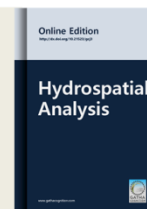




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Original Research Paper

Hydrochemical Characterisation and Groundwater Suitability for Drinking and Irrigation uses in Semiarid Region of Nashik, Maharashtra, India



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Abstract

Hydrochemical investigation was undertaken in the Kadava river basin to ascertain the groundwater quality and its suitability for drinking and irrigation purposes. In this context, forty (40) representative groundwater samples were collected from different dug/bore wells based on their importance in drinking and analyzed. Physicochemical parameters like pH, EC and TDS; cations viz., Ca, Mg, Na and K; and anions include CO₃, HCO₃, SO₄, NO₃, F, Cl were determined to authenticate the groundwater suitability for drinking. According to BIS, pH (15%), TDS (27.5%), TH (27.5%), Mg (45%), Na (15%), Cl (2.5%), NO₃ (52.5%) and F (2.5%) samples exceed the permissible limit (PL); hence, unfit for drinking. The positive loading of TDS and TH is influenced by the content of Mg, Na, Cl and SO₄ ions. The increased concentration of Na over Ca corresponds to the ion exchange process. The irrigation indices like SAR, Na (%), RSC, MAR, KR and SSP were considered to evaluate groundwater aptness for irrigation. According to SAR and RSC classification all groundwater samples are suitable for irrigation. MAR ratio suggests 97.5% samples are unfit for irrigation. The study advocates that, those aquifers which are awkward then particular remedial measures required prior to their beneficial use.

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1 INTRODUCTION

Groundwater plays an important role in water supply system for domestic, agricultural and industrial purposes in arid and semi-arid regions due to inadequate freshwater resources. It is estimated that approximately 65% groundwater used for drinking, 20% for irrigation and 15% for industrial uses in the world (Adimalla and Venkatyogi, 2018). According to United Nations Environment Programme (UNEP), one third of world population depends on groundwater for drinking particularly in India and China (UNEP, 1999). In India, groundwater is satisfying the basic needs of the society and recently overexploitation has considerable pressure on this finite natural resource due to increasing population, agricultural and industrial demands (Subramani et al., 2005). In general, the chemical

composition of groundwater is influenced by natural and anthropogenic processes viz., amount of precipitation, evapotranspiration rate, soil inputs, rock-water interaction, residence time, agricultural runoff and discharges of domestic and industrial wastes, etc. (Todd, 1980; Pawar et al., 2008; Pawar et al., 2014; Mukate et al., 2017). The consumption of contaminated water has pose serious health risk due to water contaminants like fluoride, nitrate and arsenic toxicity to millions of people (Hossain et al., 2013; Pandith et al., 2017; Adimalla and Li, 2018). Therefore, evaluation and monitoring of groundwater resources is important to prevaricates any health risk and protection of groundwater quality in natural state because it vital for public health and socioeconomic growth of the region

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(Naik *et al.*, 2008). Several studies reported that hydrochemical behavior of water is an essential to ascertain the groundwater suitability for drinking and irrigation for better human health and agricultural productivity (Tóth, 1999; Panaskar *et al.*, 2014; Mukate *et al.*, 2015; Wagh *et al.*, 2016a and b; Adimalla *et al.*, 2018).

The complete consideration of groundwater suitability for irrigation is significantly based on total ionic content of the water such as Electrical Conductivity (EC), Sodium Adsorption Ratio (SAR), Percent Sodium (% Na), Sodium (Na), Calcium (Ca), Chloride (Cl), Residual Sodium Carbonate (RSC), Magnesium Adsorption Ratio (MAR), etc. (Yidana *et al.*, 2010; Wagh *et al.*, 2016a; Panaskar *et al.*, 2016; Adimalla and Venkatayogi, 2018). In addition, it depends on salt concentration, sodium content, nutrients rate, alkalinity, acidity and hardness of water leads to loss of soil fertility and crop yield (Kirda, 1997). The poor water quality may influence the crop productivity physical condition of soil and high contents of dissolved ions in irrigation water will cause stunted plant growth and crop yield (Ayers and Westcot, 1994; Ramakrishnan, 1998). The Kadava river basin is prominent for production of cash crops like sugarcane, grapes, onion, pomegranates, vegetables, etc., due to sympathetic climate; thus, it becomes crucial to know irrigation suitability of groundwater. If groundwater quality is not protected well in time, the impact of using such contaminated water may result into the diminution of plant growth, agricultural yield and economical defeat (Ramesh and Elango, 2011). Therefore, identifying and addressing the irrigational water quality-related issues are essential to investigate at local to global scale. This study utilizes multivariate statistical techniques like Correlation Matrix (CM) and Principal Component Analysis (PCA) to identify influencing factors like geogenic and anthropogenic and there relative impacts on water quality variables. In recent times, GIS based interpolation techniques has been widely used to represent the spatiotemporal variation of ions, geomorphology, hydrogeology, land use pattern, etc., (Zolekar and Bhagat, 2015; Sahu *et al.*, 2018). Also, hydrochemical characterization of groundwater has been evaluated through dominance of ion exchange, rock weathering, evaporation, etc., to distinguish the processes distressing the groundwater chemistry. moreover, these techniques widely applied by several researchers to know the chemical composition, source of ions and relation between different variables which persuade the water quality (Rao *et al.*, 2014; Varade *et al.*, 2018; Kant *et al.*, 2018).

