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An assessment of the hydrogeochemistry of two wetlands located in Bihar State in the subtropical climatic zone of India

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Abstract A total of 30 water samples and 8 sediment samples were collected and chemically analysed for major ions (Na⁺, K⁺, Mg²⁺, Ca²⁺, HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻, silica, PO_4^{3-} , F⁻), trace elements (Fe, Mn, Ni, Cd, Zn, Pb, Cu), minerals and nutrients to determine the factors that control the chemistry of water in the Kawar-Tal and Kusheshwar-Asthan wetlands in the Bihar State of India. These analyses indicate that Ca^{2+} and HCO_3^- ions are the most dominant ions in both of the wetlands. It also indicates rock weathering is a major source of ions in these wetlands, particularly the dissolution of carbonate minerals. The hydrogeochemistry of water in Kusheshwar-Asthan is favouring kaolinite formation and in Kawar-Tal favouring kaolinite–gibbsite formation. Quartz $(\sim 36\%)$, clay minerals (\sim 21%) and chlorite (\sim 10%) are the dominant minerals in both the wetlands. Orthoclase $({\sim}12.49\%)$, calcite (${\sim}7.51\%)$ and illite (4.89%) minerals are only available in Kawar-Tal surface sediment, while albite (6.29%) and biotite (\sim 13.6%) minerals are only available in Kusheshwar-Asthan. Total carbon $(\sim 3\%)$, inorganic carbon (0.9%), organic carbon (\sim 2.1%), total sulphur ($\sim 0.0008\%$), nitrogen ($\sim 0.55\%$) and phosphate $(\sim 0.96\%)$ are available in Kawar-Tal surface sediments, while total carbon (\sim 2.38%), inorganic carbon (0.55%), organic carbon (\sim 1.84%), total sulphur (\sim 0.001%), nitrogen ($\sim 0.62\%$) and phosphate ($\sim 0.64\%$) are available

in Kusheshwar-Asthan surface sediments. The study indicates wetlands are rich in nutrient for biological activities and are sufficient to support the biodiversity, but few locations are influenced by anthropogenic activities which cause the increase of sulphur, chloride, iron and lead.

Keywords Hydrogeochemistry - Kawar-Tal - Kusheshwar-Asthan - Bihar - Wetland

Introduction

Wetlands are areas where water is the primary factor controlling the environment and the associated plant and animal life (Ramasar [2007](#page-17-0)). The UNEP-World Conservation Monitoring Center has suggested that wetlands cover a land area of about 570 million hectares, roughly 6% of the Earth's land surface, of which 2% is lakes, 30% bogs, 26% fens, 20% swamps and 15% floodplains (Ramasar [2007](#page-17-0)). India has a rich variety of wetland habitats. The total area of wetlands (excluding rivers) in India is 58,286,000 ha or 18.4% of the country, 70% of which comprises areas under paddy cultivation (Green [1990\)](#page-17-0). A total of 1193 wetlands, covering an area of about 3,904,543 ha, were recorded in a preliminary inventory coordinated by the Department of Science and Technology (DST), of which 572 were natural (Green [1990](#page-17-0)). In a recent review of the India's wetlands, 93 were identified as being of conservation importance (Scott [1989](#page-18-0)). India's 19 most important wetlands that cover a total area of 648,507 ha have been designated under the convention of wetlands of international importance as being especially significant waterfowl habitats (Ramsar Convention [2003\)](#page-18-0). The interactions of physical, biological and chemical components of a wetland, such as soils, water, plants and animals, enable the wetland to perform

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many vital functions, e.g. water storage; storm protection and flood mitigation; shoreline stabilization and erosion control; groundwater recharge and discharge; water purification through retention of nutrients in sediments; and stabilization of local climate conditions, particularly rainfall and temperature (Voogt et al. [2000](#page-17-0)).

Kawar-Tal is a largest freshwater lake in northern Bihar (Ambastha et al. [2007\)](#page-17-0). This lake has been declared and notified as a protected area under section 37 of the WildLife Protection Act 1972. Kawar-Tal has been also declared as one of the ''bird sanctuaries'' in 1989 by the State Government of Bihar (Anand and Joshi [2013\)](#page-17-0). The Ministry of Environment and Forest (1989), Government of India, has also selected this lake as one of the 16 wetlands of the country for conservation and management, mainly due to its greater and enormous productive potential for attracting numerous migratory birds coming from remote part of the country and from Siberia beyond the Himalayas. This wetland lies between the Burhi Gandak, old Bagmati and the Kareh Rivers (Kawar Lake Blogspot [2011\)](#page-17-0). This lake is formed by the meandering action of the Gandak River and is now a residual oxbow lake, one of the thousands in Bihar and Uttar Pradesh flood plains (Kawar Lake BlogSpot [2011\)](#page-17-0). In years of high rainfall, vast areas of these two states get flooded (Irrigation and Water ways Department [2000\)](#page-17-0). This causes a coalescing of wetlands form a single huge expanse of water. The floods leave behind deposits of sand, silt and clay in layers of varying thickness. In years of average rainfall, Kawar-Tal is connected with Burhi Gandak (a tributary of the River Ganga) and with nearby Nagri Jheel and Bikrampur Chaurs and unites to form a lake of about 7400 ha. By late summer, however, the water is confined to the deeper depressions and only about 300–400 ha of Kawar-Tal remains flooded and cuts off from the adjacent floodplains. The annual range of water temperature is 19.7–28.5 C. This narrow temperature variation throughout the year helps support fish life in the wetland. Kawar-Tal Lake is surrounded by 16 villages with a population of several thousands and the people undertaking land uses that have the potential to affect water quality in the lake. This lake has very dense submerged vegetation which is rich in terms of biodiversity. There were altogether 51 species of fishes belonging to 15 families and 10 orders (Sharma et al. [1994](#page-18-0)). Investigations have shown that the lake has rich biotic potential with 55 species of macrophytes (Sharma [1995\)](#page-18-0); 93 species of planktons; 87 species of macroinvertebrates (Sinha et al. [1994\)](#page-18-0); 65 species of insects (Parkash and Kumar [1996](#page-17-0)); and 11 species of gastropods being recorded. In this wetland, around 59 species of migratory birds and 107 species of local birds have been also identified (Sharma et al. [1994\)](#page-18-0).

