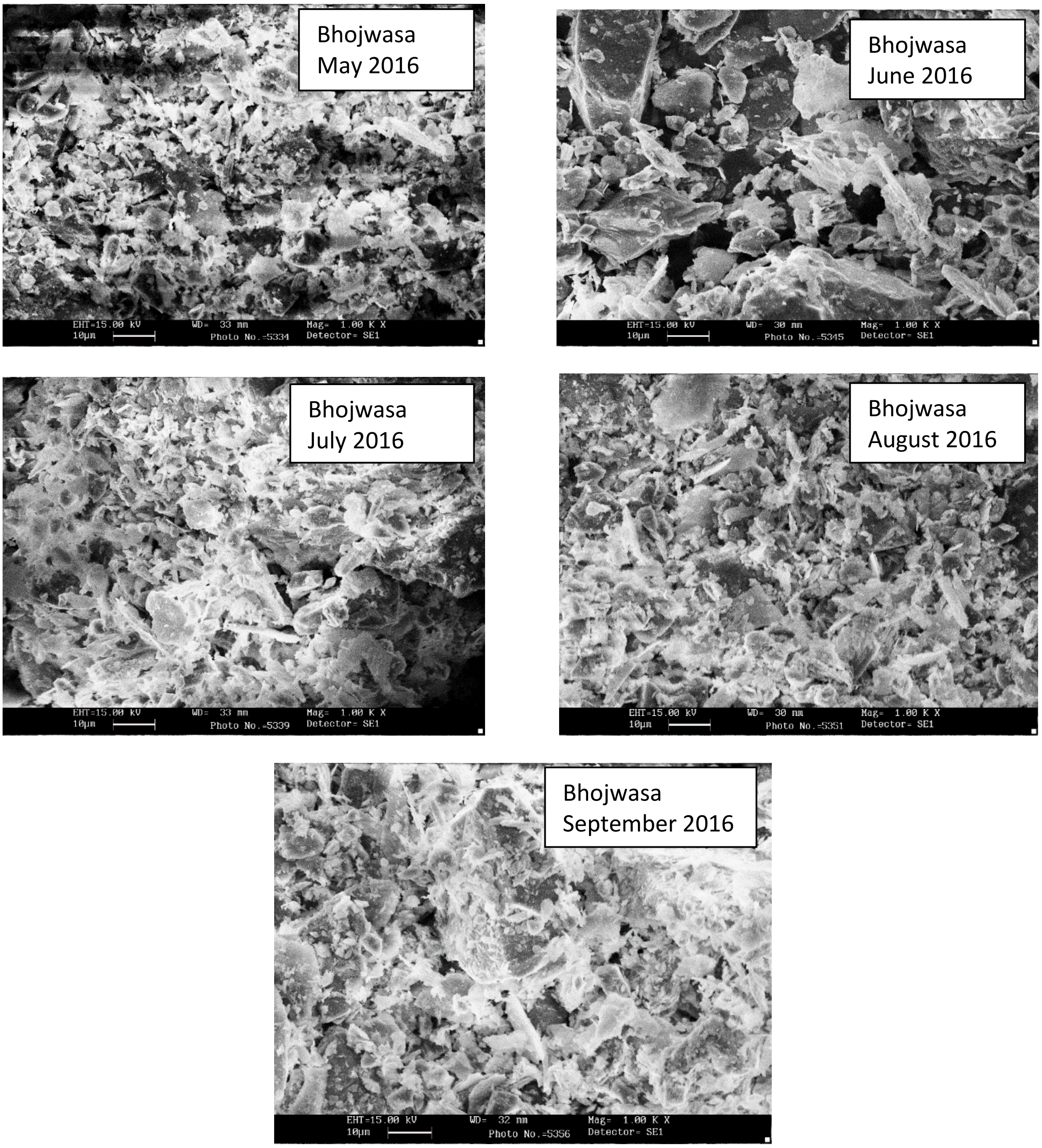


Fig. 6.2 SEM images of suspended sediments of River Bhagirathi at Bhojwasa collected during different months of ablation period of the year 2016

6.1.2 Surface characterization of bed sediments

SEM images of bed sediments collected from River Bhagirathi at Gomukh, Bhojwasa and Gangotri are given in Fig. 6.3. In the first image (Gomukh, June 2016), the grains shows one set of cleavage, possibly a micaceous mineral. The pits and grooves are the indicators of chemical weathering due to the solution. The second image (Bhojwasa, June 2016) shows two-sets of cleavage. The third image (Gangotri, June 2016) shows roundness in the mineral grains indicator of transportation by stream water.

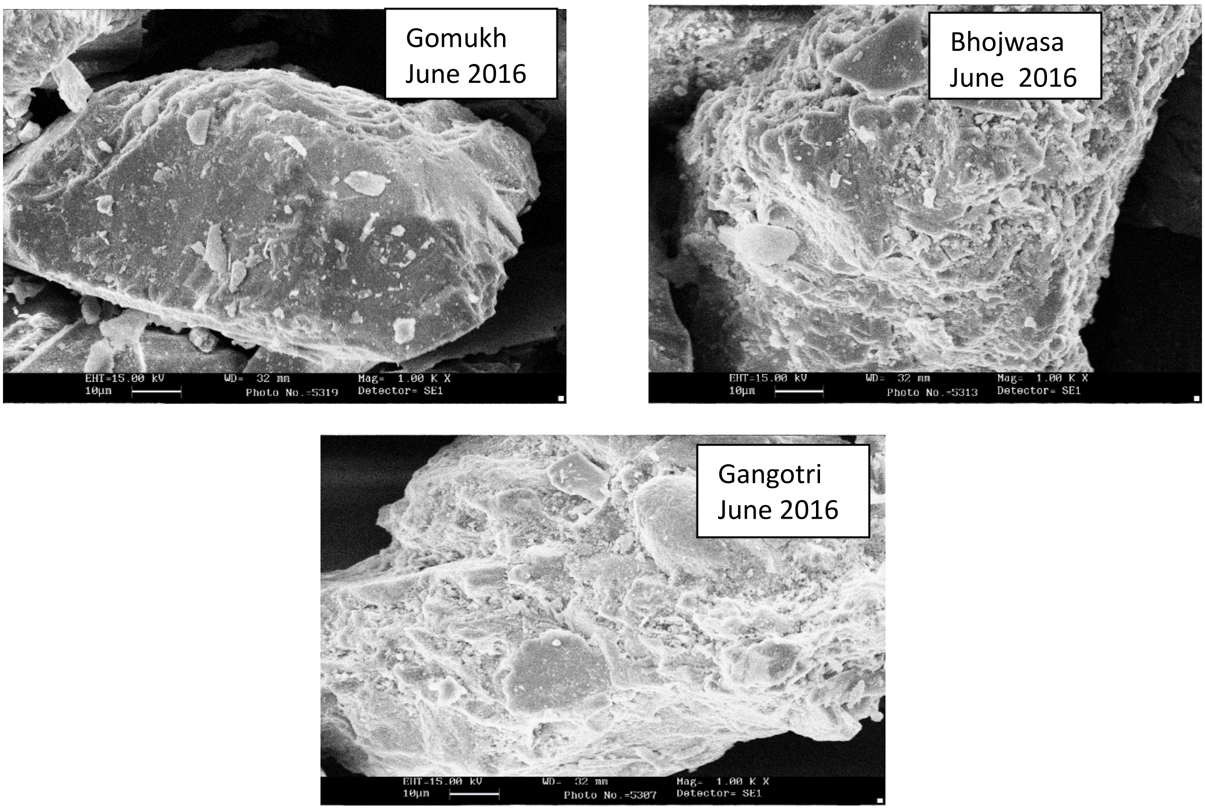


Fig. 6.3 SEM Images of bed sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri collected during the month of June 2016

6.2 Chemical Characterization of Sediments

For chemical characterization of sediments, 2.0 g of suspended and bed sediments (0-75 µm) of River Bhagirathi collected from Gomukh, Bhojwasa and Gangotri during June 2016 were put in HDPE grade plastic beaker containing 250 ml (±2 ml) of ultrapure water on a shaker with magnetic stirrer maintaining a speed of 500±20 rpm and the temperature of the solution at 3°C for 10 minutes. Solution was filtered through 0.45 µm cellulose nitrate membranes immediately and analysed for major cations and anions. Results obtained are given in Table 6.1.

Table 6.1 Chemical characteristics of suspended and bed sediment

Major ion	**Suspended sediment**			**Bed sediment**		
(µg/g)	**Gomukh**	**Bhojwasa**	**Gangotri**	**Gomukh**	**Bhojwasa**	**Gangotri**
Na	91	84	76	24	16	20
K	77	65	53	15	27	18
Ca	323	328	205	476	381	505
Mg	62	85	61	46	89	78
SO_4	1127	1008	1027	1568	3453	3245

It can be inferred from the data in the Table 6.1 that suspended sediment of the site Gomukh of River Bhagirathi has higher potential of chemical dissolution as compared to other sites i.e. Bhojwasa and Gangotri.

6.3 Metal Concentrations in Sediments

Sediment plays an important role in any solute acquisition study. Heavy metals in sediment act as bio-limiting nutrients and their potential as indicator species in solute provenance studies (Mitchell et al., 2001). Metal concentrations of Fe, Zn, Cu, Cd and Pb were analysed in the suspended and bed sediments of River Bhagirathi collected from Gomukh, Bhojwasa and Gangotri monthly during the ablation period of investigation (May to September) of the year 2016.

6.3.1 Metal concentrations in suspended sediments

Variation of metal concentrations of Fe, Zn, Cu, Cd and Pb in suspended sediment of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during May to September 2016 is shown in Fig. 6.4. The concentration of Fe, Zn, Cu, Cd and Pb in the suspended sediments of River Bhagirathi collected from Gomukh varied from 15523 to 24028 µg/g, 0 to 85.9 µg/g, 16.7 to 28.8 µg/g, 0 to 0.12 µg/g and 0 to 7.1 µg/g respectively. At Bhojwasa, the concentration of Fe, Zn, Cu, Cd and Pb in the suspended sediments of River Bhagirathi varied from 4212 to 34921 µg/g, 0 to 84.3 µg/g, 14.5 to 21.7 µg/g, 0 to 0.19 µg/g and 2.6 to 29.2 µg/g respectively. At Gangotri, the concentration of Fe, Zn, Cu, Cd and Pb in the suspended sediments of River Bhagirathi varied from 11978 to 18376 µg/g, 48.3 to 148 µg/g, 0 to 22.9 µg/g, 0 to 0.18 µg/g and 5.7 to 51.4 µg/g respectively (Table 6.2).

Table 6.2 Metal concentrations in the suspended sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during ablation period of 2016

Metal (µg/g)	**Site: Gomukh**			**Site: Bhojwasa**			**Site: Gangotri**		
	Min	**Max**	**Mean**	**Min**	**Max**	**Mean**	**Min**	**Max**	**Mean**
Fe	15523	24028	19775	4212	34921	18741	11978	18376	15418
Zn	0	85.9	42.9	0	84.3	42.6	48.3	148	95.9
Cu	16.7	28.8	22.7	14.5	21.7	19.1	0	22.9	20.8
Cd	0	0.12	0.06	0	0.19	0.06	0	0.18	0.06
Pb	0	7.1	3.5	2.6	29.2	14.8	5.7	51.4	24.7

6.3.2 Metal concentrations in bed sediments

Variation of metal concentrations of Fe, Zn, Cu, Cd and Pb in bed sediment of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during May to September 2016 is shown in Fig. 6.5. The concentration of Fe, Zn, Cu, Cd and Pb in the bed sediments of River Bhagirathi collected from Gomukh varied from 35.8 to 9161 µg/g, 25.0 to 55.2 µg/g, 15.6 to 28.2 µg/g, 0.08 to 0.17 µg/g and 1.78 to 13.2 µg/g respectively. At Bhojwasa, the concentration of Fe, Zn, Cu, Cd and Pb in the bed sediments of River Bhagirathi varied from 13.2 to 10306 µg/g, 27.2 to 40.7 µg/g, 12.3 to 30.4 µg/g, 0.10 to 0.43 µg/g and 0.89 to 14.4 µg/g respectively. At Gangotri, the concentration of Fe, Zn, Cu, Cd and Pb in the bed sediments of River Bhagirathi varied from 10.6 to 9384 µg/g, 8.2 to 64.5 µg/g, 3.8 to 27.8 µg/g, 0 to 0.14 µg/g and 0.63 to 16.8 µg/g respectively (Table 6.3).

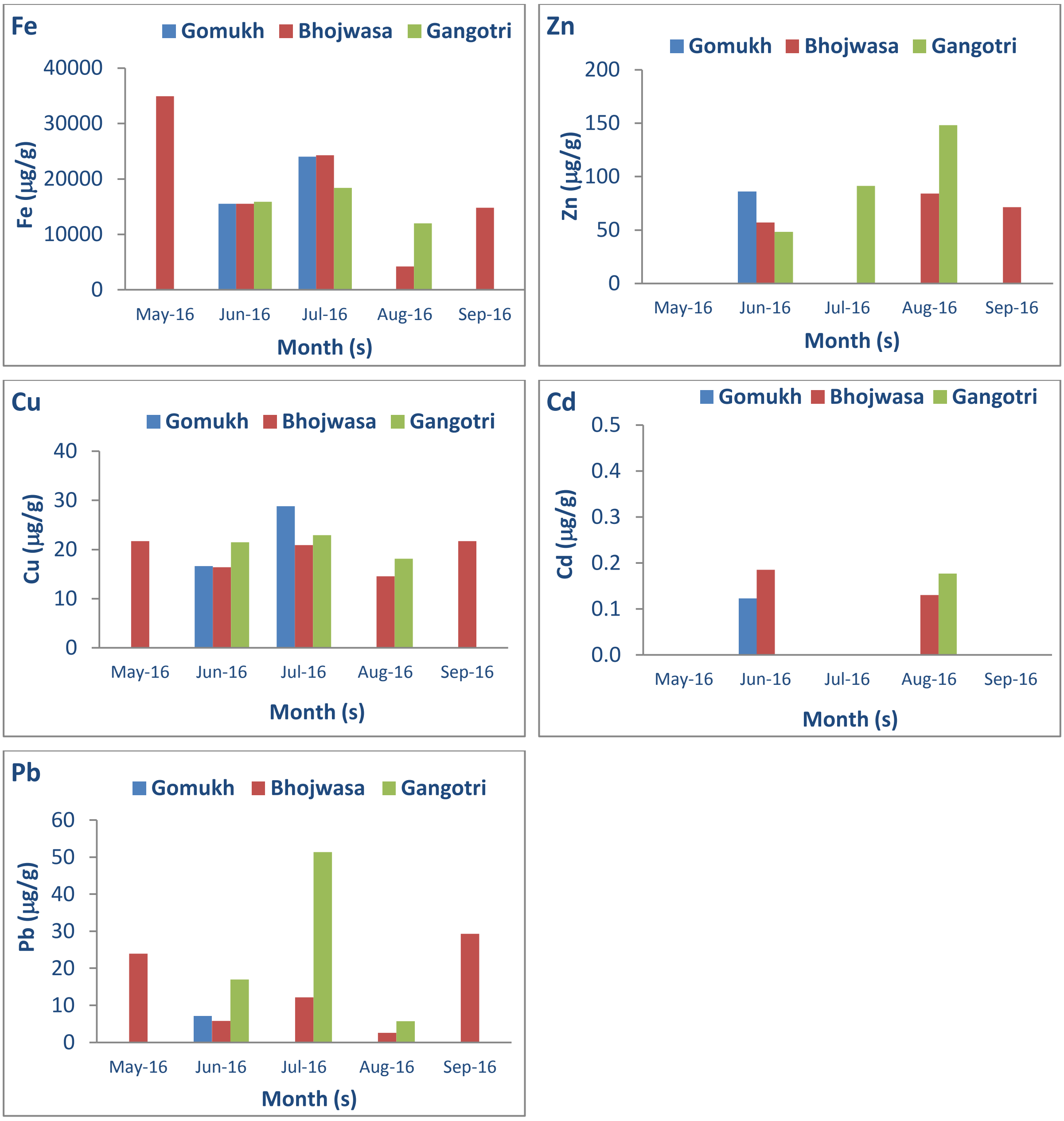


Fig. 6.4 Variation of metal concentrations in the suspended sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

Table 6.3 Metal concentrations in the bed sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during ablation period of 2016

Metal (µg/g)	Site: Gomukh			Site: Bhojwasa			Site: Gangotri		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Fe	35.8	9161	3584	13.2	10306	2178	10.6	9384	4403
Zn	25.0	55.2	43.1	27.2	40.7	35.5	8.2	64.5	35.7
Cu	15.6	28.2	22.3	12.3	30.4	19.3	3.8	27.8	19.2
Cd	0.08	0.17	0.12	0.10	0.43	0.20	0	0.14	0.09
Pb	1.8	13.2	4.9	0.89	14.4	7.7	0.63	16.8	7.5

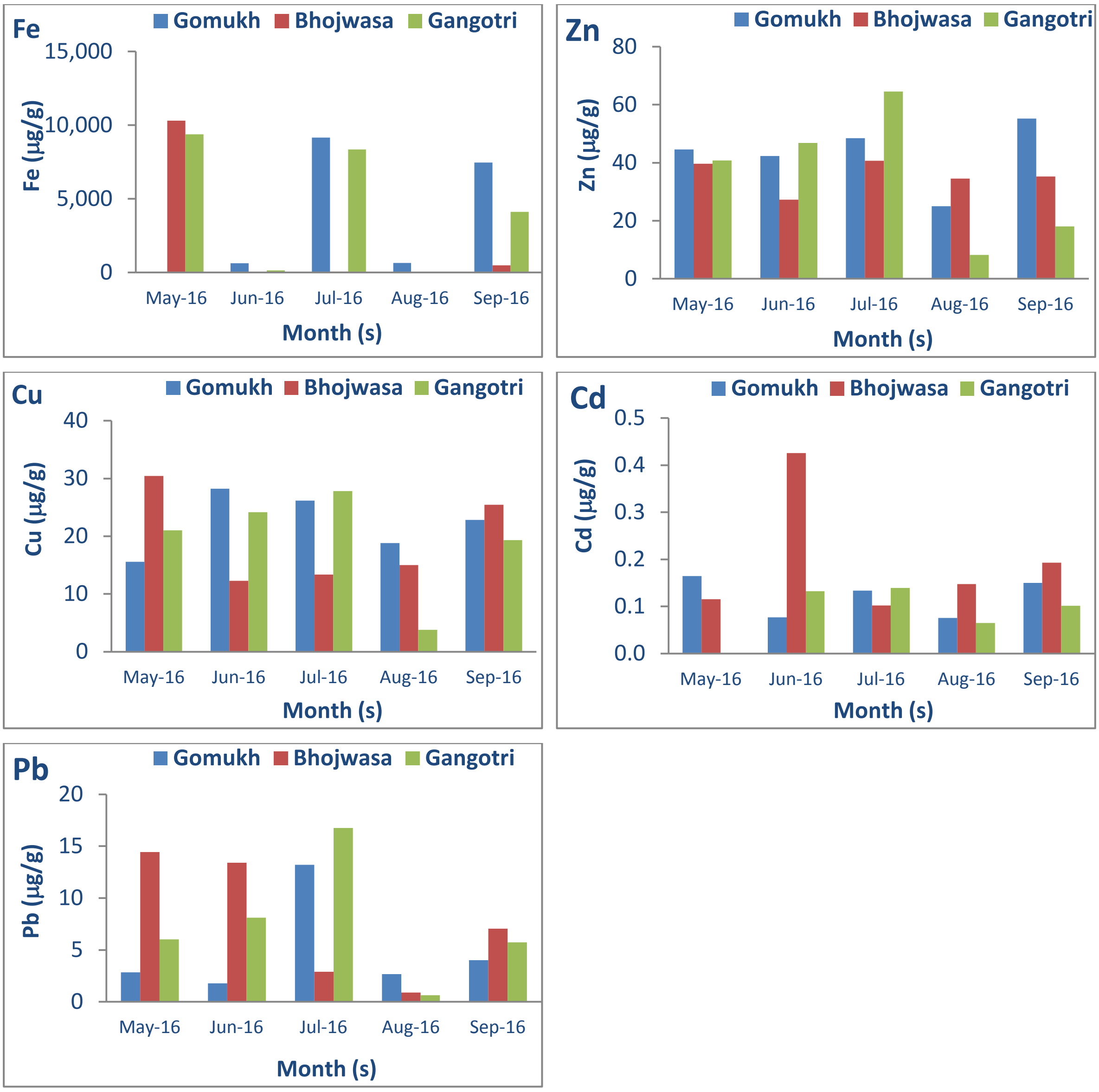


Fig. 6.5 Variation of metal concentrations in the bed sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2016