To ascertain the groundwater suitability for drinking and irrigation in the Kadava River Basin, also, it needs to understand the hydrochemical mechanisms which influencing the groundwater quality in basaltic terrain due to homogeneous lithological conditions and climatic deviation. In the study area, most of the inhabitants live in isolated villages and farm houses;

where, dug and bore wells are regularly used for drinking and irrigation. The farmers use excessive fertilizers and agrochemicals to enhance crop productivity, which results downward leaching of contaminants along with recharge water, consequently, contaminated groundwater poses a serious health risk to human. Therefore, incessant monitoring and characterisation of groundwater quality is required to prevent further groundwater quality deterioration in the future. In the basin, very partial research has been embarked on groundwater quality and health related risk; however, studies by few federal government agencies and individuals addressed water quality issues (MPCB-NEERI, 2014; Wagh *et al.*, 2017a and b; 2018a and b). Nonetheless, the connection between groundwater quality and its suitability coupled with hydrochemical mechanism was not investigated till recently. Therefore, the present study is initiated with main objectives of i) To ascertain the physicochemical characteristics of groundwater with a view to drinking and irrigation suitability; ii) To recognize the natural and anthropogenic factors which influencing on groundwater quality through multivariate statistical techniques. iii) To use of GIS based point interpolation technique to articulate the spatial extent of pollutants in the study area. Overall, integration of these techniques will help to find the source and influenced factors of water contaminants, as well, outcomes of the study may support to local water regulators to develop water suitability management plans in the Kadava river basin.

2 STUDY AREA

The study area is located within the Deccan Trap Hydrologic province, administratively situated in Chandwad and Niphad Tehsil of Nashik District, Maharashtra with lies between latitude 19°55' N to 20°25' N and longitude 73°55' E to 74°15' E, with an area of 1053km² (Figure 1). The Kadava River is the major tributary of Godavari which originates in Western Ghat, locally known as Sahyadri hills and flows towards Northwest to Southeast direction and confluence with Godavari at Nandur-Madhmeshwar dam located in Niphad Tehsil. The average rainfall of study area is 700mm rainfall and maximum from Southwest monsoonal winds (June to September). The annual temperature ranges from 5°C to 40°C with semi-arid climate and relative humidity ranges from 43 to 62% (CGWB, 2014). Alluvium deposits (20 to 25m depth) are found along the banks of river in Niphad Tehsil. In the study area, lateritic black soil, coarse shallow reddish black soil, medium light brownish black soil and reddish brown soil are reported. The black soil has high amount of alumina and carbonates of calcium and magnesium with variable concentrations of phosphorous, potash and nitrogen (CGWB, 2014). A foremost part has flat topography with gentle slopes inclined towards the southeast of the study area. The study area is well known for agricultural production of grapes, sugarcane, onions, etc., with varied cropping patterns is spread along the water courses of the River,

the Palkhed Canal and the Nandur-Madhmeshwar dam. The study area is composed of various geomorphologic units (Figure 2). The North Region composed of high level (>900 m) and middle level plateaus (550 to 900 m) elevation, Central and Northeast region have experiencing denudation. The South and Central region are prejudiced by floodplain hydrologic processes where the underlying alluvium is drained by the Kadava and Godavari Rivers. Geologically, the study area is a part of South East Deccan Volcanic Province, underlain by basalt of Upper Cretaceous to Lower Eocene age and comprised of 'pahoe' and 'aa' lava flows (GSI, 2001). Also, comprises hard rock (basalt) of the Sahyadri Group and soft rock (alluvium) which occurs in patches on the floodplains (Figure 3). Besides, Kalsubai subgroup which contains geologic markers (M1 and M2) developed on the top of the Salher and lower Ratangarh formations. Groundwater occurs mostly in unconfined, semi-confined to confined conditions in upper weathered and fractured parts down to 20-25m in depth. The yield of the wells is variable due to permeability and transmissivity of the aquifer, well location, diameter and depth. In the basalt formation, the yield of dug wells tapping upper phreatic aquifer at the depth of 12 to 15m below ground surface ranges from 45 to 90 m³/day and bore wells drilled down to 50 to 70 m depth and yields varies from 18 to 68 m³/day, based on local hydrological condition.

Alluvium occurs in discontinuous patches of thickness ranges from 7 to 21m along the river bank and floodplains area and composed of sand, gravel and kankar. Groundwater in the alluvium deposits is found under semi-confined and confined conditions; while, the water yield ranges from 13-22m³/day from dug wells and bore wells (CGWB, 2014).