Kusheshwar-Asthan is a vast wetland made up of the spilled water and river bed of the Kosi, the Kareh and the Kamla-Balan besides innumerable seasonal channels and gullies. The rivers and gullies bring silt and detrital organic matter which is deposited near river mouths, blocking their outflow. Hence, the river gets broken down into innumerable channels and rivulets. Further overbank flow of water and silt causes river diversions and creates oxbow lakes. During the rainy season, the water fills most parts (\sim 90%) of Kusheshwar-Asthan. This water logging affects 14 villages of Kusheshwar-Asthan block covering an area of 2840.80 ha. Due to their greater ecological, faunal, floral and natural importance, this area has been declared as bird sanctuary (area around 6700 ha) under the WildLife Protection Act 1972 (as amended up to 1991) on 25 August 1994 by state government of the Bihar. This is one of the 13 sanctuaries of the state Bihar with Kawar-Tal Bird sanctuary, which is included in the international list by Bird Life International and Royal Society for Protection of Birds, UK. Due to fresh alluvial deposits and rich manures and nutrients, the soil of this area is very fertile which supports the biodiversity of wetland. A variety of zooplankton and phytoplankton thrive in this wetland under warm and humid conditions. This ecosystem attracts a lot of birds of different species for feeding and breeding. Many of the birds are endemic species along with few reported migratory birds. The migratory birds begin arriving in the beginning of the October, and they reside in the wetland up to March. This wetland also reported 87 species of fishes belonging to 20 different families, and 28 species of molluscs (gastropods 18 species and bivalves 10 species) have been recorded in this area so far (Munshi and Munshi [1991\)](#page-17-0).

Both the wetlands are very important on basis of biodiversity and protected under national and international laws. It needs to be protected under this consideration; this study was carried out to predict the status of quality of lake water and sediment. By this, we can predict possible anthropogenic influences in these areas.

Study area

Water and sediment sampling was carried out in the two wetlands located in the subtropical climatic zone of the India. A total of 30 water samples and 8 sediment samples were collected from both the wetlands. Kawar-Tal is located in Manjhaul village of Cheria Bariarpur block of Begusarai District of the Bihar on the northern bank of the River Ganga. It is 22 km north of the Begusarai town. Geographically, it is located in between latitudes $25^{\circ}36'$ - $25^{\circ}39'$ N and longitude $86^{\circ}06' - 86^{\circ}10'E$ $86^{\circ}06' - 86^{\circ}10'E$ $86^{\circ}06' - 86^{\circ}10'E$ (Fig. 1). Kusheshwar-Asthan is 60 km away from the Darbhanga town. Geographically, it is located in between latitudes

Fig. 1 Study area (showing sampling locations in Kawar-Tal and Kusheshwar-Asthan wetlands)

 $25^{\circ}49' - 25^{\circ}50'$ N and longitude $86^{\circ}18' - 86^{\circ}19'E$ (Fig. 1). Being a part of the Gangetic Plain of the Indian subcontinent, these areas experience three climatic seasons—a hot and humid summer (\sim 42 °C) period from late March to mid-June, a rainy season from mid-June to October and the winter season from the November to February. The average annual rainfall in this belt of the Ganga–Burhi and Gandak is 138.4 cm, mostly (\sim 83%) in between the months of June to October (Indian Meteorological Department [1990](#page-17-0)– 2010).

Methodology

The surface is characterized by palaeolevees, swamps or flood basins (locally called ''Chaurs''), relict palaeochannels aggraded in varying degrees, meander belts, oxbow lakes and cut-off loops. Its fluvial geomorphology is dominated from west to east by the Ganga– Gandak interfluves, the Gandak–Kosi interfluves and the west by the Kosi fan belt. Some of these rivers frequently change their channels. Geomorphologically, these channels form a part of the Gandak–Kosi interfluves. The southern part of the district, except those of low-lying flood plains of the River Ganga, appears to be an elevated landmass when compared with the adjoining districts of the Khagaria and Samastipur. Hence, being a safer destination amidst the flood-drained region, it supports the human activities in a better way. In the River Ganga flood plain, which is approximately 50–55 km long and 5–6 km wide, in the southern part of the district, except those lowlying areas of ''Taals and Chaurs'', the typical fluvial characteristics of north Bihar rivers are not visible. This relatively upland area appears to be the levee of the River Ganga (Mahadevan [2002\)](#page-17-0).

Geologically, the study area is an alluvial plain in the domain of the Himalayan Rivers to the north of the Ganga. It is a part of the great Gangetic Basin. The basin was formed during late Palaeogene–Neogene times and is related to the upheaval of the Himalayas viz. flexural down warp of the Indian Plate under the supracrustal load of the Himalayas (Wadia [1966](#page-18-0)). The entire segment abounds in buried faults and grabens. The basin came into existence as a result of the collision of the India and China continental plates during the Palaeocene (Dewey and Bird [1970\)](#page-17-0). The collision has caused intraplate subduction along the main central thrust, lying in the Himalayas, raising the higher Himalaya to form source rocks and ''popping through'' the more southerly part of the Indian Plate to form the basin. This ''popping through'' might have lead to the development of longitudinal and transverse lineaments throughout the basin. With time, more southerly areas were raised, and by the mid-Palaeocene, subduction also started along the main boundary fault lying in the Himalayas.

The soil of this land unit is primarily unaltered alluvium, which is yet to undergo pedogenesis (process of soil formation). Texturally, it varies from sandy loam to loam in the meander scroll and levee (the upland bounding the flood plains of the river) areas to silt loam and silt in flood basin areas of the Himalayan Rivers and from loam in the levees of the Ganga to clayey loam and clay in the basin of the Burhi Gandak and the Bagmati River. The soil of the area is sandy loam rich with humus and is also very fertile (Mahadevan [2002](#page-17-0)).