6.4 XRF analysis of sediments

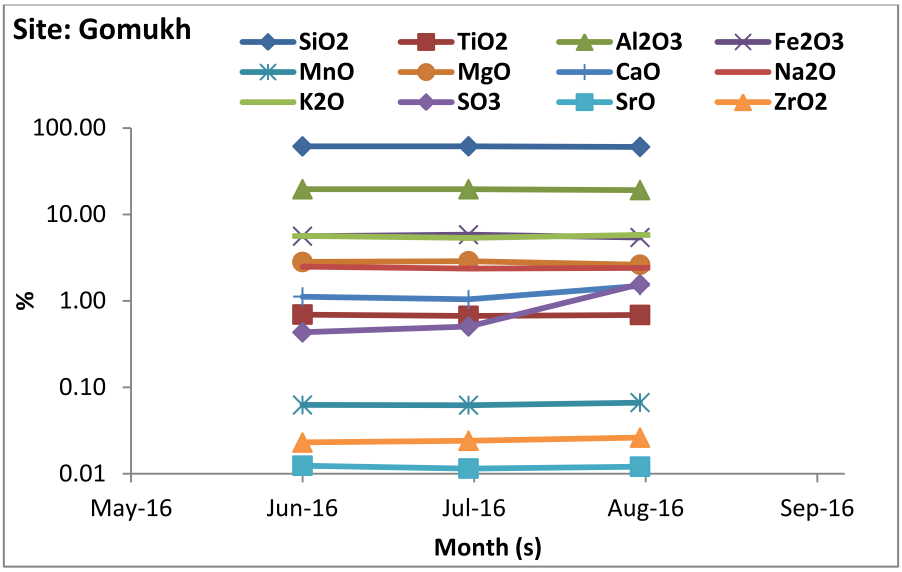
The % oxides of major and trace element are analysed in suspended and bed sediments collected from Gomukh, Bhojwasa and Gangotri during the year 2016 using XRF technique and are given in Table 6.4 and 6.5 respectively. Variation of % of elemental oxides in suspended and bed sediments are shown in Fig. 6.6 and 6.7 respectively. It can be inferred from the Table 6.4 and 6.5 that taking into account the SiO_2 and Al_2O_3 concentrations derived from the XRF technique, it can theorize the abundance of feldspar mineral in the source rock.

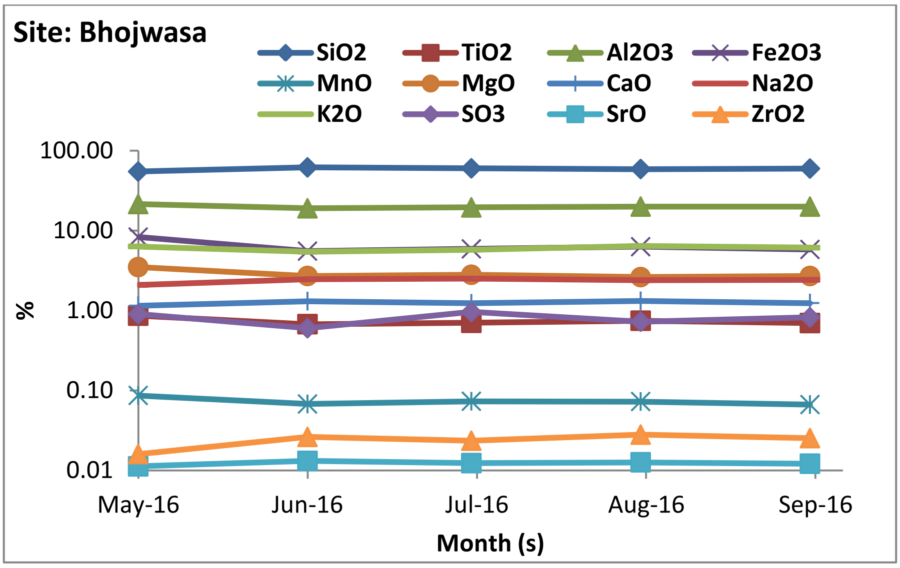
Table 6.4 Percentage of oxides of major and trace element using XRF technique in suspended sediments of River Bhagirathi

Month	**Oxides (%)**																	
	SiO_2	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**SO_3**	**Cr_2O_3**	**NiO**	**CuO**	**ZnO**	**Rb_2O**	**SrO**	**ZrO_2**
Site: Gomukh																		
May-16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jun-16	61.210	0.695	19.550	5.590	0.062	2.816	1.120	2.480	5.615	0.195	0.432	0.038	0.008	0.011	0.015	0.032	0.012	0.023
Jul-16	61.370	0.671	19.550	5.818	0.062	2.874	1.040	2.370	5.338	0.185	0.506	0.026	0.008	0.012	0.012	0.030	0.012	0.024
Aug-16	60.390	0.687	19.130	5.406	0.067	2.620	1.489	2.410	5.780	0.233	1.550	0.026	0.009	0.012	0.014	0.034	0.012	0.026
Sep-16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Site: Bhojwasa																		
May-16	54.780	0.862	21.520	8.301	0.087	3.496	1.150	2.090	6.331	0.181	0.903	0.022	0.009	0.013	0.018	0.044	0.011	0.016
Jun-16	61.760	0.675	19.020	5.533	0.068	2.704	1.310	2.470	5.434	0.209	0.600	0.034	0.008	0.018	0.013	0.032	0.013	0.026
Jul-16	60.120	0.702	19.520	5.903	0.073	2.800	1.230	2.500	5.774	0.196	0.959	0.034	0.009	0.013	0.015	0.035	0.012	0.024
Aug-16	58.940	0.745	20.010	6.286	0.073	2.618	1.320	2.390	6.407	0.217	0.724	0.050	0.010	0.013	0.018	0.042	0.013	0.028
Sep-16	59.700	0.697	19.970	5.808	0.067	2.702	1.240	2.420	6.113	0.215	0.821	0.034	0.008	0.013	0.016	0.037	0.012	0.025
Site: Gangotri																		
May-16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Jun-16	61.960	0.669	19.030	5.476	0.061	2.765	1.140	2.430	5.362	0.200	0.697	0.031	0.007	0.012	0.012	0.031	0.012	0.024
Jul-16	62.680	0.617	18.730	5.193	0.071	2.652	1.140	2.550	5.346	0.194	0.623	0.023	0.009	0.012	0.014	0.032	0.012	0.023
Aug-16	60.950	0.652	19.750	5.642	0.069	2.638	1.080	2.610	5.878	0.202	0.283	0.054	0.010	0.012	0.017	0.041	0.011	0.021
Sep-16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 6.5 Percentage of oxides of major and trace element using XRF technique in bed sediments of River Bhagirathi

Month	**Oxides (%)**																	
	SiO_2	**TiO_2**	**Al_2O_3**	**Fe_2O_3**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**P_2O_5**	**SO_3**	**Cr_2O_3**	**NiO**	**CuO**	**ZnO**	**Rb_2O**	**SrO**	**ZrO_2**
Site: Gomukh																		
May-16	69.400	0.455	14.680	2.171	0.098	0.584	2.635	4.035	3.729	1.100	0.457	0.056	0.005	0.011	0.006	0.017	0.013	0.363
Jun-16	72.170	0.414	13.880	2.152	0.053	0.686	1.934	3.742	3.526	0.586	0.607	0.046	0.006	0.012	0.007	0.017	0.014	0.107
Jul-16	71.700	0.551	13.250	2.764	0.063	0.803	1.939	3.611	3.137	0.663	1.180	0.069	0.008	0.013	0.007	0.015	0.013	0.159
Aug-16	71.030	0.468	13.870	2.996	0.055	1.110	1.686	3.483	3.430	0.522	1.090	0.048	0.006	0.014	0.010	0.016	0.013	0.097
Sep-16	71.200	0.379	14.320	2.208	0.048	0.680	2.033	3.852	3.834	0.599	0.587	0.044	0.005	0.011	0.005	0.019	0.014	0.117
Site: Bhojwasa																		
May-16	67.460	0.700	14.310	3.596	0.080	1.070	2.008	3.258	3.973	0.608	2.190	0.079	0.009	0.016	0.009	0.021	0.013	0.423
Jun-16	68.830	0.458	12.470	3.986	0.074	0.847	2.000	2.984	3.412	0.540	3.752	0.102	0.012	0.013	0.008	0.018	0.014	0.293
Jul-16	71.240	0.441	13.790	2.742	0.052	0.918	1.797	3.478	3.590	0.486	1.200	0.058	0.008	0.011	0.007	0.018	0.014	0.100
Aug-16	71.840	0.365	13.950	2.090	0.052	0.664	1.990	3.783	3.650	0.614	0.728	0.079	0.006	0.011	0.005	0.017	0.013	0.107
Sep-16	70.600	0.693	13.000	2.947	0.099	0.584	2.303	3.696	3.114	0.954	1.380	0.053	0.006	0.014	0.006	0.014	0.013	0.361
Site: Gangotri																		
May-16	70.950	0.399	14.560	1.990	0.046	0.808	2.003	3.641	4.199	0.471	0.582	0.102	0.006	0.011	0.007	0.022	0.015	0.145
Jun-16	70.340	0.534	12.990	3.145	0.076	1.160	1.920	2.993	3.356	0.596	2.470	0.111	0.009	0.014	0.010	0.017	0.013	0.194
Jul-16	70.720	0.574	13.170	2.819	0.078	0.801	2.019	3.480	3.533	0.635	1.680	0.113	0.008	0.013	0.008	0.020	0.013	0.235
Aug-16	73.190	0.325	12.940	2.005	0.063	0.548	2.075	3.626	3.564	0.533	0.757	0.092	0.006	0.018	0.005	0.018	0.014	0.184
Sep-16	71.650	0.459	13.730	2.319	0.067	0.821	2.110	3.551	3.517	0.634	0.818	0.059	0.006	0.012	0.007	0.017	0.013	0.160





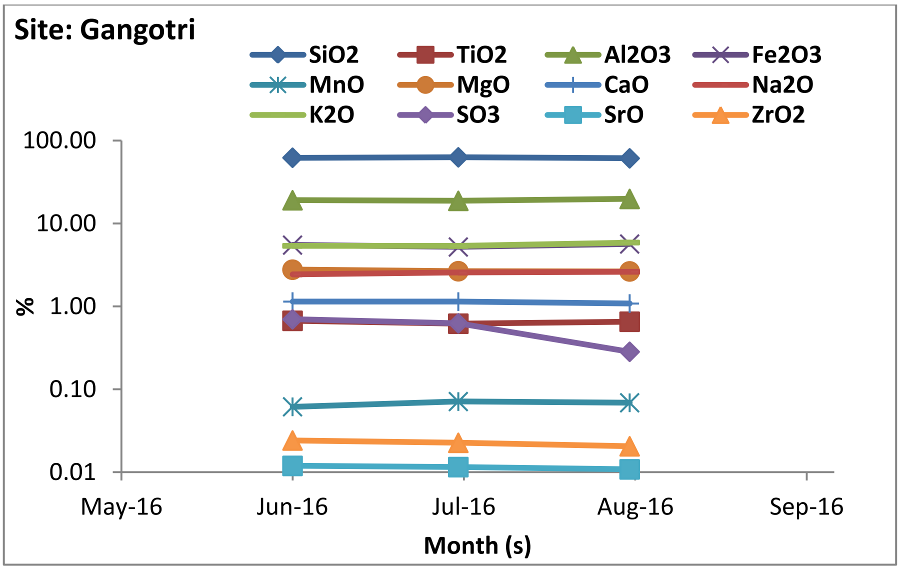
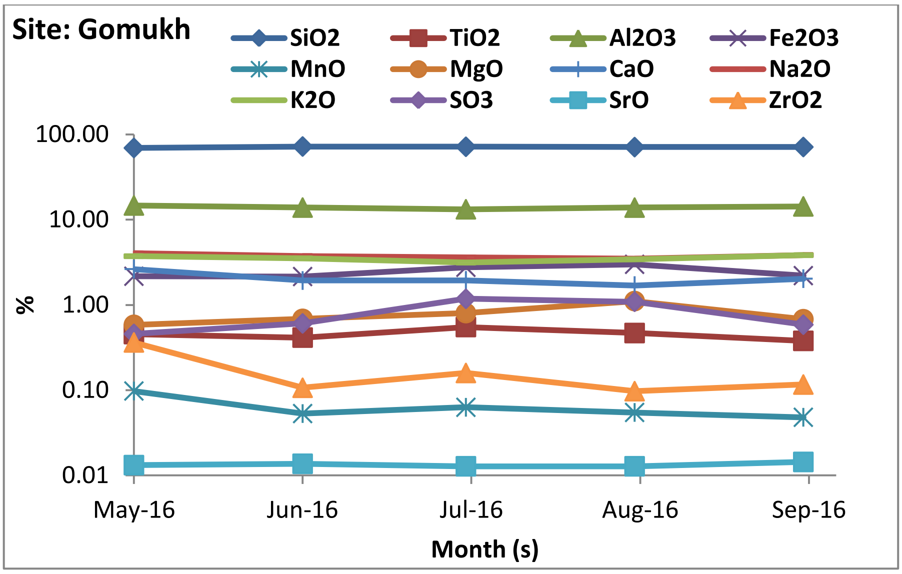
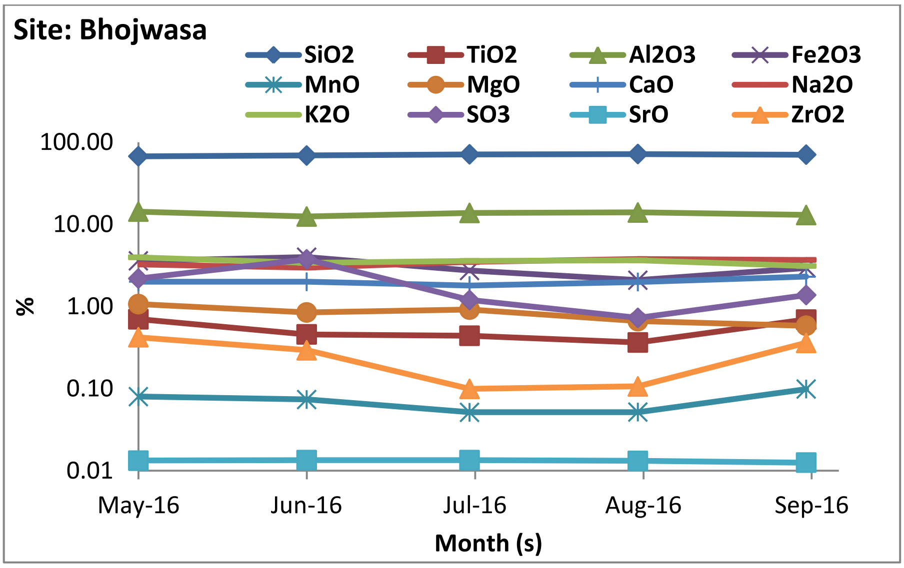


Fig. 6.6 Variation of % of elemental oxides in suspended sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri





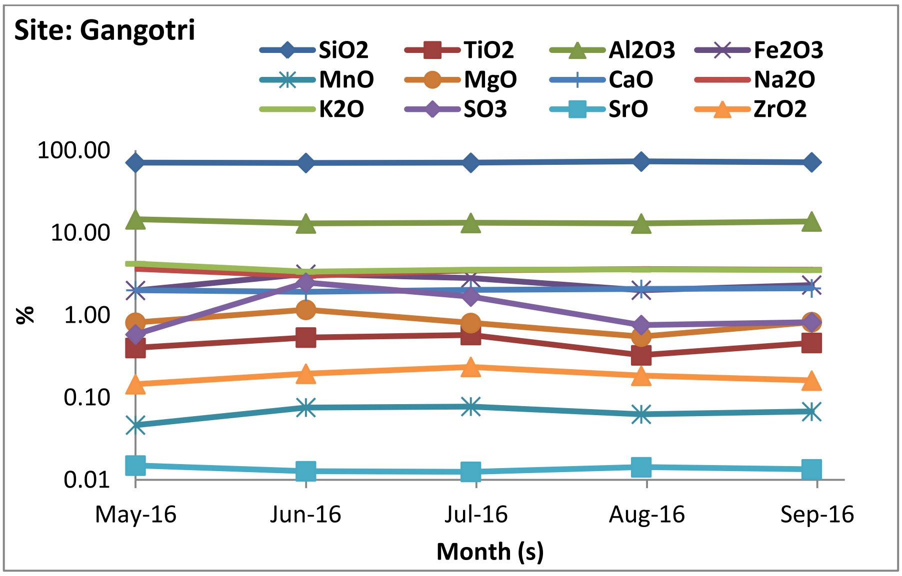


Fig. 6.7 Variation of % of elemental oxides in bed sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri

Chapter 7

MELTWATER-GLACIAL SEDIMENT INTERACTION

Laboratory experiments have been widely used to study the kinetics and mechanism of mineral dissolution (e.g. Wollast, 1967; Busenberg and Clemency, 1975; Plummer et al., 1978; Holdren and Berner, 1979; Chou et al., 1989; Nagy and Lasaga, 1992). However, the knowledge of the rates of reactions controlling meltwater composition is available only qualitatively, and there have been few studies of the sources of solutes transported by meltwaters or the way in which these are determined by the nature of the hydrological environment at the glacier portal. Therefore, in order to strengthen chemoglacial interpretations, gap needs to be filled up (Brown et al., 1994a, 1996a; Fairchild et al., 1994; Sharp et al., 1995a; Tranter et al., 1989, 1993). Controlled laboratory studies of water-rock interaction, constrained by field data from the glacier in question, have allowed the effects of different geochemical parameters (e.g. water: rock ratio, sediment particle size, crushing, repeated wetting and proton availability) on solute acquisition in subglacial channels to be isolated and quantified. For understanding of low temperature solute acquisition, dissolution experiments of glacial meltwater – suspended and bed sediment interaction were carried out considering different operating variables viz; contact time, seasonality, different sediment particle sizes, different sediment dose, effect of pH, effect of wetting and crushing of sediment. Suspended and bed sediments of River Bhagirathi collected from Gomukh, Bhojwasa and Gangotri during the month of May, June, July, August and September 2016 were used for the experiment. Maximum dissolution was observed from the suspended and bed sediments collected in the month of June. Therefore, further experiments with different operating variables viz;, different sediment particle sizes, different sediment dose, effect of pH, effect of wetting and crushing of bed sediments were carried out on the bed sediment (0-75 µm size fraction) collected from the River Bhagirathi at Bhojwasa in the month of June only. Due to paucity of suspended sediment collected during the period of investigation, the dissolution experiments were restricted to bed sediment as same dissolution trend was observed in case of contact time and seasonality for both suspended and bed sediments in test cases.