3 MATERIAL AND METHODS

To ascertain the hydrochemical composition and groundwater suitability for drinking and irrigation in Kadava River Basin, forty (40) representative groundwater samples were collected based on their importance in drinking from dug and bore wells in pre-monsoon season (April) of 2011. The study area is characterised by different geomorphic features viz., new floodplains, old floodplains, denudational landforms, and middle level plateaus. The groundwater samples were collected in sterilized plastic containers after running the water evacuation for 2 to 3 minutes to remove the influence from stored water in pipe. The parameters like pH and electrical conductivity (EC) were measured in situ by using portable multi-parameter tester. The plastic containers were labeled and sealed appropriately and transported to analytical laboratory and stored at 4°C for further analysis. The major cations viz., Ca, Mg, Na and K; and anions include CO₃, HCO₃, SO₄, NO₃, and Cl were analyzed by

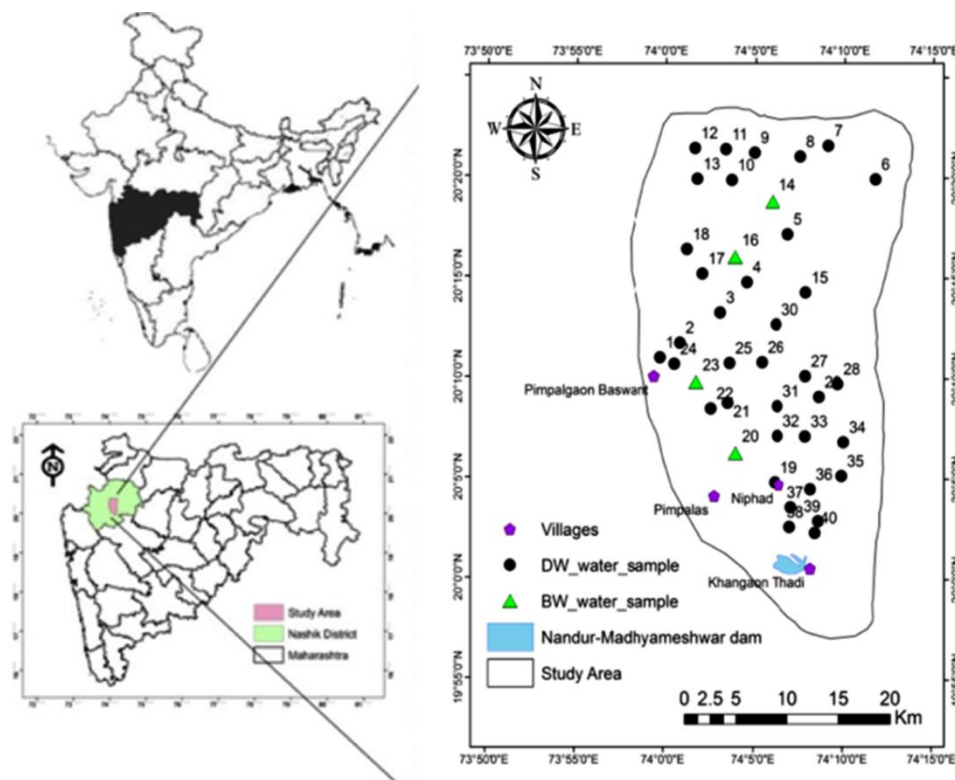


Figure 1. Study area with groundwater sample locations

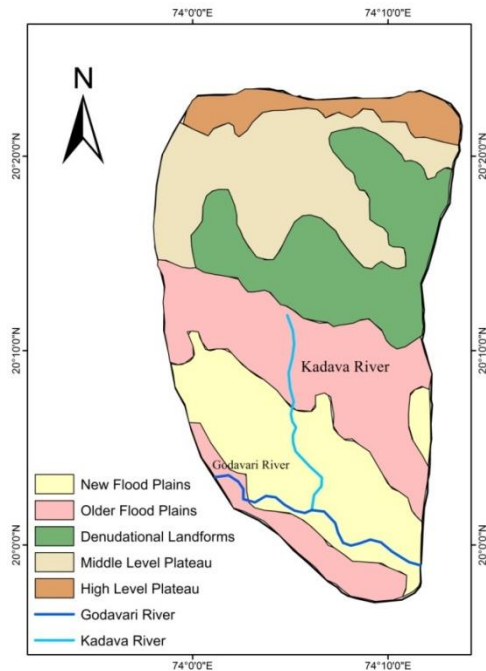


Figure 2. Geomorphology (after GSI, 2001)