A well-planned inventory survey was carried out in the study area to understand the hydrogeochemistry of the wetlands in the month of December. A Garmin Global Positioning System (GPS) was used for fixing the suitable sampling locations to determine the hydrogeochemistry of both wetlands. Thirty water samples and 8 core sediment samples were collected in January 2005. The parameters [pH, temperature, electrical conductivity (EC), dissolved oxygen (DO), oxidation–reduction potential (ORP), total dissolved solids (TDS) and total suspended matter (TSM)] were measured in the field at the time of sampling by using a water analyser kit, and these measurements were cross-checked in the laboratory. For cations, 100 mL samples were filtered using 0.45 - μ m filter paper and preserved on site with ultrapure nitric acid (boric acid was used as a preservative for nitrate) and stored at 4° C to avoid chemical alteration to samples during transport and holding (APHA [1995](#page-17-0)). Sodium and potassium were analysed by an AIMIL, PE I Flame Photometer following the standard method (APHA [1995](#page-17-0)). An atomic absorption spectrophotometer (Shimadzu-AA-6800) was used for analysis of heavy metals (Mn, Fe, Ni, Cu, Zn, Cd and Pb) and alkaline earth metals (Mg and Ca). Anions $(SO_4^2$ ⁻, NO₃⁻, F⁻, PO₄³⁻ and silicate) were analysed by using a JENWAY 6505 UV/Vis spectrophotometer, using the standard method as given in APHA ([1995\)](#page-17-0). Bicarbonate and chloride were analysed by titration method using the standard procedure as given in APHA ([1995\)](#page-17-0).

Total Carbon (TC), inorganic carbon (IC), organic carbon (OC), total sulphur (TS), inorganic sulphur (IS) and organic sulphur (OS) were analysed in cores of sediments (free from halogen) by using Eltra (CS 1000) carbon/sulphur analyser as per standard procedure. For analysis of IC and IS, samples were further treated with 30% (v/v) H_2O_2 to make it free from organic matter (Jackson [1973](#page-17-0)). Nitrogen was analysed by the Kjeldahl digestion method (Scheper et al. [2008\)](#page-18-0). Analysis of major and minor elements was carried out by the two-solution method (Shapiro and Brannock [1962\)](#page-18-0). Solution ''A'' was used for silica, phosphorous and aluminium. The mineralogy of surface sediment was studied by using X-Ray Diffractometer (XRD) (model Philips X'Pert). The slide was run through X-Ray Diffractometer (XRD) (model Philips X'Pert) at the rate of $2^{\circ}/s$. For grain size analysis of the surface sediment, all the samples were air-dried and then oven-dried at 60 \degree C for 24 h, and pebbles and very coarse materials were removed. The samples were thoroughly homogenized using a coning and quartering technique (Ingram [1971](#page-17-0)). Size separation of the sample grains was carried out

following the standard sieving and sedimentation methods (Ingram [1971](#page-17-0)). The samples were dry-sieved on an electrically controlled electromagnetic sieve shaker (Fritsch Analysette-3) for 45 min. Then, grain size fraction of 37–63 μ m and $\langle 37 \mu$ m (silt and clay); 63–125 μ m (very fine sand); $125-150 \mu m$ (fine sand); $250-600 \mu m$ (medium sand); and $>600 \mu m$ (coarse sand) was collected. The weights of all the fractions were taken out separately, and statistical calculations were made by the graph method (Krumbein and Pettijohn [1958](#page-17-0); Lindholm [1987](#page-17-0)).

Results and discussion

The distribution pattern of major cations and anions in water samples of the both wetlands was as follows: $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and HCO_3 ⁻ Cl^{-} SO_4^2 > NO_3^- > F^- = PO_4^3 ⁻. Most of the water samples showed a good charge balance with \pm 5.0% error, which is generally considered acceptable because it is very difficult to analyse all cations and anions (Berner and Berner [1987](#page-17-0); Edmond et al. [1995](#page-17-0); Huh et al. [1998;](#page-17-0) Srivastava and

Ramanathan [2012](#page-18-0)). The investigation of various physicochemical parameters like pH, EC, TDS, ORP, TSH and DO of water samples indicates about the type of physicochemical and biological processes occurring in the wetland and its surrounding in catchments area. Investigation of grain size of sediment helps to understand the sediment characteristics, soil, rock type and weathering processes in the study area. It also helps to determine the depositional pattern in the environment. The texture and mineralogy of the sediments in the aquatic environment are useful for interpreting depositional environment, provenance and nutrient occurrence of the aquatic medium. Analysis of carbon, nitrogen and phosphate in the surface sediment helps to understand the biological activities in the wetlands.

Water chemistry of wetlands

The average, maximum, minimum and standard deviation for each water quality parameter were analysed for both the wetlands as shown in Table 1. Both wetlands' water was alkaline in nature (pH \sim 8.17) (Table 1). Alkaline water in

Table 1 Summary of statistics of chemical parameters of Kawar-Tal and Kusheshwar-Asthan Wetlands

min. minimum, max. maximum, Avg. average, SD standard deviation

	pH	EC	TDS	Ca	Mg	Na	K	Cl^{-}	HCO ₃	$SO_4{}^{2-}$	$NO3-$	PO ₄ ^{3–}	\rm{F}^-
pH	$\mathbf{1}$												
EC	-0.52	1											
TDS	-0.52	1											
Ca	-0.47	0.96	0.96	1									
Mg	-0.44	0.9	0.9	0.96	$\mathbf{1}$								
Na	0.07	-0.43	-0.43	-0.41	-0.61	-1							
K	-0.17	0.61	0.61	0.68	0.76	-0.64	$\mathbf{1}$						
Cl^-	-0.43	0.26	0.27	0.27	0.27	0.13	0.07	$\mathbf{1}$					
HCO ₃	-0.6	0.81	0.8	0.85	0.73	-0.07	0.5	0.23	$\mathbf{1}$				
SO_4^2 ⁻	-0.24	-0.13	-0.13	-0.14	-0.2	0.36	0.09	0.09	0.08	1			
NO ₃	-0.33	0.28	0.29	0.45	0.53	-0.09	0.44	0.5	0.32	-0.03	$\mathbf{1}$		
PO ₄ ^{3–}	-0.36	0.03	0.03	0.12	0.13	0.26	-0.15	0.7	0.13	0.15	0.49	1	
F^-	-0.01	-0.22	-0.22	-0.28	-0.21	-0.24	0.03	0.23	-0.27	-0.07	-0.19	-0.22	-1