7.1 Dissolution Experiments

7.1.1 Effect of contact time

Dissolution experiments on suspended and bed sediments (0-75 µm size fraction) of River Bhagirathi collected from Gomukh, Bhojwasa and Gangotri were carried out upto 3600 seconds (1 hour) for different contact time with sediment dose of 8.0 g/L and equilibrium time was observed to be 600 sec (10 min) for both suspended and bed sediments of all the sites i.e. Gomukh, Bhojwasa and Gangotri (Fig. 7.1). It can be seen that the most of the dissolution occur at first few seconds and very critical for this experiment. This also demonstrates the importance of freshly grinded sediment in the glacial system and its eventual release of ions when in contact with the dilute waters from glacial system. Further progressive increase in EC was observed from Gomukh to Gangotri suggesting the change in sediment surface characteristics/or source (Fig. 7.5). Maximum dissolution was observed from the suspended and bed sediments collected in the month of June indicated by maximum EC value observed in the month of June at all three sites. The same trends were observed for cations Ca^{+2} and Mg^{+2} and anion SO_4^{-2} (Fig. 7.2, 7.3 and 7.4). These experiments indicate that glacial flour is extremely geochemically reactive and more dissolution takes place from bed sediments in comparison of suspended sediments of all three sites.

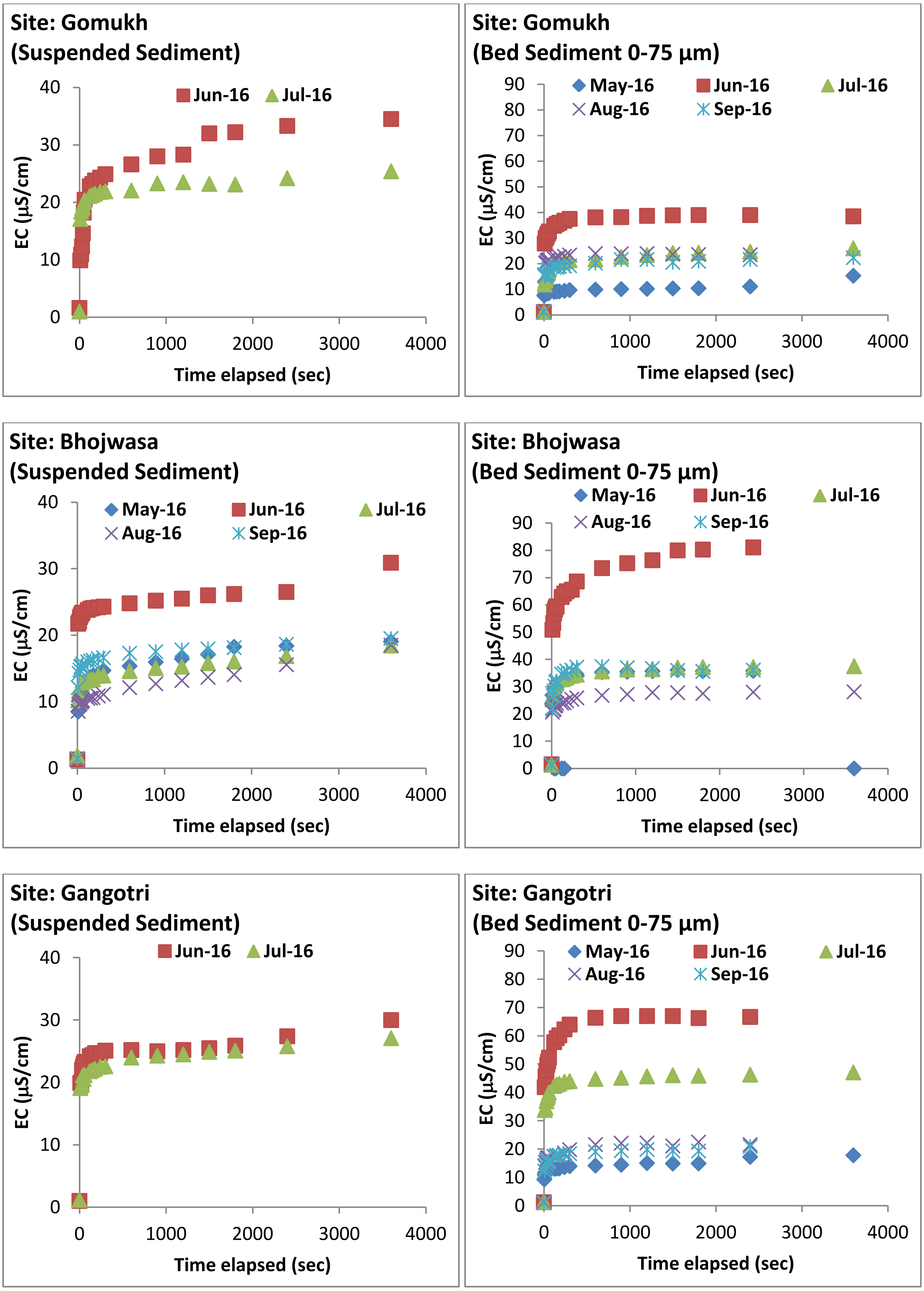


Fig. 7.1 Effect of contact time on EC for suspended and bed sediment

Volume of UPW taken = 250 ml; Background EC of UPW = 1.43 µS/cm; AT = 17.5°C, WT = 1.3°C, pH = 5.67; Sediment Dose = 8.0 g/L, RPM = 500

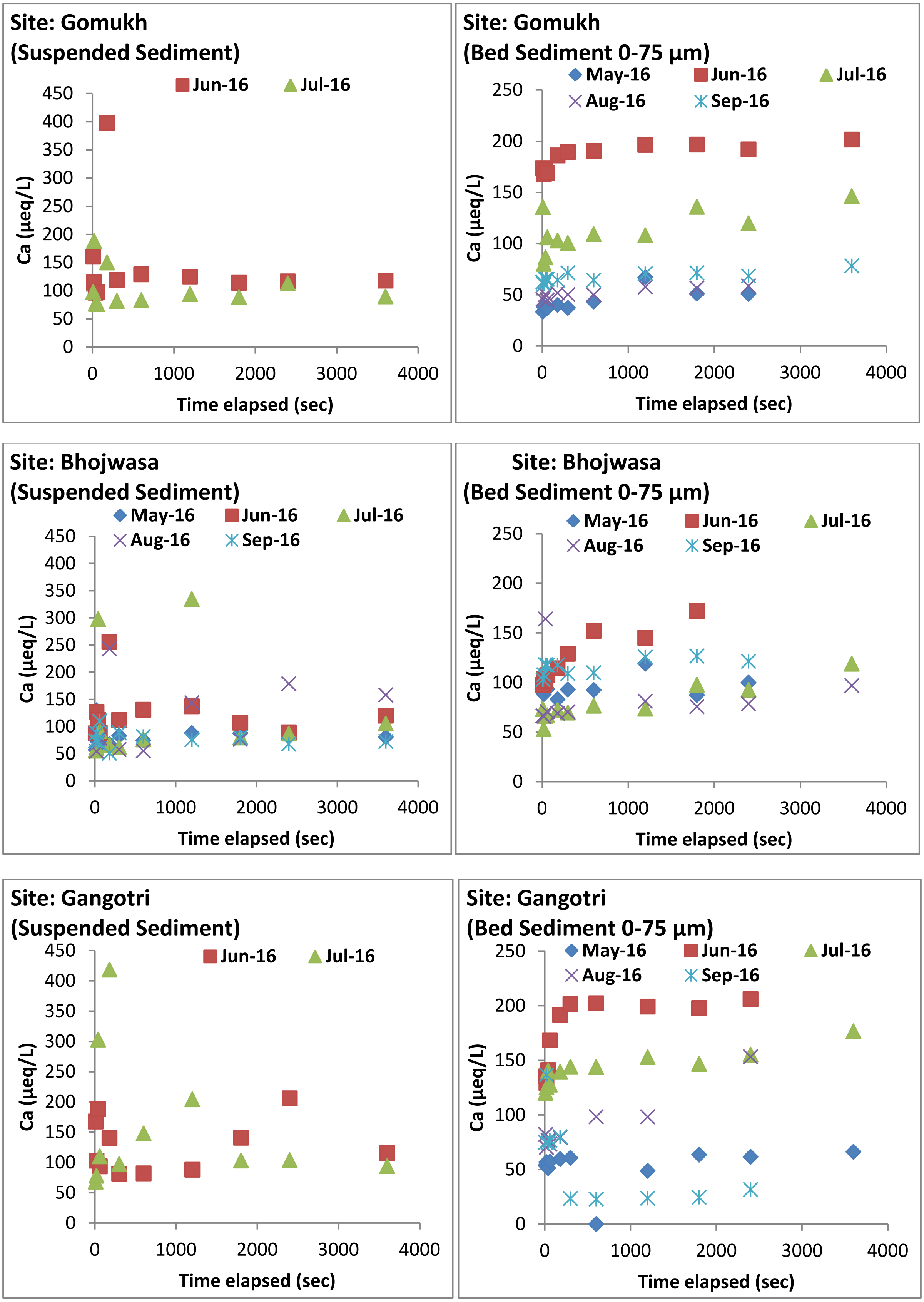


Fig. 7.2 Effect of contact time on Ca^{2+} for suspended and bed sediment
Volume of UPW taken = 250 ml; Background EC of UPW = 1.43 µS/cm; AT = 17.5°C, WT = 1.3°C, pH = 5.67; Sediment Dose = 8.0 g/L, RPM = 500

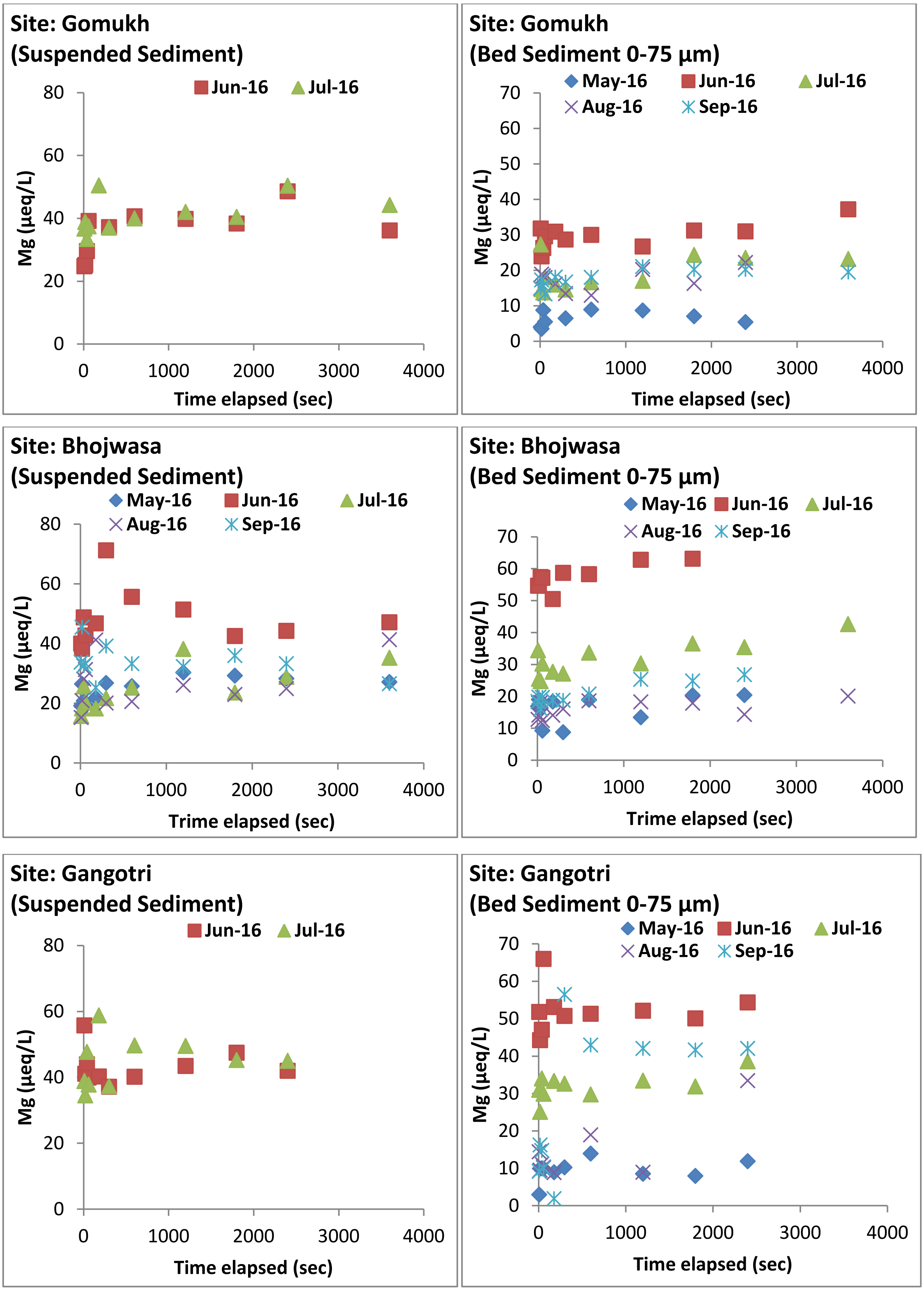


Fig. 7.3 Effect of contact time on Mg^{2+} for suspended and bed sediment
Volume of UPW taken = 250 ml; Background EC of UPW = 1.43 µS/cm; AT = 17.5°C, WT = 1.3°C, pH = 5.67; Sediment Dose = 8.0 g/L, RPM = 500

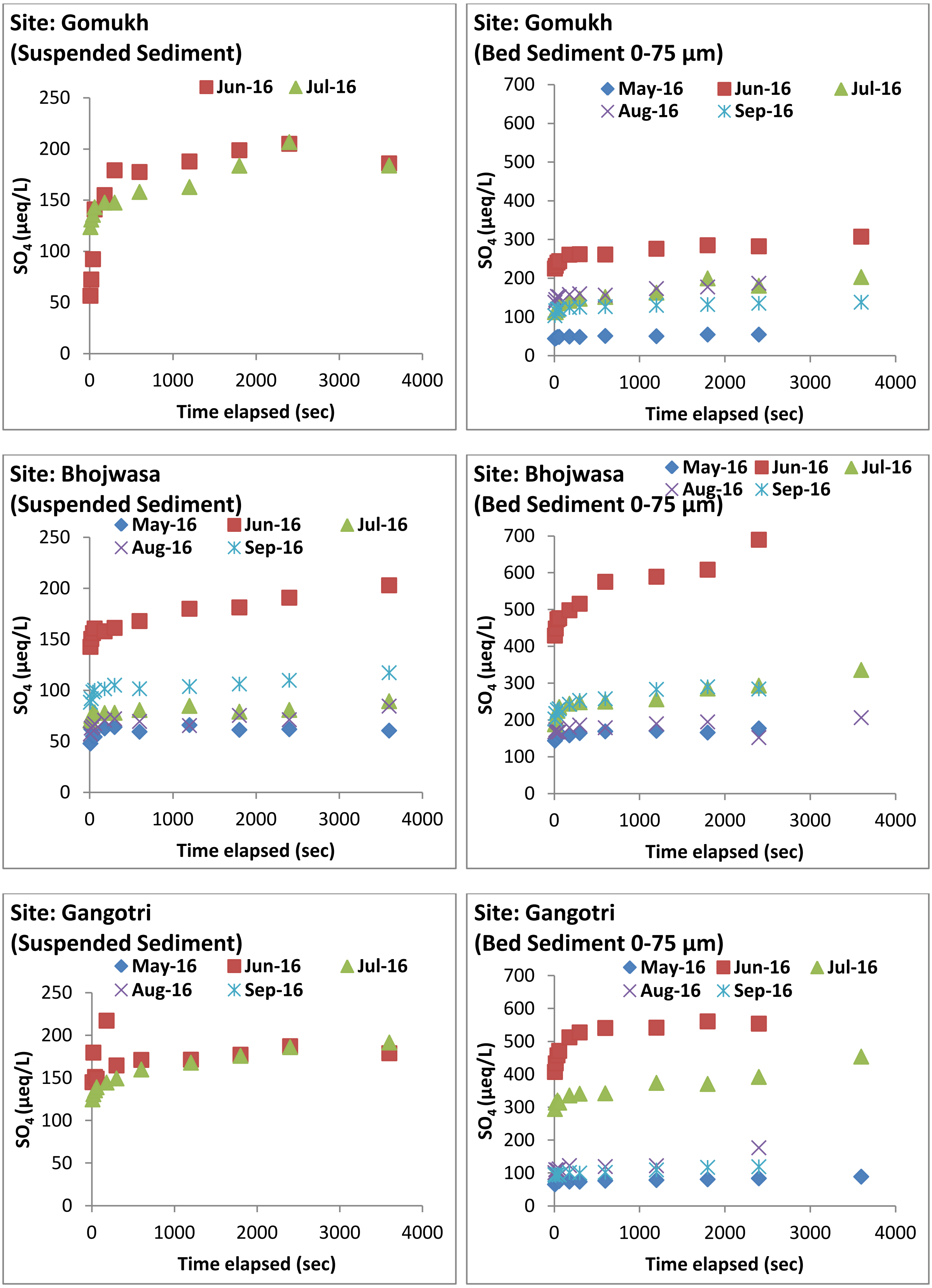


Fig. 7.4 Effect of contact time on SO_4^{2-} for suspended and bed sediment
Volume of UPW taken = 250 ml; Background EC of UPW = 1.43 µS/cm; AT = 17.5°C, WT = 1.3°C, pH = 5.67; Sediment Dose = 8.0 g/L, RPM = 500