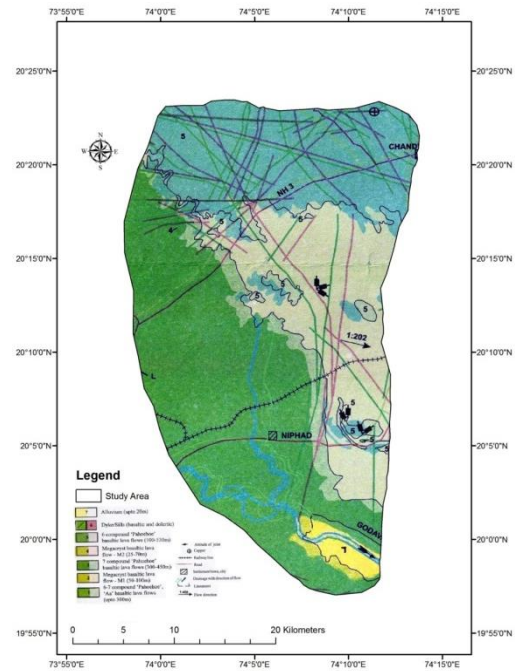


Figure 3. Hydrogeology

adopting the standard procedures of American Public Health Association (APHA, 2005). Total Hardness (TH) as CaCO_3 is computed by $\text{Ca (meq)} + \text{Mg (meq)} \times 50$. Total Dissolved Solids (TDS) is calculated from EC by multiplying with factor 0.65 (Hem, 1985). The ion balance errors (IBE) of analyzed parameters are within $\pm 10\%$ which is supposed to be acceptable (Berner and Berner, 1987). The Survey of India toposheets numbers (46 L/3, 46 L/4, 46 H/15 and 46 H/16 on scale 1:50000) used to prepared the base map of the study area. ArcGIS software is used to prepare the hydrology, geomorphology, spatial distribution maps by using Inverse Distance Weightage (IDW) technique. The MS-Excel, Statistical Package for Social Sciences (SPSS 22.0) and R software were used for statistical analysis.

4 RESULTS AND DISCUSSIONS

The summary of the groundwater parameters and comparison with the Bureau of Indian Standards (BIS) for drinking suitability is summarised in Tables 1 and 2.

4.1 Groundwater Suitability for Drinking

In the study area, pH values ranged from 7.8 to 8.9 with mean concentration of 8.3 which indicate groundwater is fairly alkaline. This nature is attributed to the loss of CO_2 , and the precipitation and dissolution of minerals from within the basalt (Kale and Pawar, 2012). Generally, elevated pH (alkaline waters) does not impact human health; but, it can alter the taste of the water and it shows a close association with ionic constituents of the water (Wagh et al., 2016a). As per the BIS Standards (2012), 15% (sample numbers 9, 32,

34, 36, 39 and 40) samples exceeded the permissible limit of pH (Table 2). In the study area, the spatial irregularity is observed in the Southern and Northern parts due to the influenced of saturation and dilution phenomenon (Figure 4a). The EC values varies from 816-7760 $\mu\text{S}/\text{cm}$ with mean concentration of 2508.5; however, it is related to the amount of total dissolved salts in water, which suggest an elevated inorganic pollution load in the water (Morrison et al., 2001). The value of EC increases with temperature and varies with the amount of soluble salts. The BIS has not prescribed any safe limit for EC; yet, the World Health Organization (WHO, 2011) designated 1500 $\mu\text{S}/\text{cm}$ EC as the permissible limit. The samples compared with WHO standards confirm that, 30 (75%) groundwater samples exceed the PL (Table 2). In view of spatial coverage, EC values are increased in the downstream portion of the Kadava River along the groundwater flow path, where alluvium deposits encountered with intense agriculture (Figure 4b). Total Dissolved Solids (TDS) is an important parameter for drinking and irrigation water suitability due to the contained ionic constituents (Davies and DeWiest, 1966). The TDS has a wide range of 530.4 to 5044.0 mg/L with mean concentration of (1630.53 mg/L) due to the semi-arid environment, lithology, agricultural and anthropogenic inputs. As per the BIS standards, all the groundwater samples exceed the desirable limit and 27.5% samples surpass the PL. High TDS is attributed from percolation of salts, dissolution of minerals from aquifer system and agricultural inputs and consumption such an elevated TDS content water may lead to gastrointestinal irritation (Panaskar et al., 2016).

Table 1. Physicochemical composition of groundwater samples (n=40)