Table 2 Correlation matrix (Kawar-Tal)

both wetlands may be due to natural processes of weathering, evaporation and $CO₂$ gas equilibrium (Garrel and Mackenzie [1967\)](#page-17-0). Araoye ([2009\)](#page-17-0), Goel et al. [\(1985](#page-17-0)) and Sarana and Adoni ([1982\)](#page-18-0) have shown the dependence of pH on the biological activities. King ([1970\)](#page-17-0); William et al. [\(1970](#page-18-0)); Olsen and Summerfield ([1977\)](#page-17-0); and Goldman [\(1972](#page-17-0)) have shown an increase in pH with active growth of phytoplankton. The high DO values in Kawar-Tal and Kusheshwar-Asthan can be related to high-level photosynthetic activity in the water bodies. A significant EC was reported in both wetlands, i.e. Kusheshwar-Asthan (4[1](#page-4-0)7.73 μ S/cm) and Kawar-Tal (374.87 μ S/cm) (Table 1). A good correlation between EC and Ca^{2+} , Mg^{2+} and K^+ observed in Kawar-Tal water samples indicates a possible source of these ions from the weathering of clay minerals, which was also justified in the mineralogical study of sediments (Tables 2, [5](#page-15-0)).

$$
4KAlSi3O8 + 4H+ + 2H2O \rightarrow 4K+ + Al4Si4O10(OH)8 + 8SiO2
$$

\nKaolinite
\n(1)

$$
CaCO3 + H2CO3 \rightarrow Ca2+ + 2(HCO3-)
$$
 (2)

TDS/EC shows good correlation in both wetlands (with correlation coefficients of ~ 0.67 ; refer to Table [4\)](#page-11-0). TDS shows some spatial variation in Kawar-Tal, but in Kusheshwar-Asthan value of TDS is almost constant throughout the wetland, possibly due to its smaller size uniform ecology. Water in Kawar-Tal (with a TDS of 0.15 mg/L) has a lower content of suspended matter than Kusheshwar–Asthan (TDS = 0.44 mg/L), maybe due to comparatively limited availability of clay minerals (Table [1](#page-4-0), [5](#page-15-0)).

Nutrients

A significant concentration of nitrate and phosphate ions that were observed in the study areas indicates possible enrichment of nitrogen and phosphorous in the two wet-lands (Table [1\)](#page-4-0). It was observed that $NO₃⁻$ ions concentrations rapidly change in a water body, and it may be due to the prevailing biological activities in the system in both wetlands (Figs. [2d](#page-6-0), [3](#page-7-0)d) (Wetzel [1979](#page-18-0)). Natural factors influencing the variability of phosphate and nitrate are considered to be associated with nitrogen and phosphorus cycle in the soil (biological sorption), especially during the growing season, when plants take up these macronutrients, mainly nitrogen, phosphorous and potassium from water (Kabata and Pendias [1999](#page-17-0)). According to Wetzel [\(1979](#page-18-0)), significant increases in the nutrient content in this wetland can be attributed to increased agricultural activities with increased use of fertilizers in the catchment areas. The contribution of nutrients by animal faeces cannot also be ruled out. Kawar-Tal is almost completely covered with aquatic vegetation; hence, concentration of nitrate and phosphate is less than Kusheshwar-Asthan, maybe due to consumption of nutrient by this aquatic vegetation. The problem of prolific growth of aquatic macrophytes in Kawar-Tal was already reported in the Conservation of Wetlands in India (Ministry of Environment and Forests [1989](#page-17-0)). A very low $(0.11-0.32 \text{ mg/L})$ concentration of fluoride has been reported in both wetlands, and spatial variations in concentrations were also low (Table [1](#page-4-0)). The chloride ions concentrations are extremely variable and depend on the rock, soil and water interaction during runoff. The availability of chloride ions in water samples was \sim 13% in Kawar-Tal and \sim 20% in Kusheshwar-Asthan of

Fig. 2 Graph of various chemical parameters (Kawar-Tal)

the total anions in the respective wetlands (Table [1](#page-4-0)). The presence of high chloride concentration in water has also been attributed to pollution (Taylor et al. [1958](#page-18-0); Wetzel [1974\)](#page-18-0). Pollution from industries and domestic effluents could also be a contributing factor to the high chloride content in the wetlands. Sulphate is often the second most abundant anion (after bicarbonate) in freshwaters considering the geology of study area, but in both wetlands, chloride is the second most anion (Table [1\)](#page-4-0). Contribution of sulphate to the total anions was not much high on both the places. The major source of sulphate in water is the weathering of rocks, particularly pyrite, anhydrite and gypsum (Bell [1994;](#page-17-0) Hounslow [1995\)](#page-17-0). The other possible source in wetlands is leaching of fertilizer (containing sulphate as important ingredient) along with rainwater through agriculture lands available in surrounding areas. These factors could have contributed to the sulphate content in the wetlands (Sigurdsson [1990;](#page-18-0) Giblin and Wieder

Fig. 3 Graph of various chemical parameters (Kusheshwar-Asthan)

[1992\)](#page-17-0). Bicarbonate ion was reported as most dominant anion in both the wetlands (Table [1\)](#page-4-0). The carbonate ion availability in water samples was $\sim 80\%$ in the Kawar-Tal and 63% in Kusheshwar-Asthan out of total anions (Table [1](#page-4-0)).

Hydrogeochemical evaluation

The geochemical variations in the ionic concentration in the water samples can be easily understood when they are plotted on X–Y cross-plots (Guler et al. [2002\)](#page-17-0). Generally, in arid climates, chemical weathering is limited and the ionic

composition of lake water is determined by the occasional precipitation (Nikanorov and Brazhnikova [1989\)](#page-17-0). Low levels of solutes in both wetlands are thought to be influenced by uptake of solute by sediment and solute loss through underground seepage (Darling et al. [1990\)](#page-17-0).