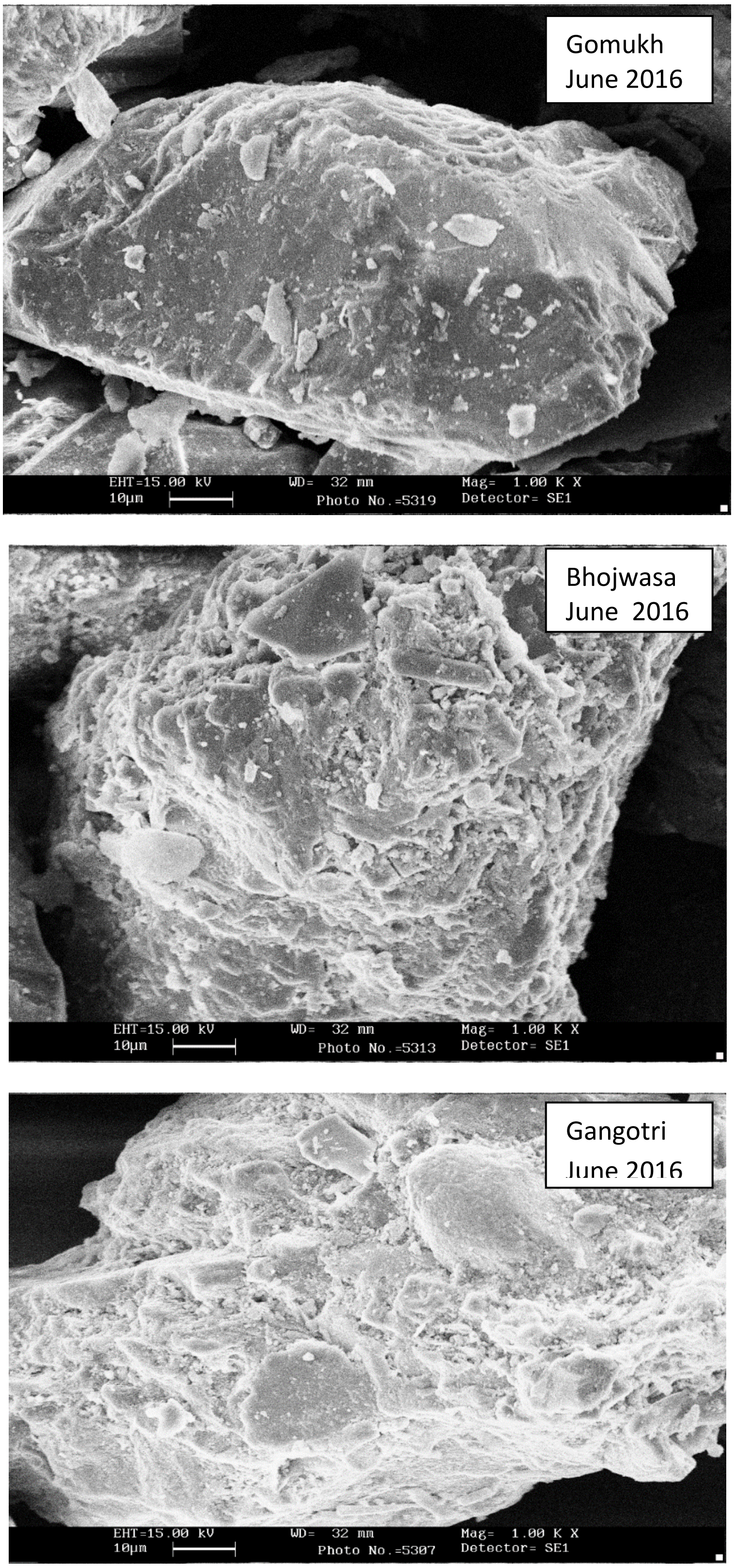


Fig. 7.5 SEM images of bed sediments of River Bhagirathi at Gomukh, Bhojwasa and Gangotri collected during the month of June 2016

7.1.2 Effect of sediment particle size

The experiments were conducted on bed sediment of River Bhagirathi collected from Bhojwasa during the month of June 2016 with different sediment particle sizes (0-75, 75-150, 150-210, 210-250 and 250-300 μm) of each sediment dose of 8.0 g/L. Surface area of the sediment particle (and hence the no. of reactive surface sites available), which increase with decreasing grain size, directly affects the rate at which meltwater acquires solute (Fig. 7.6). As dissolution progresses, the rate of solute acquisition (and resultant proton consumption) slows, which implies i) the dissolution and disappearance of microparticles ii) the disappearance of reactive calcite and aluminosilicate sites and iii) the progression towards saturation of the solution. The similar findings are arrived in the experimental investigation on the sediments from proglacial plain of Haut Glacier d'Arolla, Valais, Switzerland (Brown et al., 1996a).

7.1.3 Effect of sediment doses

The experiments were carried out on bed sediment (0-75 micron size fraction) of River Bhagirathi collected from Bhojwasa during the month of June 2016 with different sediment doses viz; 2.0, 4.0, 6.0, 8.0 and 12.0 g/L. The dissolution is faster with higher sediment dose, which reflects that reaction rate is clearly a function of the solid to solution ratio and hence the reactive solid surface area (Fig. 7.7). The similar findings are arrived in the experimental investigation on the sediments from proglacial plain of Haut Glacier d'Arolla, Valais, Switzerland (Brown et al., 1996a).

7.1.4 Effect of crushing of sediment

Very large tractive forces operate at the base of a glacier, favouring in crushing and grinding of subglacial bedrock and sediments. These subglacial physical weathering processes produce an abundance of fine particles with fresh, reactive mineral surfaces, which are susceptible to dissolution. These processes have further important effects on the morphology of the individual mineral grains which may enhance the solubility of the solid and the rate constant for dissolution (Brown et al., 1996a). To investigate this hypothesis, bed sediment of River Bhagirathi collected from Bhojwasa during the month of June 2016 was crushed from 75-150 micron to 0-75 micron and the dissolution experiment was carried out on this sediment fraction. Higher solute acquisition was observed from crushed sediment because of abundance of fine particles with more fresh, reactive mineral surfaces which are susceptible to dissolution (Fig. 7.8). The similar findings are arrived in the experimental investigation on the sediments from proglacial plain of Haut Glacier d'Arolla, Valais, Switzerland (Brown et al., 1996a).

7.1.5 Effect of wetting of sediment

The characteristic rate laws defining solute release during dissolution experiments may change over time. Power law dissolution kinetics is linked with high initial solute release, followed by slower quasi-linear release as the duration of rock to water contract increases. This indicates the destruction of microparticles adhering to mineral grains, the removal of fresh reactive surface sites, dissolution of rapidly weathered minerals such as calcite and evolution towards to equilibrium of the solution. Wetting history of the sediment in the hydrological system may also affect rates of solute aquisition. To investigate this hypothesis, bed sediment (0-75 micron size fraction) of River Bhagirathi collected from

Bhojwasa during the month of June 2016 was wetted for 2 hours and then dried at 50ºC. The dissolution experiment was carried out on this dried sediment. The solute released from wetted sediment is significantly lower than the fresh sediment which may be attributed to the destruction of microparticles adhering to mineral grains, the removal of fresh reactive surface sites, dissolution of rapidly weathered minerals such as calcite and evolution towards to equilibrium of the solution (Fig. 7.9). The similar findings are arrived in the experimental investigation on the sediments from proglacial plain of Haut Glacier d'Arolla, Valais, Switzerland (Brown et al., 1996a).

7.1.6 Effect of pH

The effect of initial water composition on the rate of dissolution operates mainly through the hydrogen ion concentration (H^+) of the solution, which promote acid hydrolysis reactions (Raiswell et al., 1980; Raiswell, 1984; Curtis, 1976). These aqueous protons are derived from two main sources in the glacier system; the dissolution and dissociation of atmospheric carbon dioxide, and the oxidation of sulphide minerals such as pyrite. Protons may also be derived from the dissolution of acid deposition [e.g. $H_2SO_4(s)$, $HNO_3(s)$] (Tranter et al., 1993), especially early in the snowmelt season when snowmelt is most acidic. Another important dissolved substance in the glacier meltwater is dissolved oxygen, as the decay of oxidizable minerals such as sulphides requires the presence of dissolved O_2 (Tranter et al., 1993; Brown et al., 1994a).

The role of solution chemistry in laboratory dissolution studies has been widely reported (e.g. Wollast, 1967; Deju and Bhappa, 1965; Petrovic et al., 1976; Holdren and Berner, 1979). Such studies show that the initial reaction rate is a simple function of pH and hence distinctly lower rate laws apply to higher pH solutions. Thus variability in the source and abundance of protons may have important implications for the rate and magnitude of solute acquisition from suspended sediment in glacial environments (Brown et al., 1996b). To investigate this hypothesis, the experiments were carried out on bed sediment (0-75 micron size fraction) of River Bhagirathi collected from Bhojwasa during the month of June 2016 with sediment dose of 8.0 g/L at different pH viz; 4.23, 4.94, 5.76 and 7.20 and higher dissolution was observed with decrease in pH, which may be attributed to availability of more hydrogen ion concentration of the solution, which favours more solute acquisition from sediment into meltwater (Fig. 7.10). The similar findings are arrived in the experimental investigation on the sediments from proglacial plain of Haut Glacier d'Arolla, Valais, Switzerland (Brown et al., 1996a).

The relationship between mineral weathering rates derived under laboratory conditions and rates of geochemical reactions in natural systems requires careful consideration (cf. Casey et al., 1993; Velbel, 1993), and has received comparatively little attention in the glaciological literature. Chemical weathering rates calculated from mass-balance studies in natural watersheds may be more than 3 orders of magnitude slower than in the laboratory (e.g. Schnoor, 1990; Drever, 1994; Hoch et al., 1999) suggesting that either rate constants may be lower in nature or that environmental factors alter some other term in the rate equation (Velbel, 1993). Velbel (1993) suggests that, rather than compositionally- or chemically-driven differences between weathering rates in nature and in the laboratory, physical processes (e.g. hydrological) factors are responsible. This may reduce the reactive surface area available for weathering as a result of processes such as heterogeneous flow in pore/fracture networks and soils.