Sample No.	Type	pH	EC	TDS	TH	Ca	Mg	Na	K	Cl	F	CO ₃	HCO ₃	SO ₄	NO ₃	IBE
G1	DW	7.8	1664	1081.6	590.41	48.1	114.72	60.4	1	68.46	0.5	300	60	37.87	50.14	-0.26
G2	DW	8	2336	1518.4	764.12	71.05	143.11	51.3	2.5	215.88	0.2	60	190	199.85	44.38	4.43
G3	DW	8.2	1414	919.1	354.85	50.1	56.02	63.8	1	110.76	0.1	40	120	87.82	50	4.4
G4	DW	8.4	816	530.4	302.68	51.3	42.56	26.5	4.6	108.28	0.3	20	140	22.61	19.38	3.62
G5	DW	8.3	1000	650	577.58	28.46	123.57	25.46	1.2	167.89	0.5	40	120	147.46	29.74	4.45
G6	DW	8.3	1426	926.9	454.28	50.5	80.04	42.1	1.5	119.36	0.4	20	120	145.14	61.7	4.38
G7	DW	8.2	1752	1138.8	473.89	53.73	82.85	42.7	1.5	126.88	1	20	110	166.28	51.81	4.48
G8	DW	8	4340	2821	1101.4	130.43	189.18	108.5	3	582.2	0.4	20	160	196.63	44.26	4.48
G9	DW	8.6	1024	665.6	367.98	30.46	71.21	15.6	3.5	42.6	0.5	100	90	39.51	40.54	3.93
G10	DW	8.2	2620	1703	671.26	71.36	120.26	53.4	1.5	223.06	0.2	40	120	197.8	51.91	4.06
G11	DW	8.4	1436	933.4	593.14	55.52	110.86	21.3	1	199.4	0.2	20	130	125.99	44.2	4.28
G12	DW	8.3	2620	1703	591.21	61.01	107.04	73	1	194.92	0.2	40	180	167.81	66.98	2.25
G13	DW	8.4	900	585	237.71	29.87	39.78	47.37	1.3	75.66	0.5	0	90	81.95	58.62	4.27
G14	BW	8.3	1664	1081.6	239.83	12.22	51.06	74.5	5.2	84.2	2	20	110	96.07	41.66	3.47
G15	DW	8.4	1083	703.95	389.44	33.63	74.51	31.36	7.5	145.6	0.6	0	160	58.65	57.63	2.39
G16	BW	8.5	992	644.8	237.65	32.06	38.43	52.4	1	61.12	0.1	40	140	52.69	59.94	-2.51
G17	DW	8.1	3770	2450.5	840.85	74.02	160.02	74.2	0.9	307.46	0.2	60	200	180	67.26	3.3
G18	DW	8.4	1844	1198.6	306.91	38.82	51.21	43.1	1.9	95.44	0.2	20	120	67.48	41.42	4.23
G19	DW	8.4	2198	1428.7	430.66	19.04	93.47	130.06	3.5	188.98	0.4	40	160	145.89	59.15	3.85
G20	BW	8.3	5680	3692	1281.79	44.89	285.37	299.8	1	627.64	0.5	300	200	172.91	53.49	4.38
G21	DW	8.2	2500	1625	497.5	33.05	101.23	65.02	1.1	159.82	0.4	40	140	155.95	59.65	1.76
G22	DW	8.1	1580	1027	189.73	29.47	28.32	150.33	1.3	239.67	0.4	0	120	69.51	42.35	-2.39
G23	BW	8.4	3414	2219.1	597.41	52.01	114.04	207.01	4.5	297.1	0.4	200	160	98.85	56.88	0.98
G24	DW	8	1368	889.2	572.18	68.15	98.04	52.3	1.5	197.78	0.3	40	180	158.89	58.99	-1.35
G25	DW	8.2	1774	1153.1	652.39	60.92	122.02	23.2	1.4	138.76	0.3	0	300	161.28	44.3	4.35
G26	DW	8.4	1689	1097.85	632.69	117.42	82.75	23.36	4.3	189.6	0.4	20	180	148.65	53.66	3.13
G27	DW	8	2400	1560	565.46	67.14	97.01	106.1	1.5	238.98	0.1	40	200	123.94	44.75	4.27
G28	DW	8.1	3244	2108.6	805.49	122.71	121.69	70.5	1	267.12	0.3	20	400	112.77	43.11	3.76
G29	DW	8.4	2314	1504.1	545.07	72.02	89.07	56.4	5.2	199.8	0.2	40	180	132.84	44.37	0.3
G30	DW	8.5	1638	1064.7	338.95	80.56	33.56	66.1	3	98.3	0.1	20	200	87.77	43.85	2.5
G31	DW	8.2	4060	2639	690.1	64.05	129.32	108.8	1.4	307.52	0.3	20	150	217.33	44.37	4.27
G32	DW	8.6	1640	1066	546.41	63.07	94.85	219.8	2.8	261.08	0.5	180	160	120.09	19.31	4.42
G33	DW	8.1	7080	4602	573.56	48.05	110.64	142.3	1.5	355.2	0.5	20	180	205.23	52.62	-2.95
G34	DW	8.8	1516	985.4	395.99	34.87	75.35	32.5	1.4	118.96	0.3	20	110	109.91	45.09	2.83
G35	DW	8.4	3410	2216.5	407.23	23.45	85.06	150.01	1	235.9	0.6	20	140	141.97	68.62	3.48
G36	DW	8.6	2014	1309.1	482.81	68.34	76.12	101.09	3	199.78	0.5	100	100	84.8	44	3.77
G37	DW	8.4	5100	3315	767.66	29.66	169.22	281.6	3.5	502.68	0.6	200	100	118.99	61.74	3.19
G38	DW	8.4	7760	5044	1033.99	38.08	229.07	583.4	4.5	1057.9	0.8	100	200	239.01	61.75	4.21
G39	DW	8.7	3240	2106	535.39	12.02	123.3	219.2	2.3	352.16	0.6	100	100	159.24	41.17	3.55
G40	DW	8.9	2020	1313	501.8	44.09	95.54	102.3	1	192.2	0.5	20	210	166.9	20.58	4.13
Minimum		7.8	816	530.4	189.73	12.02	28.32	15.6	0.9	42.6	0.1	0	60	22.61	19.31	-2.95
Maximum		8.9	7760	5044.0	1281.79	130.43	285.37	583.4	7.5	1057.9	2	300	400	239.01	68.62	4.48
Mean		8.3	2508.50	1630.53	553.49	52.89	102.79	102.45	2.32	233.90	0.43	60.00	155.75	130.11	48.63	2.90

G: Groundwater; **DW:** Dug Well; All the values are expressed in mg/l except pH on scale and EC in $\mu\text{S/cm}$.