Most of the samples of both wetlands have a $Na^+/Cl^$ molar ratio around 1, indicating straight evaporative concentration with no ion-exchange process in study area (Figs. [2](#page-6-0)a, 3a). The graph between $(Ca^{2+} + Mg^{2+})$ and $(SO_4^{2-} + HCO_3^-)$ follows a nearly 1:1 line in both wetlands (Figs. [2b](#page-6-0), 3b). These linear relationships between these ions would be expected with evaporative

concentration. The graph of $TZ + (total cation)$ versus $(Ca^{2+} + Mg^{2+})$ shows most of the samples very close to theoretical line (1:1) indicate weathering of rock minerals that are dominant in both wetlands (Figs. [2c](#page-6-0), [3c](#page-7-0)). The graph of $Na⁺$ versus $NO₃⁻$ shows few water samples scattered and falling away from theoretical line (1:1), possibly indicating the effects of anthropogenic activities. The source of Ca^{2+} and Mg²⁺ ions in wetlands water can be deduced from the meq $(Ca^{2+} + Mg^{2+})/$ meq (HCO_3^-) ratio. If calcium and magnesium originate solely from dissolution of carbonate in the aquifer from the weathering of accessory pyroxene and amphibole minerals, the ratio would be about 0.5. The graph between meq(Ca^{2+} + Mg^{2+})/meq(HCO₃⁻) and meqCl⁻ indicates contribution of anthropogenic input in both wetlands (Figs. [2](#page-6-0)f, [3f](#page-7-0)). The graph between $(SO_4^{2-} + Cl^-)$ and $(Na^+ + K^+)$ in Kawar-Tal water samples is scattered, indicating some other source input along with natural weathering process (Fig. [2](#page-6-0)e). The graph between $(SO_4^{2-} + Cl^-)$ and $(Na^{+} + K^{+})$ in Kusheshwar-Asthan shows most of water samples falling close to the theoretical line and very few away from line, indicating natural weathering is the dominant process (Fig. [3e](#page-7-0)). Potassium contribution to the total cations was low in both wetlands $\sim 2.57\%$ (Kawar-Tal) and \sim 3.49% (Kusheshwar-Asthan) (Table [1\)](#page-4-0). Evaporation plays a greater role in the concentration of potassium in lake waters; its resistance to weathering and its use in the formation of clay minerals cause the concentration of the element to be much lower than that of sodium (Nelson 2014). A significant amount of $CaCO₃$ was reported in wetlands water, but it is one of the least soluble compounds in water. However, in weak acidic condition, $CaCO₃$ can be converted to soluble CaHCO₃. In this study, Ca^{2+} comprises about 56% (Kawar-Tal) and 52% (Kusheshwar-Asthan) of the total cations (Table [1\)](#page-4-0).

Statistical analysis

Numerical analysis of hydrogeochemical data has been attempted to determine the geochemical factors that influence the chemical evolution of water (Lawrence and Upchurch [1982](#page-17-0)). A three-step approach was used to assess the data for both wetlands. The steps used were: the use of a univariate statistical analysis (analysis of individual chemical parameters); characterization of major ion concentrations using traditional geochemical plotting tools; and multivariate analysis (principal component analysis and cluster analysis). Multivariate statistics have been widely applied in the earth and environmental sciences (Schuenemeyer and Drew [2011\)](#page-18-0). Multivariate methods involve the simultaneous analysis of multiple variables rather than an examination of commonalities as well as difference between large data sets. The major objectives of

this evaluation were to delineate the study areas based on chemical signature and to identify the variables (chemical parameters) that best explain the underlying difference. The concentrations of major ions in respective areas were depicted using Piper (trilinear) and Stiff diagrams.

Correlation matrix

The correlation matrices for water samples collected from Kawar-Tal and Kusheshwar-Asthan are shown in Tables [2](#page-5-0) and [3,](#page-9-0) respectively. In the Kawar-Tal water samples, Ca^{2+} ion shows strong correlations with Mg^{2+} (0.96) and $HCO₃⁻$ (0.85) ions, suggesting a common source of origin (Table [2\)](#page-5-0). Calcium ion also shows good correlations with EC (0.96) and TDS (0.96). Similarly, Mg^{2+} ions show good correlations with EC (0.90) and TDS (0.90); $HCO_3^$ ions show good correlations with EC (0.81) and TDS (0.80), indicating that Ca^{2+} , Mg^{2+} and HCO_3^- ions are the major contributors to the EC and TDS content of the water. Good relationships between these ions also indicate natural weathering processes occur in situ in the Kawar-Tal wetland. Potassium ions show significant correlations with Mg^{2+} (0.76), Ca^{2+} (0.68), EC (0.61) and TDS (0.61), indicating K^+ ions contribute significantly to the hydrochemistry of the wetlands. Nitrate ions show significant correlations with Ca²⁺ (0.45), Mg²⁺ (0.53) and K⁺ (0.44) ions, indicating the possibility that nitrate in water may be from run-off containing fertilizer during the monsoon period from agriculture land (Table [2\)](#page-5-0). The low nitrate was observed may be due to active denitrification in the Kawar-Tal wetland sediments. The other ions Na^+ , Cl^- , SO_4^{2-} , $PO₄³⁻$ and F⁻ do not show any significant correlation among each other or with other ions (Table [2\)](#page-5-0). In Kusheshwar-Asthan water samples, Ca^{2+} shows a significant correlation with Mg^{2+} (0.79), suggesting that there is a common mineral source of these ions in water (Table [3](#page-9-0)). Calcium ion also shows average correlations with $HCO_3^ (0.35)$ and Cl⁻ (0.34) ion, indicating equal contributions of natural weathering and other source of these ions in water (Table [3\)](#page-9-0). Sodium ion shows a very good correlation with F^{-} (0.76) ions and average correlation with NO_3^- (0.35) ions, indicating possibility of anthropogenic input in Kusheshwar-Asthan water samples (Table [3\)](#page-9-0). EC shows average correlation with K^+ (0.41), Mg^{2+} (0.32) and SO_4^{2-} (0.27) (Table [3](#page-9-0)).