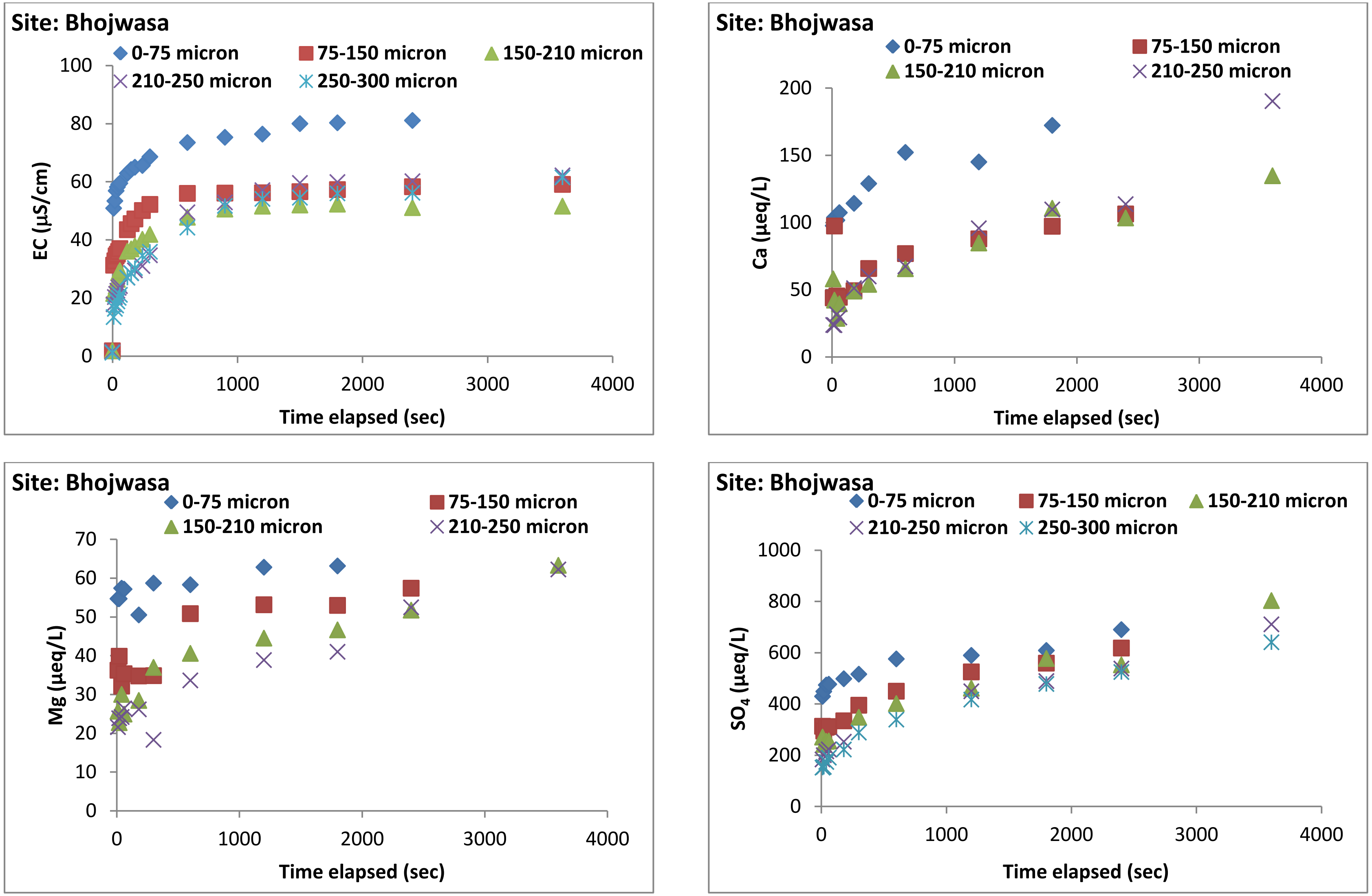


Fig. 7.6 Effect of sediment particle sizes on EC, Ca^{+2}, Mg^{+2} & SO_4^{-2}

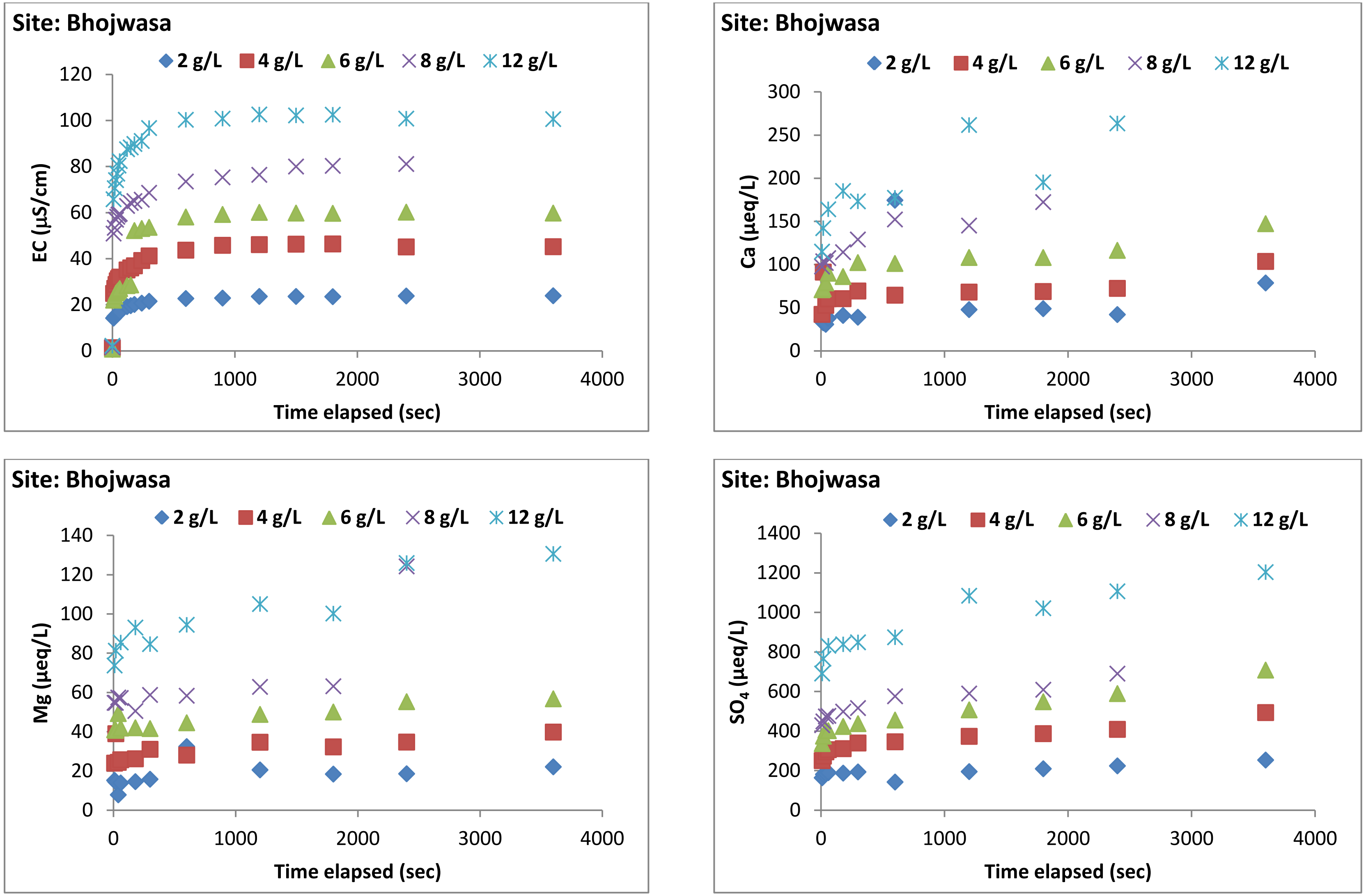


Fig. 7.7 Effect of sediment particle doses on EC, Ca^{+2}, Mg^{+2} & SO_4^{-2}

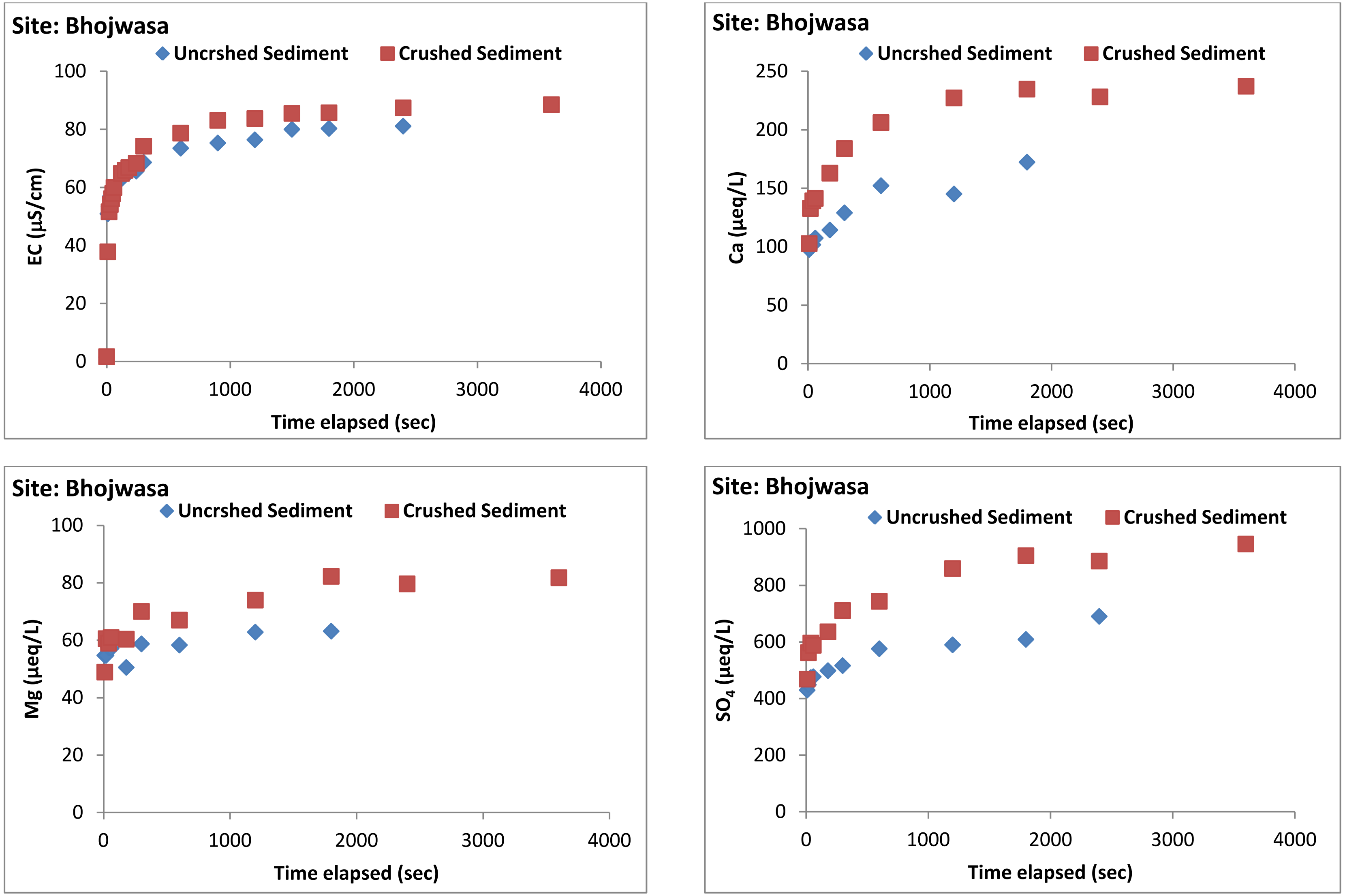


Fig. 7.8 Effect of crushing of sediment on EC, Ca^{+2}, Mg^{+2} & SO_4^{-2}

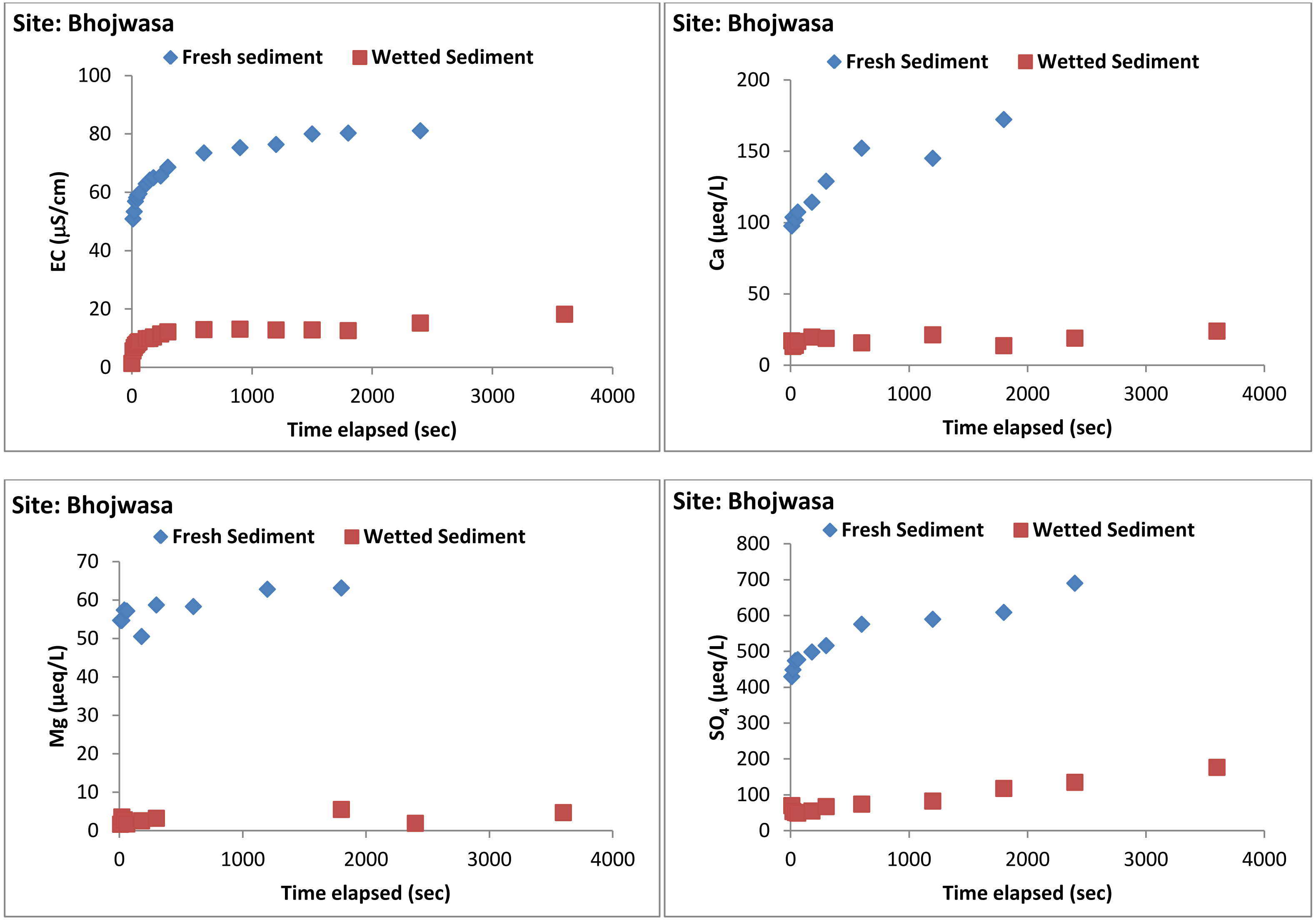


Fig. 7.9 Effect of wetting of sediment on EC, Ca^{+2}, Mg^{+2} & SO$_4^{-2}$

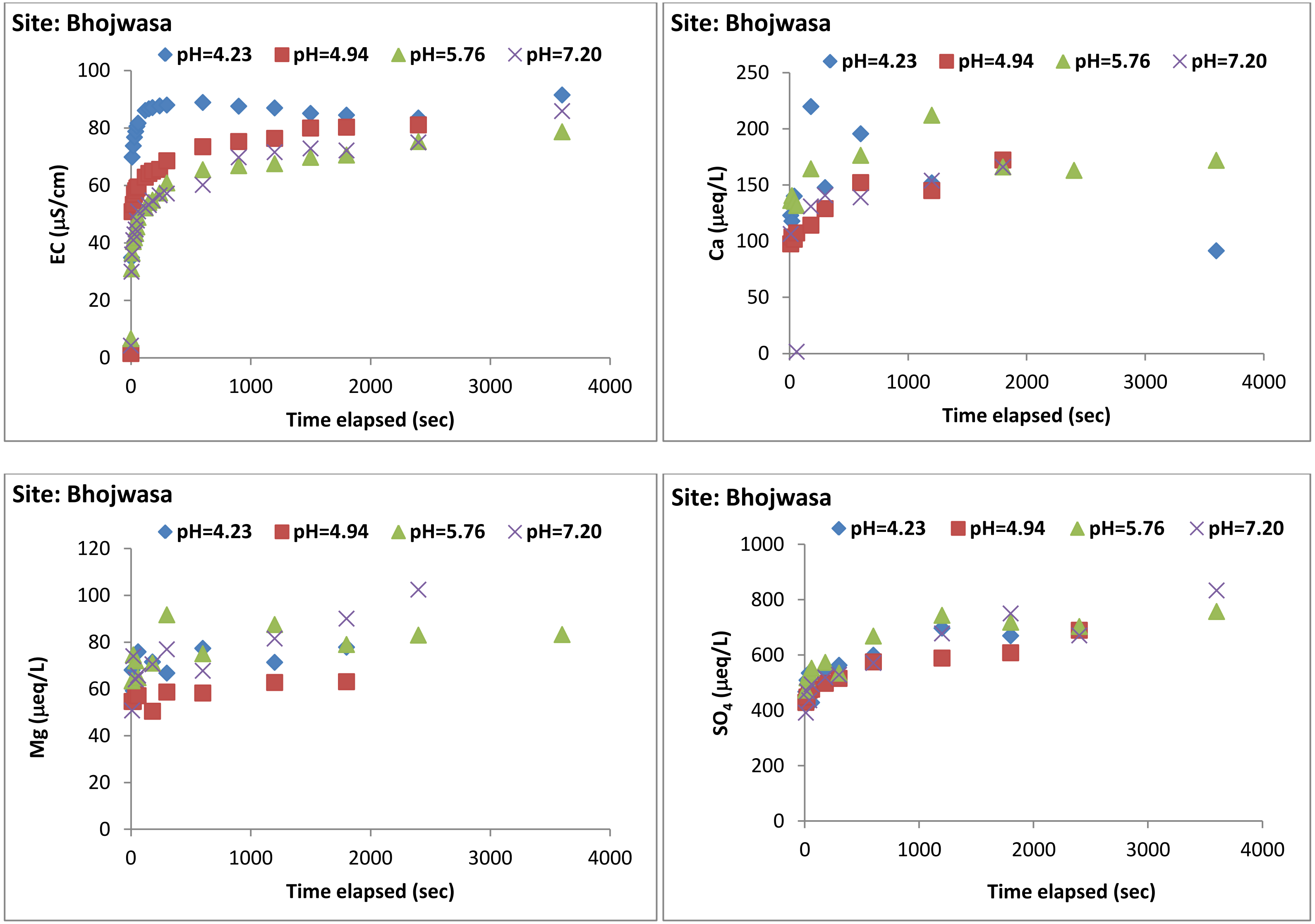


Fig. 7.10 Effect of pH on EC, Ca^{+2}, Mg^{+2} & SO_4^{-2}

Chapter 8

OPEN- AND CLOSED-SYSTEM CHARACTERISTICS

Low temperature ionic enrichment and dissolution in a glacial environment is unique in many ways. Melt water received at the glacier snout is being transported through number transport pathways in the glacier. Big glaciers are perennial source of water with pressure melting sustaining the flow during the cold winter months which has high ionic concentrations due to its contact with the subglacial sediments and also due to higher residence time within the glaciers due to slow velocity. As melting period starts, significant amount of meltwater is transported through the glacier surface. As snow cover recede over the glacier surface, the subglacial distributed channel system also get integrated. This system receives meltwater from the glacier's surface and depending on the development of the englacial conduit system including moulins and crevasses. This multiple transport pathways of meltwater in a glacial system are seasonally evolving. Gangotri glacier is a large glacier and with a length of about 28 km, the largest of the Ganga system. About 4-5 kms of glacial surface is heavily debris covered limiting the chances of developing extended supraglacial channels system. Hence these meltwaters generated at the higher elevations contribute to the subglacial drainage system and undergo slow movement within the distributed network. This allows the water to be in contact with the freshly grinded subglacial sediments within the glacier and under ionic enrichment process mostly probably under the closed system environment. Once the meltwater emerge at the snout mixed with high sediment concentration, the system gets exposed in the open environment. Such closed system characteristics may be modified by re-equilibration with atmospheric CO_2 or ground water mixing to give bulk meltwaters with open-system characteristics (Thomas and Raiswell, 1984). In the present investigation, the study of open- and closed-system characteristics of the Gangotri glacier system at Gomukh, Bhojwasa and Gangotri have been attempted using observed comparative data of HCO_3, SO_4, C-ratio and $p(CO_2)$ value.

8.1 Effective CO_2 Pressure

The open and closed system are defined based on the relationship between the partial pressures of atmospheric CO_2 (g) with that of aqueous CO_2 (aq). In the aqueous system proton consumption is mainly controlled by carbonate equilibria (Raiswell, 1984). Thus, continued weathering of the rock minerals in contact with the meltwater depends on H^+ supply through the dissolution of $CO_2(g)$ to form $H_2CO_3^*$ [where $H_2CO_3^* = CO_2(aq) + H_2CO_3(aq)$]. However, the reaction $CO_2(g) \leftrightarrow CO_2(aq)$ is generally slower than the reactions which consume $H_2CO_3^*$. Therefore the amount of CO_2 in solution [$CO_2(aq)$] relative to the partial pressure of CO_2 in the overlying gas phase [$p(CO_2)$] provides a relationship between reactions that supply protons and those that consume them, establishing a natural basis for the classification of subglacial weathering regimes (Raiswell, 1984; Tranter et al., 1993; Brown, 2002). The effective CO_2 pressure or internal CO_2 pressure [log $p(CO_2)$]can be evaluated from pH values and HCO_3^- concentration using the following equation:

$$logp(CO_2) = \log(HCO_3^-) - pH + pKCO_2 + pK_1 \quad (5)$$

Where $pKCO_2 = 1.11$, and $pK_1 = 6.58$, assuming a water temperature of 0°C (Ford and Williams, 1989).

Since the values of constants (i.e. pKCO$_2$ = 1.11, and pK$_1$ = 6.58) have been taken assuming a water temperature of 0°C, but in case of Gangotri glacier system, water temperature varies from 0.3 to 1.5°C at Gomukh, from 0.1 to 4.0°C at Bhojwasa and from 1.0 to 7.0°C at Gangotri and not 0°C. Therefore, the values of these constants at different temperatures were calculated using the values given in Table 8.1 and p(CO$_2$) values of meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri for 0830 hour, 1730 hour and their mean during the year 2014, 2015 and 2016 were calculated and plotted in Fig. 8.1(a-c). The p(CO$_2$) trend for 0830 hour and 1730 hour is same as that for their mean value, therefore, for further discussion, mean value of p(CO$_2$) is taken.

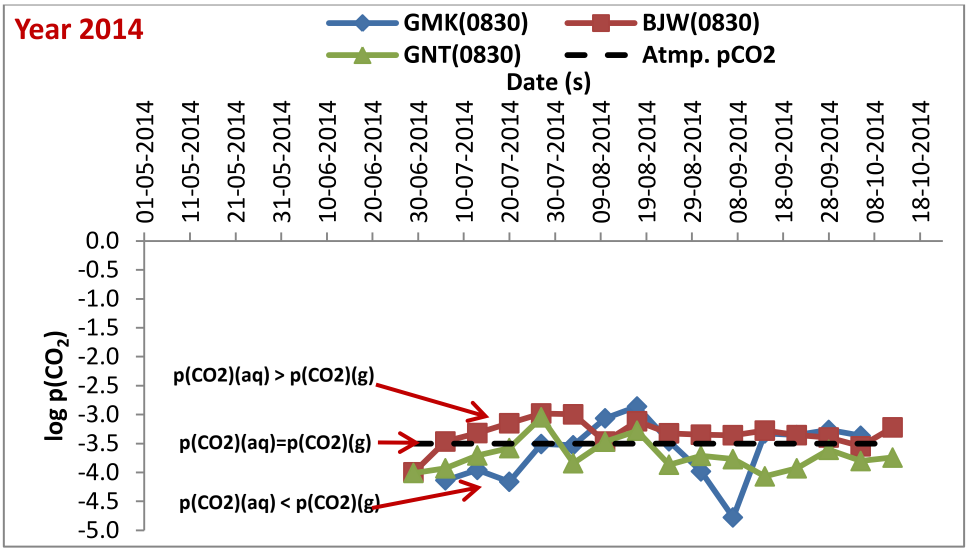
Table 8.1 Equilibrium constants for the carbonate system

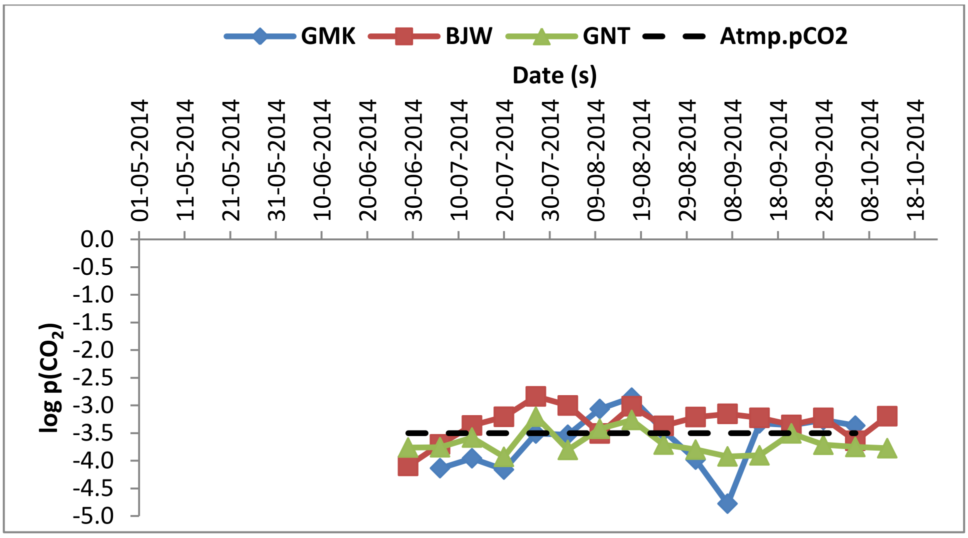
T (°C)	pKCO$_2$	pK$_1$
0	1.11	6.58
5	1.19	6.52
10	1.27	6.46
15	1.34	6.42
20	1.41	6.38
25	1.47	6.35
30	1.52	6.33
45	1.67	6.29
60	1.78	6.29
80	1.90	6.34
90	1.94	6.38

Source: Drever (1997)

The p(CO$_2$) of a solution reveals the rate at which CO$_2$ diffuses into or out of solution relative to the rate of other chemical weathering reactions (Raiswell 1984; Raiswell and Thomas, 1984; Thomas and Raiswell, 1984). The p(CO$_2$) signature of meltwater can characterize different glacial hydrological weathering environments (Sharp 1991; Wadham et al., 1998). The system is said to be open when proton supply equals the consumption, the p(CO$_2$) of the solution remains in the equilibrium with the atmosphere i.e. $[p(CO_2)(aq) = p(CO_2)(g)]$. While the system is said to be closed if p(CO$_2$) of solutions is not equal to atmospheric pCO$_2$ ($10^{-3.5}$atm), it can be said to be in disequilibrium with respect to the atmosphere and the two sets of reactions proceed at different rates, $[p(CO_2)(aq) \neq p(CO_2)(g)]$. Closed system low p(CO$_2$) conditions arises when protons are consumed more rapidly than they are supplied. This may happen when large quantities of reactive rock material comes into contact with relatively pure water (Tranter et al., 1993). This decreases the p(CO$_2$) of the meltwater so the solution is in apparent equilibrium with an atmosphere which is depleted in CO$_2$, favouring CO$_2$ influx across the air-meltwater interface. Conversely, closed system high p(CO$_2$) conditions occur when protons are supplied to solution more rapidly than they are consumed (Tranter et al., 1993). In glacial system, this may occur from an input of aqueous protons (e.g. from snowmelt or sulphide oxidation), freezing of meltwaters (which excludes CO$_2$ from the growing ice lattice), and /or the neutralization of acidity by bicarbonates.