The calcium content varies from 12.02 to 130.40mg/L (mean 52.89mg/L) (Table 1). According to BIS standards, all the groundwater samples are within permissible limit; hence, beneficial use for drinking. Conversely, 4 samples (numbers 8, 26, 28 and 30) are beyond the BIS desirable limit (75mg/L) (Table 2). Spatial distribution map demonstrated that high value of calcium occurred in patches of central and Southern parts due to local geological influences (Figure 4c). The magnesium content varies widely from 28.32mg/L to 285.37mg/L with mean value of 102.79mg/L. In the study area, 45% groundwater samples exceeded the PL (100mg/L) of the BIS. The high content of magnesium is encountered in patches of downstream of the Kadava River Basin catchment area (Figure 4d) owing to

geological control and the presence of the Thakurwadi Formation containing picritic horizons (MgO of 3.5% to 11.86 %) (Beane et al., 1986). Average Ca+Mg value (meq/l) contributes 73.53% of total cations and signifies the major supply of mafic minerals such as olivine and pyroxene from weathering of basalt (Pawar et al., 2008; Rabemanana et al., 2005). TH content is ranges from 189.73-1281.79mg/L with mean value of 553.49mg/L (Table 1). As per the BIS standards, prescribed permissible limit of TH for drinking is 600mg/L. TH content of 27.5% (sample numbers 2, 8, 10, 17, 19 and 25, 26, 28, 31, 37 and 38) groundwater samples exceed the PL of drinking (Table 2). The sodium content of groundwater samples are ranges between 15.6mg/L to 583.4mg/L with mean 102.45mg/L. As per BIS

standards, 15% samples (number 20, 23, 32, 37, 38 and 39) beyond the PL; hence, unfit for drinking (Table 2). The drinking of high content sodium water may cause human health effects like high blood pressure, arteriosclerosis, edema, hyperosmolarity, vomiting, etc (Prasanth et al., 2012). The high content of sodium is due to basalt weathering and dissolution of soil salts are redeposit by evaporation and sodium exhibits high solubility behavior (Stallard and Edmond, 1983). The high sodium content is likely derived from the Salher Formation which contains plagioclase feldspar and forms the solution between anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) and albite ($\text{NaAlSi}_3\text{O}_8$) having a mole ratio of different cations and anions (Garrels and Christ, 1967). The South part has more accumulation of sodium due to the hydro-geomorphologic features such as slope and groundwater flow path (Figure 4e). The K content is varies from 0.9-7.5mg/L with mean value of 2.32mg/L, As per BIS standards, all the samples are within allowable range. However, high content in groundwater is mainly influenced by agricultural activities, which relies on K-rich fertilizers; however, its diminutive content is due to a lack of naturally-occurring K bearing minerals within the study area. The cation abundance in the study are descending order of $\text{Mg} > \text{Ca} > \text{Na} > \text{K}$.