DUROV diagram

According to DUROV diagram of water sample of the study areas, the concentration of Ca^{2+} , Mg²⁺ and $HCO_3^$ ions mainly influences water quality (Fig. [4\)](#page-10-0). It indicates dominance of natural weathering in both wetlands, while lesser effect of Na⁺, Mg²⁺, Cl⁻ and SO₄²⁻ ions is

Table 5 Correlation matrix (Trabiteshwar Troutan)													
	pH	EC	TDS	Ca	Mg	Na	K	Cl^-	HCO ₃	SO_4^{2-}	NO_3 ⁻	F^-	PO ₄ ³
pH	$\mathbf{1}$												
EC	-0.09	1											
TDS	-0.2	0.97	1										
Ca	-0.12	0.03	0.07	1									
Mg	-0.13	0.32	0.37	0.79	-1								
Na	-0.21	-0.31	-0.25	-0.12	0.27	$\mathbf{1}$							
\mathbf{K}	-0.03	0.41	0.44	-0.15	0.22	0.22	$\mathbf{1}$						
Cl^{-}	-0.38	$\overline{0}$	0.01	0.34	0.1	-0.23	0.06	1					
HCO ₃	-0.01	-0.22	-0.15	0.35	0.39	0.22	0.19	-0.08	1				
$SO_4{}^{2-}$	-0.48	0.27	0.34	0.12	0.12	-0.19	-0.02	-0.2	0.02	$\mathbf{1}$			
NO_3^-	-0.58	0.02	0.11	0.13	0.2	0.35	0.17	-0.09	0.39	0.52	1		
F^-	0.01	-0.49	-0.44	-0.14	0.05	0.76	0.08	-0.21	-0.06	-0.38	0.15	1	
PO ₄ ^{3–}	-0.09	-0.17	-0.07	0.14	0.14	0.04	0.22	0.02	0.3	-0.09	-0.22	0.17	-1

Table 3 Correlation matrix (Kusheshwar-Asthan)

observed (Fig. [4\)](#page-10-0). A very small variation was observed in both the wetlands due to similar subtropical climate and geology. Geologically, both wetlands are similar to small variation of few minerals.

Piper diagram

Piper diagrams are often used to classify water types. Each data point on a Piper diagram reflects relative molar proportions of major ions, rather than their absolute concentrations. Water samples from both wetlands have a water composition that is dominated by the cations Ca^{2+} and Mg^{2+} and by the anion HCO_3^- (Fig. [5](#page-10-0)).

Mechanisms controlling water chemistry (Gibbs diagram)

The source of major ions in water can be defined by plotting the samples according to the variations in weight ratios of $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$ as function of TDS (Gibbs [1970](#page-17-0)). Rock weathering appears to be the principal mechanism controlling the ion chemistry of both wetlands (Fig. [6\)](#page-12-0). In both wetlands, sulphate/chloride ratio is below 0.50 [ranging from 0.24 to 0.30 (Kawar-Tal) and 0.36 to 0.47 (Kusheshwar-Asthan)], suggesting that there is a limited anthropogenic input of sulphur and limited in situ leaching of this element (Table [4\)](#page-11-0). In Kusheshwar-Asthan, the Na^{+}/Cl^{-} ratio is 0.85, while in Kawar-Tal it is 1.28 (Table [4\)](#page-11-0), indicating some additional sodium source must be there other than precipitation. The calcium/bicarbonate ratio is less than 1.00 at both wetlands, suggesting that these ions were sourced by microbial respiration of organic carbon in sediments (Table [4](#page-11-0)). The

bicarbonate/total anion ratio is less than 1.00 in both wetlands, suggesting that there is only a limited anthropogenic influence on both the study sites. Nitrate/total anion ratio is 0.1–0.2 in Kawar-Tal and 0.01–0.02 in Kusheshwar-Asthan, indicating most of nitrate is consumed by denitrification in both wetlands (Table [4\)](#page-11-0). The fluoride/magnesium ratio is 0.01–0.03 in Kawar-Tal and 0.01–0.02 in Kusheshwar-Asthan, indicating fluoride is devoid of natural weathering (Table [4](#page-11-0)).

Stability diagrams

Mineral stability offers an opportunity to study the equilibrium between silicate minerals and natural waters. The principle behind such an approach is that water derives its composition from the parent rock in the weathering region and suspended sediments owe their mineralogical composition partly to the parent rock and partly to the chemical reaction of rock and water (Garrel and Christ [1966](#page-17-0)). Thus by studying the water chemistry, stable mineral assemblages can theoretically be predicted. In the current study, an attempt has been made to apply this approach to the studied wetland (Figs. [7,](#page-13-0) [8](#page-14-0)).

The plot of the silicate diagram of Kawar-Tal waters is mainly in the range of stability field of gibbsite with a few points in the kaolinite range (Fig. [7](#page-13-0)). For water samples from the Kusheshwar-Asthan, the silicate stability diagrams show most of the samples in kaolinite range (Fig. [8](#page-14-0)). This implies that hydrochemistry of water in Kusheshwar-Asthan is favouring kaolinite formation and in Kawar-Tal favouring kaolinite–gibbsite formation. This was also justified by dominance of clay minerals (18–24%) in surface sediment of both wetlands (Table [5\)](#page-15-0).

Fig. 4 DUROV diagram of Kawar-Tal and Kusheshwar-Asthan Fig. 5 Piper diagram of Kawar-Tal and Kusheshwar-Asthan
wetlands

Heavy metal analysis

Only a limited number of chemical analyses were carried out in this study for the metals Fe, Mn, Ni, Cd, Cu, Pb and Zn. Kawar-Tal lake water contains Fe (~ 0.06 mg/L), Mn $(\sim 0.03 \text{ mg/L})$, Ni $(\sim 0.06 \text{ mg/L})$, Cu $(\sim 0.002 \text{ mg/L})$, Zn $(\sim 0.02 \text{ mg/L})$, Cd $(\sim 0.02 \text{ mg/L})$, Pb($\sim 0.46 \text{ mg/L}$), while Kusheshwar-Asthan lake water contains Fe $(\sim 0.65 \text{ mg/L})$, Mn $(\sim 0.04 \text{ mg/L})$, Ni $(\sim 0.05 \text{ mg/L})$, Cu $(\sim 0.004 \text{ mg/L})$, Zn $(\sim 0.02 \text{ mg/L})$, Cd $(\sim 0.02 \text{ mg/L})$ and Pb (\sim 0.49 mg/L) (Table [1](#page-4-0)). High iron concentration in Kusheshwar-Asthan may be due to local input or probably associated with local microbial reductive dissolution of iron oxide in wetland sediments. Lead concentrations are

wetlands

significant in both wetlands, maybe due to some local anthropogenic input. Other heavy metals concentrations are under permissible limit of World Health Organization [\(2006](#page-18-0)).