$$CaCO_3(s) + 2H^+(aq) \leftrightarrow Ca^{2+}(aq) + H_2O(l) + CO_2(g) \qquad (6)$$





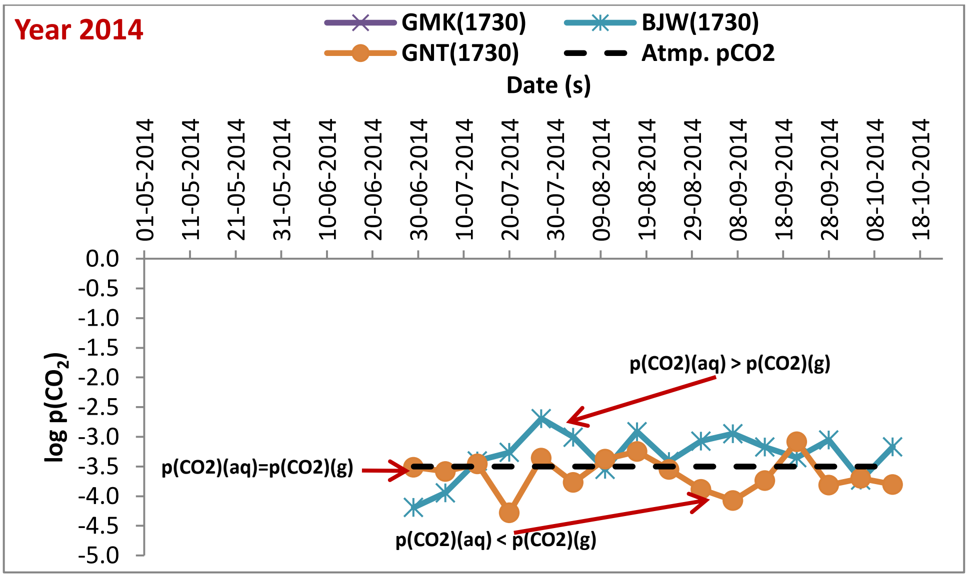


Fig. 8.1(a) Variation of $p(CO_2)$ in the meltwater of River Bhagirathi at 0830, 1730 hours and mean at Gomukh, Bhojwasa and Gangotriduring the year 2014

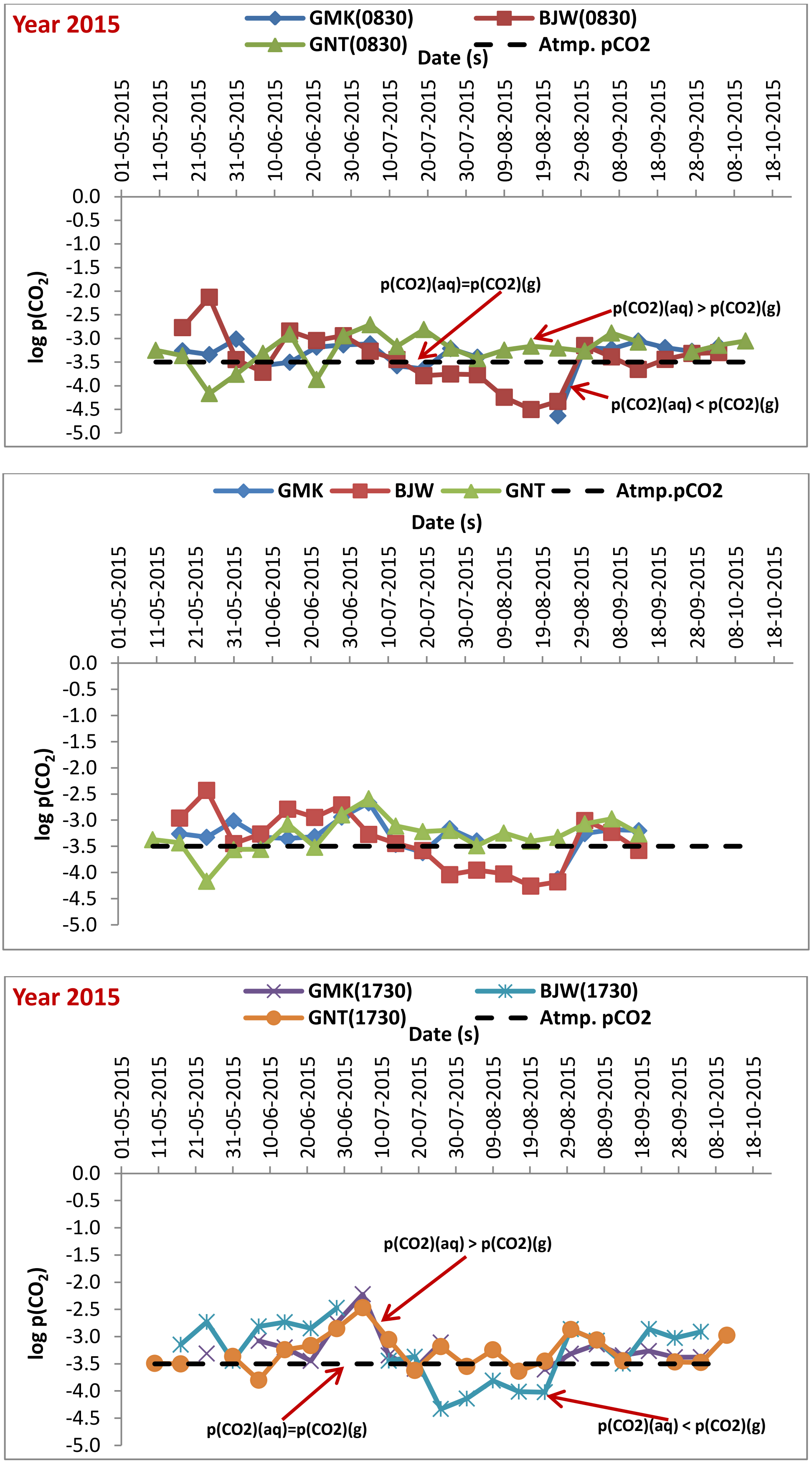


Fig. 8.1(b) Variation of $p(CO_2)$ in the meltwater of River Bhagirathi at 0830, 1730 hours and mean at Gomukh, Bhojwasa and Gangotriduring the year 2015

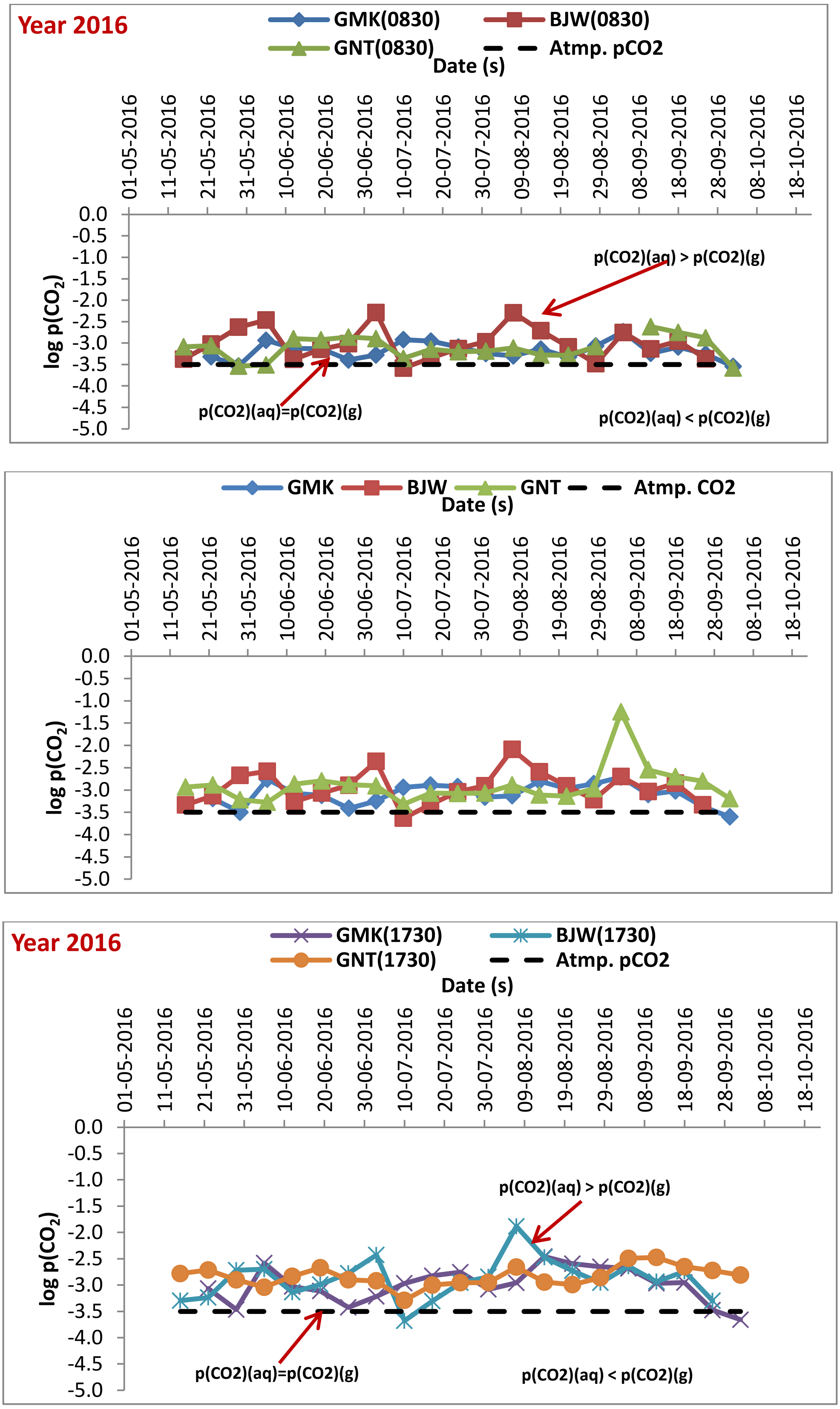


Fig. 8.1(c) Variation of $p(CO_2)$ in the meltwater of River Bhagirathi at 0830, 1730 hours and mean at Gomukh, Bhojwasa and Gangotriduring the year 2016

Note that closed system $p(CO_2)$ conditions may arrise from either physical conditions (e.g. closed channel flow, where there is no air-meltwater interface for CO_2 influx or efflux) or kinetic factors (e.g. when the rate of CO_2 transfer across the gas-water interface is slower than H^+ consumption during acid hydrolysis reactions) (Brown, 2002).

8.2 Assessment of Open- and Closed-System Response of Gangotri Glacier Meltwater

As mentioned in the previous section, the assessment of inter-annual and seasonal variations of open- vs closed- system behaviour of Gangotri glacier meltwater is carried out at Bhojwasa, around 4 km downstream of glacier snout, where discharge is monitored. The system characteristics were assessed by the $pCO_2(aq)$ variations. The $pCO_2(aq)$ values are determined weekly and shown in the Fig. 8.2. The system assessment also carried out from Gomukh to Gangotri along the stream continuum to study nature of CO_2 dissolution in open environment and resultant changes in the stream chemistry. Fig. 8.2 clearly suggests that the stream at Bhojwasa show the characteristics of high $p(CO_2)$ closed system for all the years and seasons except for short durations especially during a month (August) in 2015. There are very few random sample which showed open system characteristics. The high pCO_2 closed system is produced by a combination of factors. The closed system characteristics in the open environment, after the stream left from its glacier confines, is driven by the sulphate dominant rock in the study area and suspended sediment concentration and supported by C-ratio, pH apart from $p(CO_2)$. For example, short duration low pCO_2 closed system prevalence in the year 2015 is associated with low suspended sediment concentration (SSC) and high pH. This is also linked with prolonged snow cover in the higher altitude region during the year, which lead to the under development of the subglacial drainage system and resultant low sulphide oxidation.

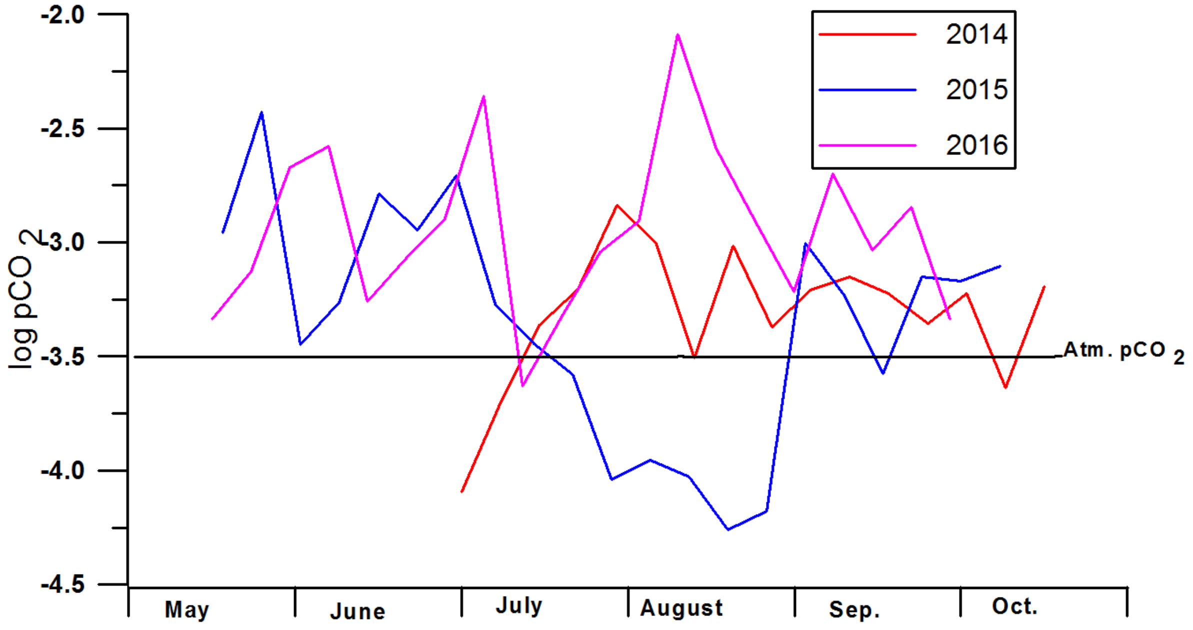


Fig. 8.2 Inter-annual seasonal variations on $p(CO_2)$ proglacial stream of Gangotri glacier at Bhojwasa

8.3 Inter-annual and Seasonal Variations of Closed-System Process in Meltwater of River Bhagirathi at Bhojwasa

Daily variation of discharge, TSS, pH, HCO_3, SO_4 and C-ratio in the meltwater of River Bhagirathi at Bhojwasa is shown in Fig. 8.3. The following insight dominance of high $p\mathrm{CO}_2$ on closed system characteristics of River Bhagirathi, its origin could be derived from Fig 8.3.

Discharge hydrograph of 2014 shows sharp rising and falling limb and persistent high flow period covering entire month of July. Year 2015 shows a prolonged rising limb with delayed peak flows occurring in the months of August (7th August). This suggests that the snow cover in the catchment persisted for longer duration in 2015. Peak discharge was subdued with discharge peaking on 15th July in the year 2016. The delay in peak discharge in the year 2015 may attributed to the delayed snowmelt from higher elevations of the Gangotri catchment as revealed from the assessment of snow cover variations during these three years. The discharge characteristics in a glacial system have direct bearing on the sediment transfer characteristics. It is also linked with the development and progression of subglacial channel network (Thayyen et al., 1999) as subglacial zone is the major source area of glacial sediments. The sediments, which get deposited throughout the winter period gets evacuated during the early stages of subglacial channel development. In 2014 and 2016, this early evacuation of sediment is clearly visible in the data. However, the year 2015 did not experience any significant sediment evacuation neither during the initial stage nor later. Low sediment flux was observed in the year 2015, which may be attributed to the under development of subglacial drainage system. Study of snow cover persistence over the glacier vindicated this assessment as the year 2015 experienced prolonged snow cover at higher elevations of the basin as suggested earlier. This high discharge low SSC scenario has influenced the comparatively high pH (>7.0) observed during the high flow period in the year 2015, which may be attributed to the higher surface melt contribution from prolonged snow cover in the basin and also associated with under development of subglacial zone during the year, limiting the pyrite oxidation which results in less production of proton (H^+) ions and thereby increasing the pH.

In the year 2014 and 2016, HCO_3 concentration did not show any significant seasonal variations as expected of a glacial system. Generally, rising and falling limb of the hydrograph is associated with concentrated waters dominated from subglacial system. This suggests the domination of subglacial enrichment and sediment interaction throughout the ablation season. Given the large glacier cover in the catchment, this suggests that most of the surface melt, even during the peak flow period is routed through the subglacial system. While during the year 2015, high HCO_3 concentration associated with a delayed discharge peak is observed (Fig.8.3) which may be attributed to contribution from supraglacial system having debris and prolonged snow cover at higher elevations of the basin. The main source of SO_4 concentration in meltwater is pyrite oxidation in sublacial system. During 2014 and 2016, SO_4 concentration did not show significant seasonal variation as in the case of HCO_3. But during the year 2015, SO_4 concentration is attenuated during seasonal high flows suggesting reduced transit time within the subglacial zone supporting our pervious observation that the subglacial system is under developed during 2015. This is also supported by the absence of major sediment peaks during 2015 neither during the initial stage nor later. The relative importance of two major proton producing reactions - carbonation and sulphide oxidation can be evaluated on the basis of the C-ratio. During rising limb of the hydrograph in the year

2014 and 2016, C-ratio varies from low value 0.17 to 0.45 overwhelming sulphide oxidation within the glacier and resulting into a high *p*(CO_2) closed system conditions. In the year 2015, C-ratio attains upto 0.62 value during rising limb of hydrograph following trend of discharge and higher values compared to the year of 2014 and 2016 during falling limb of the hydrograph implying contribution from supraglacial system. Higher pH observed during the higher HCO_3 during the 2015 peak flow period suggest domination of carbonation reaction during this specific period, which resulted into a low *p*(CO_2) closed system conditions. The results can be summarised that the Gangotri glacier system is dominated by high *p*(CO_2) closed system associated due to higher proton release from oxidation of sulphides and low *p*(CO_2) closed system during the times of prolonged snow cover and under developed subglacial drainage system.

8.4 Inter-annual and Seasonal Variations of Closed-System Process in Meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri

Similar exercise was carried out to study how the observed closed system characteristics propagate from glacier snout at Gomukh to Gangotri along the stream continuum. Weekly variations of pH, TSS, HCO_3, SO_4, C-ratio and log *p*(CO_2) in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016 are shown in Fig. 8.4(a-d).