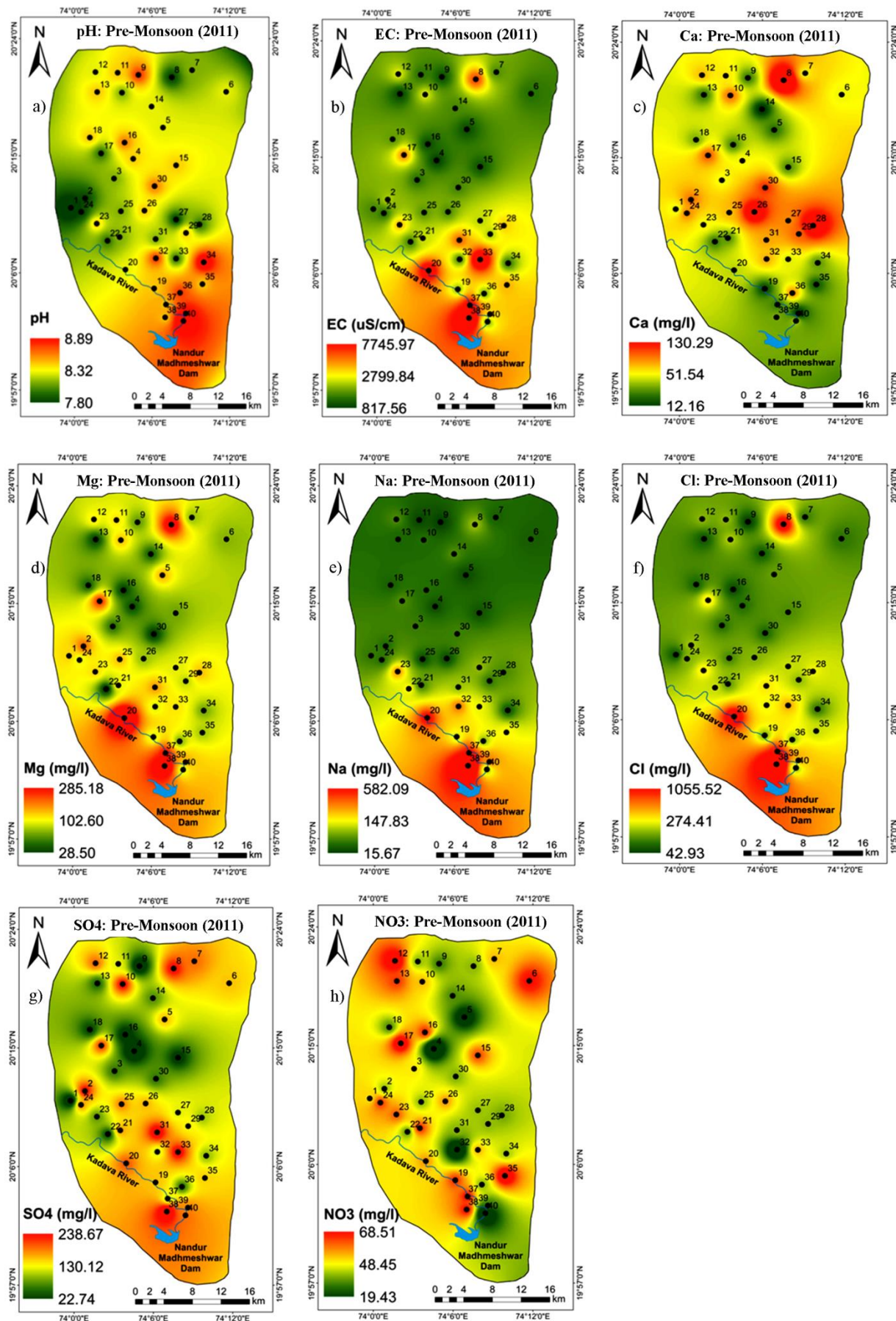
The chloride value ranges from 42.6-1057.9mg/L with mean value of 233.90mg/L (Table 1). As per BIS standards, 39 groundwater samples are within the PL, except sample number 38. Nonetheless, only 11 (27.5%) groundwater samples (numbers 20, 33, 37 to 39) exceed the DL for chloride (250mg/L) (Table 2). The high content of Cl in groundwater is contributed from natural and anthropogenic processes such as weathering of chloride minerals such as halite, domestic waste, fertilizers, etc. (Loizdou and Kapetnois, 1993). The spatial distribution map of Cl depicts that South part is mostly influenced by leaching of fertilizers and animal

waste and agricultural runoff (Figure 4f). The sulphate content is varies from 22.61 to 239.01mg/L with mean value of 130.11mg/L (Table 1). It is observed that all of the groundwater samples are within the PL of sulphate; conversely, only 7.5% samples (numbers 31, 33, 38) exceed the DL (200mg/L) of drinking (Table 2). The source of sulphate content in groundwater is contributed from gypsum-containing fertilizers (Todd, 1980). The spatial variation map of sulphate demonstrated that the lower reaches of catchment area has been mostly affected; while, the northern region is influenced in few places, this area also has a prolonged agriculture and excessive use of fertilizers to increase crop yield (Figure 4g). The nitrate content varies from 19.31mg/L to 68.62mg/L with mean concentration of 48.63mg/L (Table 1). The analytical results compared with BIS standards confirm that 52.5% samples exceed the permissible limit (45mg/L) of the BIS (Table 2). The elevated nitrate concentration corresponds to nitrogen-phosphorus-potassium (NPK) complex fertilizers; Urea, animal excreta, domestic waste and organic compost (Wagh et al., 2017a; 2018a and b). The spatiotemporal map of nitrate illustrates the uneven distribution at South, Central and North region based on changing cropping pattern (Figure 4h). The fluoride content ranges from 0.1 to 2mg/L with mean concentration of 0.4 mg/L. The analytical results illustrated that only one sample (number 14) which contained 2mg/L fluoride; so, all the groundwater samples have allowable levels of fluoride for drinking as they show a fluoride content below the PL (Table 2). The fluoride content source is anthropogenic like phosphate fertilizer use in agricultural field. In general, anions in the groundwater are reflecting the influence of geochemical and anthropogenic inputs. It is illustrated that chloride is the primary anion followed by bicarbonate, sulphate and nitrate. The mean concentrations of all the anions are within permissible limits set by the BIS, except nitrate.