Mineralogy of surface sediments

The mineralogical study was carried out by X-ray Diffractometer (XRD). The results indicate that the major mineral present in all the samples of both wetlands surface sediment is quartz (Table [5\)](#page-15-0). The most abundant minerals in Kawar-Tal sediments (in order of decreasing abundance) are quartz (34.78–38.02%), chlorite (10.62–12.13%),

Table 4 Summary of various statistical relations between chemical parameters of Kawar-Tal and Kusheshwar-Asthan

min. minimum, max. maximum, Avg. average, SD standard deviation

muscovite (6.43–7.64%), orthoclase (11.99–13.02%), calcite $(6.94-8.13\%)$, illite $(4.19-5.69\%)$ and other clay minerals (18.25–22.88%) (Table [5\)](#page-15-0). The most abundant minerals in the Kusheshwar-Asthan surface sediments are quartz (33.43–37.13%), chlorite (8.12–11.43%), muscovite (12.11–14.07%), albite (5.12–7.11%), biotite (12.11–14.07%) and other clay minerals (20.11–24.11%) (Table [5](#page-15-0)). Orthoclase, calcite and illite minerals are only reported in Kawar-Tal wetland core sediments. Similarly, albite and biotite minerals are only reported in Kusheshwar-Asthan core sediment and not in Kawar-Tal core sediment (Table [5](#page-15-0)).

High silica concentrations that were measured in surface sediments of the Kawar-Tal (\sim 35%) and Kusheshwar-Asthan (32.88%) may be due to dominance of quartz in surface sediment (Table [6\)](#page-15-0). At both sites, silica concentrations are higher than the Indian river average, i.e. 24.5%. The significant aluminium concentration was observed in surface sediment of the Kawar-Tal $(\sim 6.63\%)$ and Kusheshwar-Asthan (4.8%) (Table [6](#page-15-0)). At both the places, concentration of aluminium is less than the world average aluminium concentration of river, i.e. 9.40% in surface sediment. This indicates that most of sediments are derived from quartz-rich components as orthoquartzites in the area. The low aluminium content in the sediments also indicates low amount of clay minerals and hence dominance of quartz in the sediments.

Carbon/nitrogen ratio

In the Kawar-Tal surface sediments, the C/N ratio is higher than that in the Kusheshwar-Asthan surface sediments. The range of C/N ratio is 4.80–5.92 in Kawar-Tal and 2.43–5.40 in Kusheshwar-Asthan (Table [6](#page-15-0)). According to the surface sediment analysis in Kawar-Tal,

percentage of TC ranges between 2.40 and 3.49%, with mean value 3.00%; in Kusheshwar-Asthan, TC ranges between 1.53 and 3.25%, with mean value 2.38% (Table [6\)](#page-15-0). The TS in the sediments ranges between 0.0003 and 0.0014%, with value almost similar in both wetlands. Sample analysis data show that IC percentage in Kawar-Tal ranges between 0.42 and 1.31%, with mean value 0.90%. In Kusheshwar-Asthan, IC ranges between 0.39 and 0.72%, with a mean value 0.55%. At both sites, IS is available in very less quantity (0.0001–0.0006%). The OC and OS are present in more quantity than IC and IS, in both the study areas (Table 6). The OC ranges between 1.73 and 2.29%, with mean value 2.1% in Kawar-Tal and 1.14–2.53%, with mean value 1.84% in Kusheshwar-Asthan. OS ranges between 0.0002 and 0.0009% in both the places (Table 6). The nitrogen percentage is slightly more in Kusheshwar-Asthan than in Kawar-Tal. In Kawar-Tal sediments, nitrogen varies from 0.50 to 0.59%, with mean value 0.55%, and in Kusheshwar-Asthan, range is 0.57–0.67%, with mean value 0.62%. Phosphate percentage is more in Kawar-Tal $(\sim 0.96\%)$ than in Kusheshwar-Asthan $(\sim 0.64\%)$.

Sediment analysis

Grain size is the most fundamental property of sediment particles affecting their environment, transport, deposition and biodiversity. Grain size analysis helps to understand the sediment provenance, transport history and depositional conditions (Folk and Ward [1957](#page-17-0); Friedman [1979](#page-17-0); Bui et al. [1990](#page-17-0)). The grains distribution in the surface sediment of both the wetlands Kawar-Tal and Kusheshwar-Asthan is poorly sorted. Statistical calculation was made in laboratory by the standard method (Krumbein and Pettijohn [1958](#page-17-0); Lindholm [1987](#page-17-0)). The Kawar-Tal surface sediment

grains are moderately sorted and symmetrically skewed, and sediments grains are very platykurtic (Table [7\)](#page-15-0). In Kusheshwar-Asthan, sediments are moderately well sorted, coarse-skewed, and sediment grains are very platykurtic (Table [7](#page-15-0)).

Conclusion

The distribution pattern of major cations and anions in water samples of the both wetlands was as follows: $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and

Fig. 7 Stability diagram of water samples (Kawar-Tal wetland)

 $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > F^- = PO_4^{3-}$. Most of the water samples showed good charge balance with $\pm 5\%$ error. The classification of hydrochemical facies of both wetlands shows dominance of chemical facies Ca^{2+} + Mg^{2+} , $SO_4{}^{2-}$ -Cl⁻ and HCO₃⁻-CO₃²⁻ (Fig. [9\)](#page-16-0). The analysed data show Ca^{2+} ion and HCO_3^- ion are the most dominant ions in both the wetlands water. Most of the samples of both wetlands have a Na^+/Cl^- ratio around 1, indicating straight evaporative concentration with no ionexchange process in study area. The graph between $(Ca^{2+} + Mg^{2+})$ and $(SO₄²⁻ + HCO₃⁻)$ was featured a

nearly 1:1 line in both wetlands, indicating evaporative concentration. The graph of $TZ + (total cation)$ versus $(Ca^{2+} + Mg^{2+})$ shows most of the samples very close to theoretical line (1:1) indicate weathering of rock minerals that are dominant in both wetlands. The graph of $Na⁺$ versus $NO₃⁻$ shows few water samples scattered and falling away from theoretical line (1:1), indicating interference of anthropogenic activities. The source of Ca and Mg in wetlands water can be deduced from the meq(Ca^{2+} + - Mg^{2+})/meq(HCO₃⁻) -) ratio. The graph between $meq(Ca^{2+} + Mg^{2+})/meq(HCO_3^-)$ and meq Cl^- indicates