HCO_3 concentration was found to be increasing steadily from Gomukh to Bhojwasa during the complete ablation period of the year 2014, while during the year 2015 and 2016, it was higher at Bhojwasa followed by Gomukh and Gangotri during rising limb of the hydrograph and it was higher at Gangotri followed by Gomukh and Bhojwasa during falling limb of the hydrograph (Fig. 8.4). Overall HCO_3 concentration was higher either at Bhojwasa or at Gangotri**,** which may be attributed to the dominance in stream carbonate dissolution or from the contributions from non- glacierized areas of the catchment. Higher value of SO_4 concentration was observed in the meltwater of River Bhagirathi at Gomukh followed by Gangotri and Bhojwasa during the complete ablation period of the year 2014, 2015 and 2016 suggesting that the sulphide oxidation attenuate from glacier portal to downstream**.**

As mentioned earlier, the C-ratio, evaluates the relative importance of two major proton producing reactions - carbonation and sulphide oxidation, was estimated in the meltwaters of river Bhagirathi at Gomukh, Bhojwasa and Gangotri during the period of investigation of the year 2014, 2015 and 2016. Higher value of C-ratio was observed in the meltwater of River Bhagirathi at Gangotri followed by Bhojwasa and Gomukh during the complete ablation period of the year 2014, while during the year 2015 and 2016, it was higher at Bhojwasa followed by Gangotri and Gomukh during rising limb of the hydrograph and it was higher at Gangotri followed by Bhojwasa and Gomukh during falling limb of the hydrograph (Fig. 8.3). Overall C-ratio was very low at the mouth of the glacier i.e. at Gomukh, followed by Gangotri and Bhojwasa in rising limb of hydrograph and at Bhojwasa and Gangotri in falling limb of the hydrograph, which suggest that pyrite oxidation remain as major proton producing reaction throughout the river stretch from Gomukh to Gangotri. Further, higher C-ratio at Gomukh, Bhojwasa and Gangotri during peak flow period during the year 2015 implies that the effect of glacier system persist up to Gangotri and beyond.

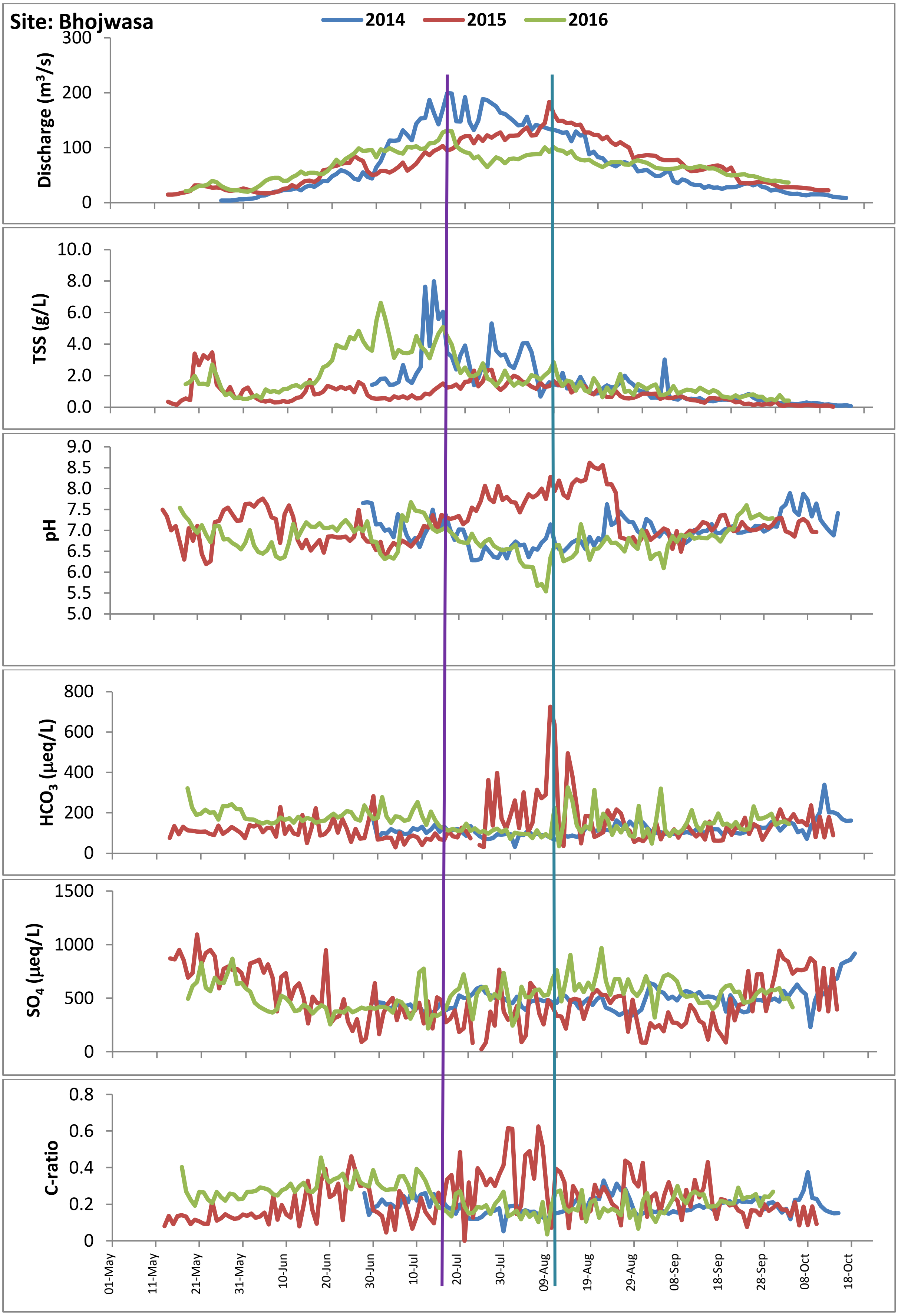


Fig. 8.3 Daily variation of discharge, TSS, HCO_3, SO_4 and C-ratio in the meltwater of River Bhagirathi at Bhojwasa

In the year 2014, the $p(CO_2)$ value for meltwater at Gomukh shows seasonal variations moving between low $p(CO_2)$ closed system conditions and high $p(CO_2)$ closed system conditions. During the year 2015 & 2016, $p(CO_2)$ value for meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri was higher than the atmospheric value indicating closed system high $p(CO_2)$ condition except closed system low $p(CO_2)$ at Bhojwasa during peak flow period of the year 2015. This is a global trend that river water shows disequilibrium with the atmosphere (Garrels and Mackenzie, 1971; Raymahasay, 1986). The slightly higher values of $p(CO_2)$ could be explained by the relative higher rate of solubility in comparison to release of excess of CO_2 gas in a turbulent and low temperature environment (Stumm and Morgan, 1970). High $p(CO_2)$ values are likely to arise from the coupling of sulphide oxidation and carbonate dissolution (Wadham et al., 1998) and low $p(CO_2)$ values may be attributed to large supply of comminuted rock material plus pure water in the system. Over all this study concludes that from the origin at Gomukh to 14 km downstream at Gangotri, River Bhagirathi remains under closed system conditions, in which high $p(CO_2)$ closed system conditions dominates. The sediment concentration and subglacial activities play a major role in this process and influence of glacier system extend to downstream reaches as well. How far this influence persists beyond Gangotri needs to be studied further. Persistence of high $p(CO_2)$ closed system implies that the excess proton (H^+) is continued to be available in the system further downstream of glaciers and may have significant impact on further evolution of chemistry of headwater tributaries of River Ganga. The higher sulphate flux during the seasonal high flows was suggested as unique characteristics of River Ganga headwaters in a study conducted on Dokriani glacier in the Bhagirathi catchment earlier (Hasnain and Thayyen, 1999) as compared to its Alpine counterparts. Similar observations during this study for the largest glacier of the basin underline this characteristic and suggest that it is a regional phenomenon. Further studies are required to assess its impact on biotic systems in the upper reaches and its downstream effect.

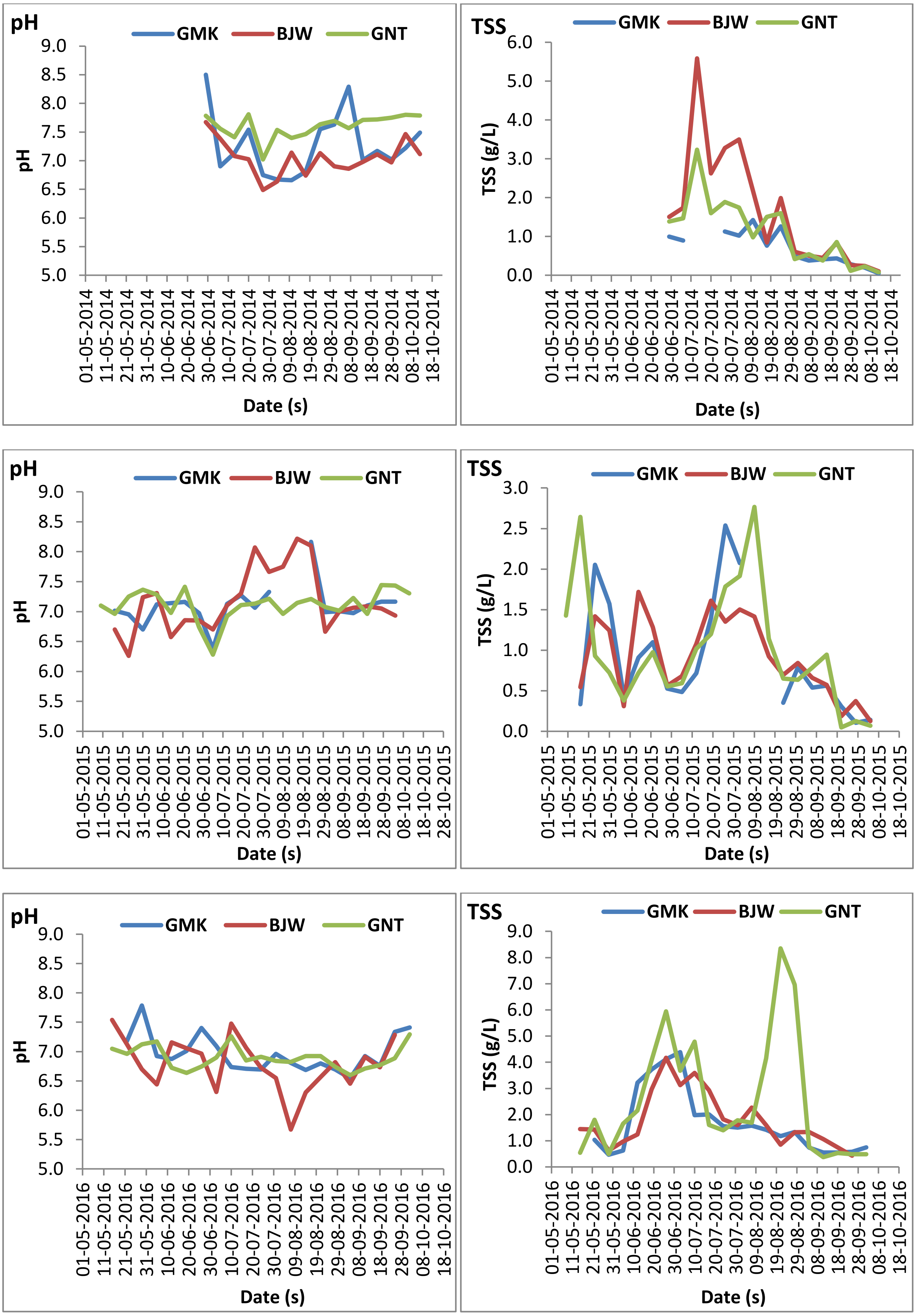


Fig. 8.4(a) Weekly variation of pH and TSS in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016

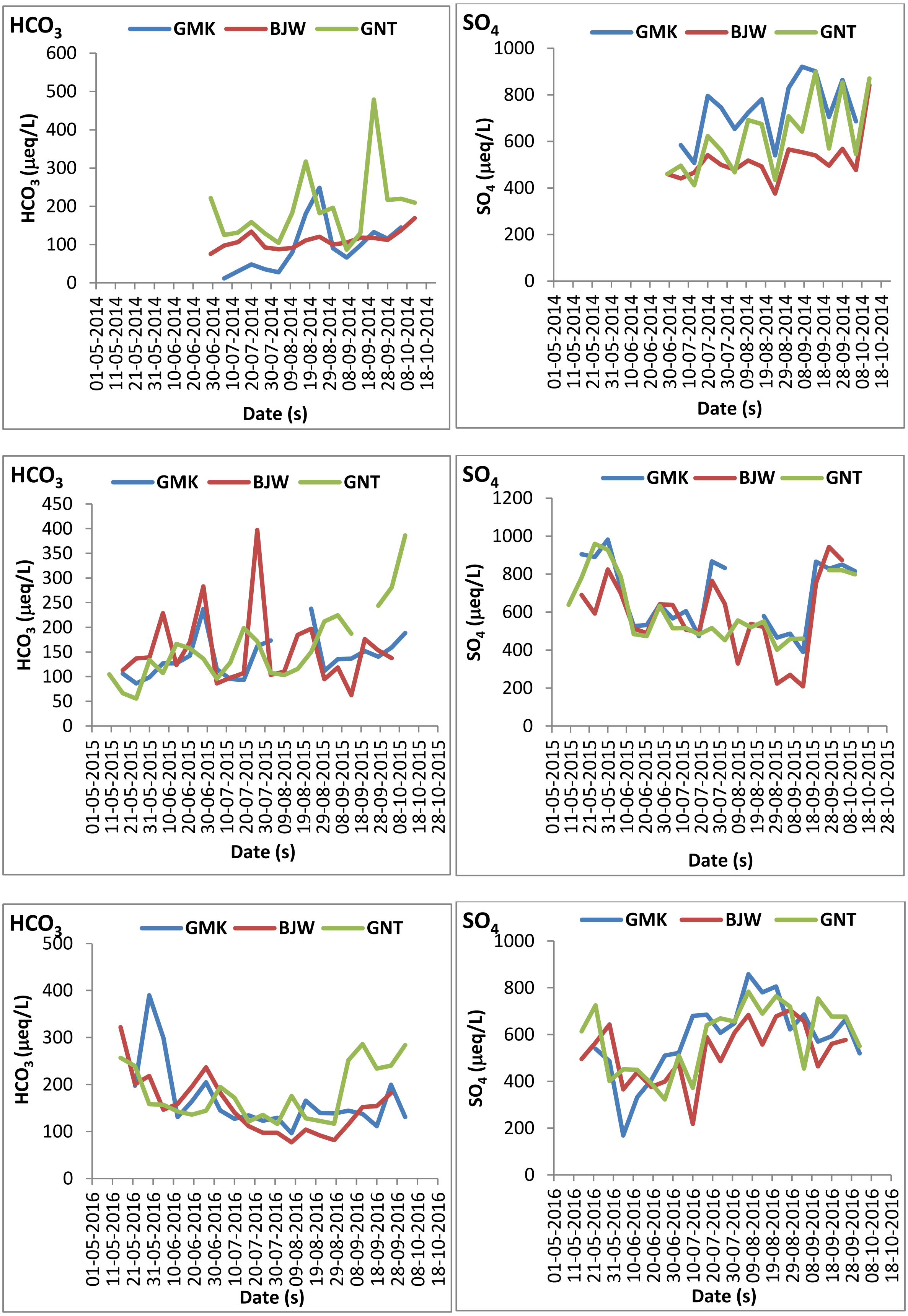


Fig. 8.4(b) Weekly variation of HCO_3 and SO_4 in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016

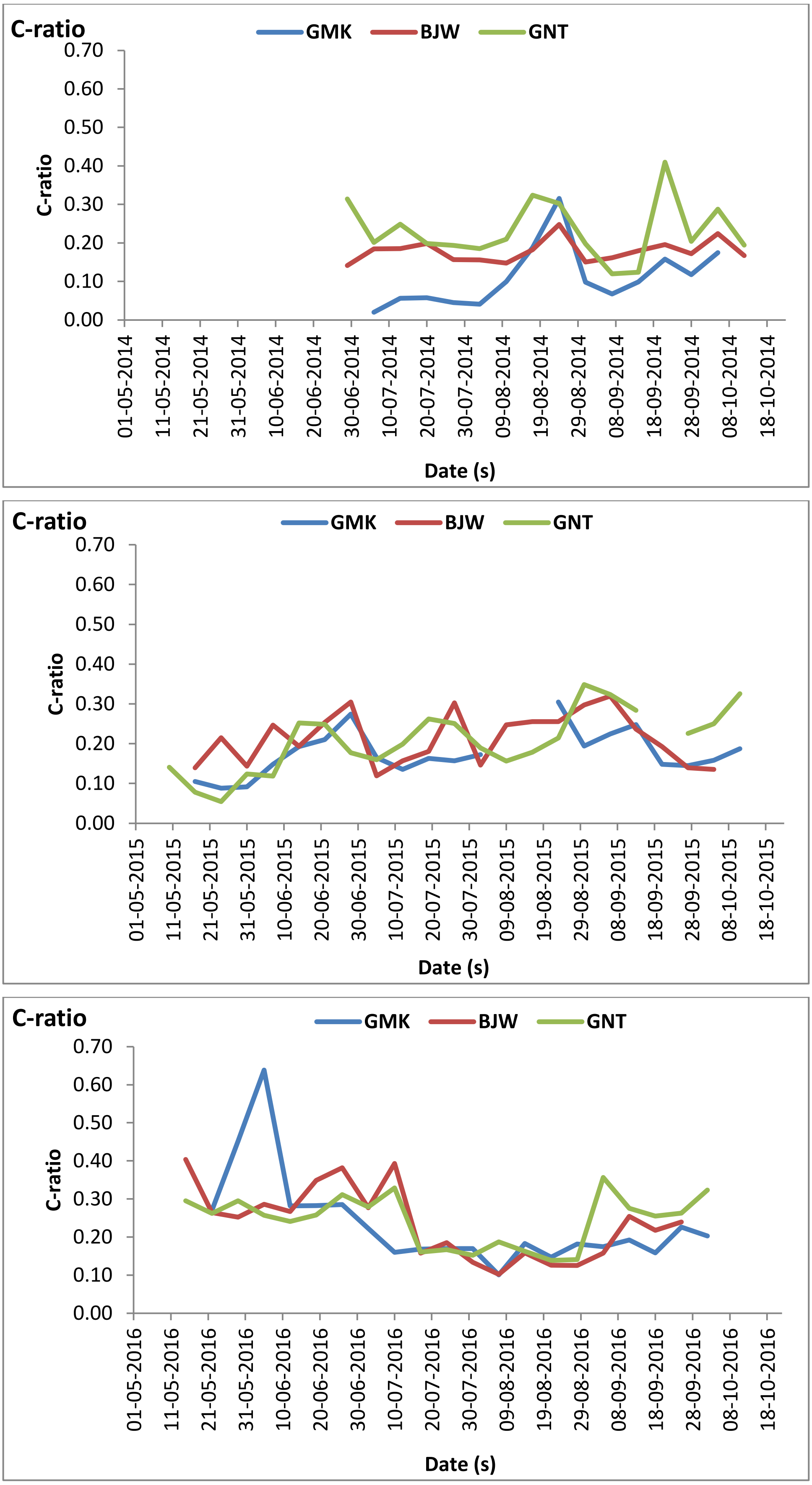


Fig. 8.4(c) Weekly variation of C-ratio in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016