Fig. 8 Stability diagram of water samples (Kusheshwar-Asthan wetland)

dominance of weathering over anthropogenic inputs in both wetlands. The graph between $(SO_4^{2-} + Cl^-)$ and $(Na^{+} + K^{+})$ in Kawar-Tal water samples is scattered, indicating some other source input along with natural weathering process. Rock weathering is the principle mechanism controlling the water chemistry of both wetlands. The stability diagram of Kawar-Tal wetland water indicates that water is in equilibrium with gibbsite and kaolinite, but in Kusheshwar-Asthan, it is in equilibrium with kaolinite. This indicates that the hydrogeochemistry of water in Kusheshwar-Asthan is favouring kaolinite formation and in Kawar-Tal favouring kaolinite-gibbsite formation. All the water samples of Kawar-Tal wetland are in

''good'' quality range (20–40%) on the basis of percentage of sodium. Few samples (20%) were even recorded in "excellent" quality range. But in Kusheshwar-Asthan, all the water samples are in ''good'' quality range only. Based on conductivity suggested, both the locations' water quality is in "good" range, i.e. 250 to $750 \mu S/cm$. The cationic composition indicates that water of both the wetlands is dominated by calcium ions. The anionic composition indicates that water of both the wetlands is dominated by bicarbonate ions.

Quartz (\sim 36%) and clay minerals (\sim 21%) are the most dominant minerals in both wetlands. Total carbon concentrations at both the sites indicate that there is sufficient Table 5 Summary of statistics of mineral (%) in sediment of Kawar-Tal and Kusheshwar-Asthan

min. minimum, max. maximum, Avg. average, SD standard deviation

Table 6 Summary of statistics of biogeochemical parameters (%) in sediment of Kawar-Tal and Kusheshwar-Asthan

Biogeochemical	Kawar-Tal			Kusheshwar-Asthan					
parameter $(\%)$	Min.	Max.	Avg.	SD	Min.	Max.	Avg.	SD	
Total Carbon (TC)	2.4	3.49	3	0.53	1.53	3.25	2.38	0.72	
Inorganic Carbon (IC)	0.42	1.31	0.9	0.42	0.39	0.72	0.55	0.14	
Organic Carbon (OC)	1.73	2.29	2.1	0.25	1.14	2.53	1.84	0.58	
Total Sulphur (TS)	0.0003	0.0014	0.0008	0.0005	0.0008	0.0013	0.001	0.0002	
Organic Sulphur (OS)	0.0002	0.0009	0.0005	0.0003	0.0007	0.0009	0.0008	0.0001	
Inorganic Sulphur (IS)	0.0001	0.0005	0.0003	0.0002	0.0001	0.0006	0.0003	0.0002	
Nitrogen	0.5	0.59	0.55	0.04	0.57	0.67	0.62	0.04	
Phosphate	0.84	1.12	0.96	0.12	0.61	0.67	0.64	0.03	
Silicon	34	36	35	0.91	31.5	34.5	32.88	1.38	
Aluminium	6.25	7	6.63	0.32	4.45	5.5	4.8	0.48	
Carbon/Nitrogen (C/N)	4.8	5.92	5.44	0.57	2.43	5.4	3.9	1.31	

min. minimum, max. maximum, Avg. average, SD standard deviation

Table 7 Statistics of grain size by using graphical method

organic matter available to sustain biological activities. Sulphur was reported in significant concentration in both places. The presence of nutrients, i.e. nitrogen and phosphates, is in good amount in both the places showing ideal environment for vegetation and biological productivity. Silica concentrations in the sediment samples of both the places exceed the average for Indian rivers. Aluminium is present in lower concentrations than the world average for surface sediments at both sites. Kawar-Tal lake water contains Fe (\sim 0.06 mg/L), Mn (\sim 0.03 mg/L), Ni (\sim 0.06 mg/ L), Cu (\sim 0.002 mg/L), Zn (\sim 0.02 mg/L), Cd (\sim 0.02 mg/ L), Pb(\sim 0.46 mg/L), while in Kusheshwar-Asthan water contains Fe $({\sim}0.65 \text{ mg/L})$, Mn $({\sim}0.04 \text{ mg/L})$, Ni $(\sim 0.05 \text{ mg/L})$, Cu $(\sim 0.004 \text{ mg/L})$, Zn $(\sim 0.02 \text{ mg/L})$, Cd (\sim 0.02 mg/L) and Pb (\sim 0.49 mg/L). The study indicates wetlands are rich in nutrients for biological activities and are

Classification of Hydrogeochemical Facies & Environment

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4- Recent Dolomitic Waters

- 5- Recent Recharge Waters
- 6- Ca+Mg, Na+K & HCO3+CO3
- 7- Na+K, Ca+Mg & HCO3+CO3
- 8- High Na+K & HCO3+CO3
- SO₄ 9- Concentration and precipitation of Na+K, HCO3+CO3 & Cl
- ÷ 10- CI+SO4 & HCO3+CO3
- ᠊ᠣ 11- Sea Water High Na+K & Cl+SO4
	- 12- Water Contaminated with Gypsum
	- 13- Static and Disco-ordinated Regimes
	- 14- Dissolution & Mixing
	- 15- Dynamic and coordinated Regimes

Kusheshwar-Asthan

Fig. 9 Classification of hydrochemical facies (Kawar-Tal and Kusheshwar-Asthan)

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6

Ion Exchange

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 $Na + K$ \subset

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4

5

20

HCO3 + CO3

50

80

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sufficient to support the biodiversity, but few locations are influenced by local anthropogenic activities which cause the increase of sulphur, chloride, iron and lead.

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