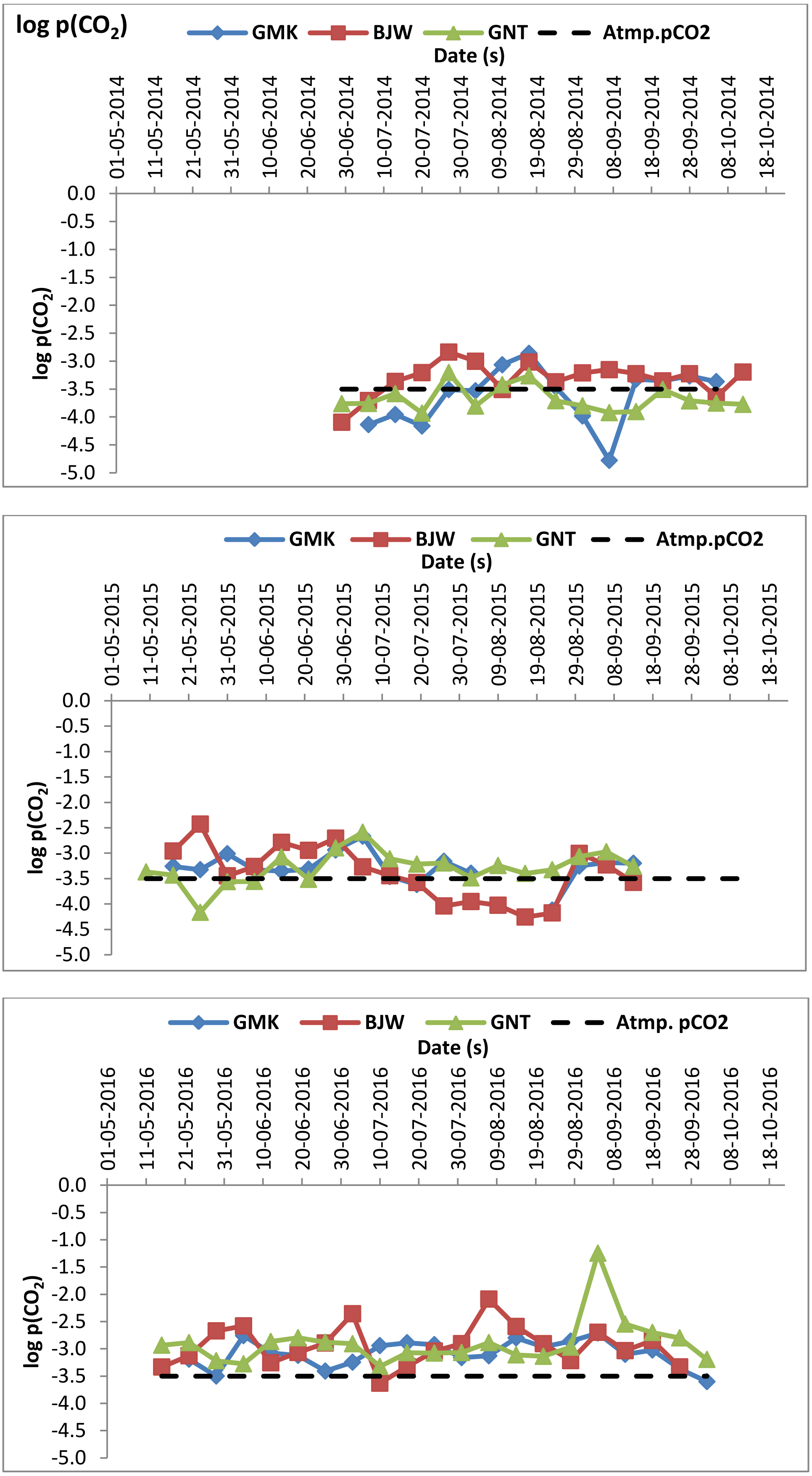


Fig. 8.4(d) Weekly variation of *p*(CO_2) in the meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri during the year 2014, 2015 and 2016

Chapter 9

CONCLUSIONS

The Gangotri glacier is one of the biggest and most important glaciers in the Himalayan region as well as the source of River Ganga. In the present investigation, the study of the dynamics of solute acquisition by dilute glacier waters in interaction with freshly grinded glacier sediments was carried out at snout at Gomukh, 4 km downstream at Bhojwasa and further 14 km downstream at Gangotri under prevailing low temperature conditions. The main sources of production of sediment from the glacier fed channels are bedrock system (glacier bottom ice and bed rock), glacier system (sedimentation from different part of glacier such as snout, ablation zone, accumulation zone and lateral moraines) and channel system. High suspended sediment concentration in melt season was observed in the meltwater of River Bhagirathi from Gomukh to Bhojwasa, mainly driven by the subglacial processes.

pH plays an important role in low temperature chemical process in controlling the solute acquisition during suspended sediment-meltwater interaction and also indicative of the processes producing protons. Lowest pH value in the meltwater of River Bhagirathi was observed at Gomukh followed by Bhojwasa and Gangotri, which may be attributed to dominance of oxidation of sulphide at Gomukh followed by Bhojwasa and Gangotri, which contributes large number of protons (H^+) during oxidation in the meltwater of River Bhagirathi at Gomukh and thereby reducing the pH. Electrical conductivity (EC) represents the ionic enrichment characteristics of the meltwater. High value of EC in the meltwater of River Bhagirathi was observed at Gomukh followed by Bhojwasa and Gangotri, which may be attributed to interaction of meltwater with freshly grinded sediment at Gomukh resulting high solute acquisition of meltwater of River Bhagirathi at Gomukh.

The hydro-chemical analysis of collected filtered meltwater samples from River Bhagirathi at Gomukh, Bhojwasa and Gangotri revealed that Ca^{2+} and Mg^{2+} were the dominant cations of total cations at all the three sites, followed by K^+ and Na^+ at Gomukh and by Na^+ and K^+ at Bhojwasa and Gangotri during the period of investigation (2014-2016). While SO_4^{2-} and HCO_3^- were the dominant anions followed by Cl^- and NO_3^- at all the three sites. Two major anions, HCO_3 and SO_4, in glacial meltwaters are mainly derived from the dissolution of atmospheric carbon dioxide and carbonates weathering and the oxidation of sulphides. HCO_3 concentration was highest at Bhojwasa followed by Gangotri and Gomukh, suggesting enhanced carbonate dissolution at Bhojwasa as compared to Gangotri and Gomukh while SO_4 concentration was highest at Gomukh followed by Gangotri and Bhojwasa, suggesting dominance of oxidation of sulphide within the glacier system as appeared at Gomukh followed by Gangotri and Bhojwasa. Further, average metal concentration of Fe, Zn and Cu was observed higher in meltwater of River Bhagirathi at Gomukh as compared to Bhojwasa and Gangotri because of evolution of Gangotri glacier from Gomukh.

Inter-annual variations of solute and sediment fluxes in a glacial system are closely linked to the discharge variations. On a year to year basis, these variations could be linked to the variations in the atmospheric temperature or winter and summer precipitation. Snow cover variations play a crucial role in glacial systems as it is widely accepted that the development of subglacial drainage system closely follows that of snow cover in upper elevations, which in turn is responsible for chemical and sediment flux in these rivers.

Discharge hydrograph of the year 2014 and 2016 shows sharp rising and falling limb and persistent high flow period covering entire month of July. Year 2015 shows a prolonged rising limb with delayed peak flows occurring in the months of August (7th August). The delay in peak discharge in the year 2015 may attributed to the delayed snowmelt from higher elevations of the Gangotri catchment as revealed from the assessment of snow cover variations during these three years. Suspended sediment concentration (TSS) in glacial meltwaters is directly linked with the discharge variations. TSS concentration is also linked with the development and progression of subglacial channel network as subglacial zone is the major source area of glacial sediments. Generally, in glacial systems, TSS concentration peaks just before the discharge peak and seasonal hysteresis between discharge and TSS concentration is often reported. The sediments, which get deposited throughout the winter period gets evacuated during the early stages of subglacial channel development. In 2014 and 2016, this early evacuation of sediment is clearly visible in the data. TSS in the year 2015 was remarkably low as compared to 2014 and 2016. Under development of subglacial drainage system could be the reason for such a low sediment flux during 2015.

The relative importance of two major proton producing reactions – sulphide oxidation and carbonation can be calculated on the basis of the ($HCO_3/HCO_3 + SO_4$) ratio, called the C-ratio. Very low average C-ratio for meltwater of River Bhagirathi at Bhojwasa (0.20-0.24) indicates that the major proton producing reaction is oxidation of sulphide. The coupled reaction involving carbonate and CO_2 dissolution and oxidation of sulphide minerals derived protons, which control the chemistry of meltwater draining from Gangotri glacier.

Solute fluxes usually increase with discharge in an aquatic system. The largest solute fluxes are transported by the most dilute meltwater as solute concentration is usually inversely related to discharge in a glacial system. Fluxes of all major dominating cations (Ca^{+2} and Mg^{+2}) and major dominating anions (HCO_3^- and SO_4^{-2}) follow the same trend as that of discharge and highly correlated. TSS flux and TDS flux are also highly correlated with discharge. The seasonal variations in suspended sediment concentration during the study period may be attributed to the progression of subglacial drainage network development. The distributed channel system in the subglacial zone is dormant during winter season with less water availability and high overburden pressure of glacier ice. As melt season progresses, more and more snow and glacier melt routed to the subglacial zone and the distributed channel spread to the higher elevations of the glacier. Higher sediment flux events from glacier are also indicative of good integration of distributed system. These processes are also linked with the solute acquisition in the meltwater, which could be distinctly different for Alpine and Himalayan glacier systems.

Chemical and physical denudation rates are important in solute acquisition studies. These rates are very high in high altitude Himalayan drainage system. The cation denudation rate of Gangotri glacier meltwater at Bhojwasa were evaluated to be 34.1, 67.3 and 30.7t km^{-2} y^{-1} for rising limb, peak flow and falling limb of the annual hydrograph respectively. This is higher than the recorded value at other glaciers of the world which lie in the range of 9.7 to 17.4 t km^{-2} y^{-1}. The physical weathering rate of the Gangotri glacier catchment was evaluated to be 3864, 11805 and 1230 t km^{-2} y^{-1} for rising limb, peak flow and falling limb of the annual hydrograph respectively. This is much higher than the average erosion rate of Indian sub-continent (327 t km^{-2} y^{-1}) and world (150 t km^{-2} y^{-1}). The presence of large and active glaciers and relatively younger age of the Himalayan mountains with their high seismicity, intense monsoon rainfall and steep valleys with frequent avalanching are responsible for this high rates of erosion in the Himalayan region.

In glacierized catchments, large ablation-driven diurnal discharge variations affects glacier meltwater chemistry. Diurnal variation in hydro-chemistry of meltwater revealed that a sharp change (decrease) in the electrical conductivity of meltwater between 1200 hours to 1500 hours was observed, which may be attributed to dilution effect due to higher rate melting because of higher air temperature during this period. Almost same trend are observed for major cations and anions. Variability in the dilution of solute rich subglacial flow with respect to the ground environment by dilute surface glacier meltwater causes variation in the dissolved ion concentration of meltwater draining from the glacier.

Surface characteristics of sediments play an important role in solute acquisition during freshly grinded sediment-meltwater interaction. The sediments derived from Gangotri glacier are mineral grains and not rock fragments. Further, suspended sediment of the site Gomukh of River Bhagirathi has higher potential of chemical dissolution as compared to other sites i.e. Bhojwasa and Gangotri. XRF analysis of suspended and bed sediments revealed that taking into account the SiO_2 and Al_2O_3 concentrations, it can theorize the abundance of feldspar mineral in the source rock.

For understanding of low temperature solute acquisition, Dissolution experiments of glacial meltwater- sediment interaction were conducted on bed sediments of River Bhagirathi considering different operating variables viz; contact time, seasonality, different sediment particle sizes, different sediment dose, effect of pH, wetting and crushing of bed sediments. Equilibrium time was observed to be 600 sec (10 minute). Further progressive increase in EC was observed from Gomukh to Gangotri suggesting change in sediment surface characteristics/or source. Maximum dissolution was observed from the bed sediments collected in the June. Dissolution increases with increase in sediment doses but decreases with increase in sediment particle size fraction. Higher solute acquisition was observed from crushed sediment because of abundance of fine particles with fresh, reactive mineral surfaces which are susceptible to dissolution. The solute released from wetted sediment is significantly lower than the fresh sediment, which may be attributed to the destruction of microparticles adhering to mineral grains, the removal of fresh reactive surface sites, dissolution of rapidly weathered minerals such as calcite and evolution towards to equilibrium of the solution. Further, higher dissolution was observed with decrease in pH, which may be attributed to availability of more hydrogen ion concentration of the solution, which favours more solute acquisition from sediment into meltwater.

Low temperature ionic enrichment and dissolution in a glacial environment is unique in many ways. Melt water received at the snout is being transported through number transport pathways in the glacier. This multiple transport pathways of meltwater in a glacial system are seasonally evolving. Gangotri glacier is a large glacier and with a length of about 28 km, the largest of the Ganga system. About 4-5 kms of glacial surface is heavily debris covered limiting the chances of developing extended supraglacial channels system. Hence these meltwaters generated at the higher elevations contribute to the subglacial drainage system and undergo slow movement within the distributed network. This allows the water to be in contact with the freshly grinded subglacial sediments within the glacier and under ionic enrichment process mostly probably under the closed system environment. Once the meltwater emerges at the snout mixed with high sediment concentration, the system gets exposed in the open environment. Such closed system characteristics may be modified by re-equilibration with atmospheric CO_2 or ground water mixing to give bulk meltwaters with open-system characteristics. The study of open- and closed-system characteristics of the

Gangotri glacier system at Gomukh, Bhojwasa and Gangotri have been attempted using observed comparative data of SO_4, C-ratio and $p(CO_2)$ value as follows:.

- Higher value of SO_4 concentration was observed in the meltwater of River Bhagirathi at Gomukh followed by Gangotri and Bhojwasa during the complete ablation period of the year 2014, 2015 and 2016 suggesting that the sulphide oxidation attenuate from glacier portal to downstream.
- Overall C-ratio was very low at the mouth of the glacier i.e. at Gomukh, followed by Gangotri and Bhojwasa in rising limb of hydrograph and at Bhojwasa and Gangotri in falling limb of the hydrograph which may be attributed to overwhelming pyrite oxidation within the subglacial environment under high $p(CO_2)$ closed system condition at Gomukh and which continued upto Gangotri. Further, improvement in C-ratio at Gomukh, Bhojwasa and Gangotri during peak flow period during the year 2015, which is not observed in case of the year 2014 and 2016, implies the contribution from supraglacial system having debris and prolonged snow cover at higher elevations of the basin.
- The $p(CO_2)$ signature of meltwater can be used to characterize different glacial hydrological weathering environments. When proton supply equals the consumption, the $p(CO_2)$ of the solution remains in the equilibrium with the atmosphere, the system is said to be open. If $p(CO_2)$ of solutions are not equal to atmospheric pCO_2 ($10^{-3.5}$atm), it can be said to be in disequilibrium with respect to the atmosphere and the system is said to be closed. The $p(CO_2)$ value for meltwater of River Bhagirathi originating from Gangotri Glacier at Bhojwasa was slightly higher than the atmospheric value ($10^{-3.5}$) indicating closed system high $p(CO_2)$ weathering while $p(CO_2)$ value for meltwater at Gomukh and Gangotri was slightly lower than the atmospheric value indicating closed system low $p(CO_2)$ condition during the year 2014. During the year 2015 & 2016, $p(CO_2)$ value for meltwater of River Bhagirathi at Gomukh, Bhojwasa and Gangotri were higher than the atmospheric value indicating closed system high $p(CO_2)$ condition except closed system low $p(CO_2)$ at Bhojwasa during peak flow period of the year 2015, which may be attributed to fact that due to under development of subglacial system, significant sediment evacuation could not take place resulting into reduced pyrite oxidation.

Knowledge gaps and future research directions

As per our research findings, closed system conditions persist along the River Bhagirathi from its origin at Gomukh to Gangotri and supported by the prevailing chemical processes of sulphide oxidation, C-ratio and $p(CO_2)$ values. How far this influence persists beyond Gangotri along the river continuum further downstream upto Ganga plain at Hardwar needs to be studied. Further studies are required to assess the impact of this closed system on biotic systems in the upper reaches and its downstream effect.

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PROJECT COMPLETION REPORT

1. Title of the project: Ionic Enrichment Dynamics of Glacial Sediment and Meltwater of Gangotri Glacier, DST No: SB/DGH-49/2013

2. Principal Investigator(s): Dr. M. K. Sharma, Scientist D
Co-Investigator(s): Dr. C. K. Jain, Scientist G
Dr. Renoj J. Thayyan, Scientsit D
Dr. Manohar Arora, Scientistv D
3. Implementing Institution(s): National Institute of Hydrology (NIH), Roorkee
Other collaborating Institution(s): None

4. Date of commencement: 19.05.2014

5. Planned date of completion: 27.07.2017

6. Actual date of completion: 27.07.2017

7. Objectives as stated in the project proposal:

i) To characterize the seasonal variability of the major-ion chemistry of glacial meltwater
ii) Chemical characterization of the suspended sediment of Gangotri glacial system
iii) To study Ionic enrichment dynamics of meltwater-glacial sediment interaction
iv) To investigate open and closed system low temperature ionic enrichment process

8. Deviation made from original objectives if any, while implementing the project and reasons there of: Nil

9. Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs: Please see the Chapters for details.

10. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject: Please see the Chapters for details.

11. Conclusions summarizing the achievements and indication of scope for future work: Please see the Chapter-9 for details.

12. S&T benefits accrued:

i. List of Research publications

1. Sharma, M. K., Thayyen, R. J., Jain, C. K., Arora, M. and Kumar, Naresh (2016) Study of Hydro-chemical Characteristics and Controlling Processes of Meltwater in Gangotri Glacier System, Uttarakhand, India, Presented in 21st Int. Conf. on

Hydraulics, Water Resources and Coastal Engineering (HYDRO 2016 International), 8-10 Dec., 2016 organized by CWPRS, Pune at Pune, Abstract Souvenir pp. 127.

ii. Manpower trained on the project:

a) Research Scientists or Research Associates: Nil

b) No. of Ph.D. produced: Nil

c) Other Technical Personnel trained: One JRF was trained on the operation of Ion Chromatograph

iii. Patents taken, if any: Nil

13. Financial Position: Presented in the SE & UC

14. Procurement/ Usage of Equipment

S. No.	Name of the equipment	Make/ Model	Cost (FE/Rs.)	Date of installation	Utilization rate (%)	Remarks regarding Maintenance /breakdown
1.	Low Temperature pH meter – 1	Hach, HQ 11d	1,89,395.00	30.04.15	100%	Working
2.	Low Temperature Conductivity meter – 1	Hach, HQ 14d	2,08,560.00	30.04.15	100%	Working
3.	Deep freezer with variable temperature – 1	Remi, RQV-600 Plus	1,83,351.00	27.04.15	100%	Working
4.	Computer Note Book (Laptop) - 1	Panasonic, CF-AX2	1,22,850.00	28.11.14	100%	Working

b) Plans for utilizing the equipment facilities in future: All the equipments procured under the project are being used in other in-house funding project.

Name and Signature:

a. Principal Investigator_____________

b. Co-Investigator___________________