Table 2. Groundwater suitability for drinking based on BIS drinking standards

Parameters	DL-PL	Samples above DL (%)	Sample numbers	Samples above PL (%)	Sample numbers
pH	6.5-8.5	100	1-40	15	9, 32, 34, 36, 39, 40
EC	-	-	-	-	-
TDS	500-2000	100	1-40	27.5	8, 17, 20, 23, 28, 31, 33, 35, 37, 38, 39
TH	300-600	90	1-12, 15, 17-21, 23-40	27.5	2, 8, 10, 17, 19, 25, 26, 28, 31, 37, 38
Ca	75-200	10	8, 26, 28, 30	0	
Mg	30-100	97.5	1-20, 22-40	45	1, 2, 5, 8, 10, 11, 12, 17, 20, 21, 23, 25, 28, 31, 33, 37-39
Na	200	-	-	15	20, 23, 32, 37, 38, 39
K	12	0	-	0	
Cl	250-1000	27.5	8, 17, 20, 23, 28, 31, 32, 33, 37, 38, 39	2.5	38
SO ₄	200-400	7.5	31, 33, 38	0	
NO ₃	45	-	-	52.5	1, 3, 6, 7, 10, 12, 13, 15-17, 19-21, 23-24, 26, 34-36, 37, 38
F	1-1.5	2.5	14	2.5	

DL: Desirable Limit; PL: Permissible Limit.

Figure 4. Spatial distributions: a) pH, b) EC, c) Ca, d) Mg, e) Na, f) Cl, g) SO₄ and h) NO₃

4.2 Irrigation Suitability of Groundwater

The absolute consideration of groundwater suitability for irrigation is significantly based on total ionic content of the water such as EC, SAR, % Na, Na, Ca, Cl, RSC, MAR, etc. In addition, it depends on salt concentration, sodium content, nutrients rate, alkalinity, acidity and hardness of water leads to loss of soil fertility and crop yield (Kirda, 1997). The area under investigation is

renowned for agriculture due to sympathetic climate; thus, it is important to know water quality of irrigation. If groundwater quality is not protected properly then the impact of using such polluted water may leads to diminution of plant growth, crop productivity (Ramesh and Elango, 2011). As a result, the suitability of groundwater for irrigation has been attempted on the basis of various irrigation indices and their classification is represented (Tables 3 and 4).

Table 3. Irrigation suitability indices for groundwater

Sample No.	SAR	RSC	MAR	KR	Na(%)	SSP
G1	1.07	-0.98	79.90	0.22	18.14	18.00
G2	0.80	-10.36	77.05	0.14	12.91	12.60
G3	1.46	-3.87	65.08	0.39	28.07	27.89
G4	0.66	-3.15	58.03	0.19	17.21	15.86
G5	0.46	-8.42	87.86	0.09	8.85	8.63
G6	0.85	-6.56	72.54	0.20	16.89	16.60
G7	0.85	-7.12	71.99	0.19	16.50	16.22
G8	1.41	-19.00	70.74	0.21	17.70	17.47
G9	0.35	-2.65	79.58	0.09	9.34	8.34
G10	0.89	-10.29	73.74	0.17	14.80	14.59
G11	0.38	-9.22	76.89	0.08	7.34	7.16
G12	1.30	-7.69	74.52	0.27	21.09	20.96
G13	1.33	-3.33	68.94	0.43	30.33	29.99
G14	2.08	-2.40	87.44	0.67	40.94	39.96
G15	0.69	-5.27	78.69	0.17	16.47	14.73
G16	1.47	-1.18	66.64	0.47	32.41	32.16
G17	1.11	-11.76	78.28	0.19	16.02	15.92
G18	1.06	-3.57	68.74	0.30	23.65	23.19
G19	2.70	-4.78	89.11	0.65	39.66	39.28
G20	3.61	-12.75	91.38	0.50	33.41	33.37
G21	1.26	-6.46	83.62	0.28	22.06	21.89
G22	4.72	-1.87	61.56	1.70	63.15	63.03
G23	3.66	-2.81	78.52	0.74	42.96	42.65
G24	0.95	-7.29	70.57	0.20	16.65	16.42
G25	0.39	-8.30	76.95	0.08	7.33	7.09
G26	0.40	-9.15	54.01	0.08	8.10	7.37
G27	1.93	-6.83	70.66	0.40	28.90	28.73
G28	1.07	-9.05	62.30	0.19	15.96	15.85
G29	1.04	-6.74	67.33	0.22	19.00	18.20
G30	1.56	-2.88	40.98	0.42	30.19	29.63
G31	1.79	-10.85	77.09	0.34	25.43	25.28
G32	4.06	-2.43	71.48	0.86	46.55	46.36
G33	2.57	-8.01	79.33	0.53	34.88	34.74
G34	0.71	-5.55	78.27	0.18	15.30	14.98
G35	3.21	-5.30	85.81	0.79	44.22	44.12
G36	1.99	-4.79	64.99	0.45	31.42	31.05
G37	4.39	-7.28	90.48	0.79	44.18	44.00
G38	7.83	-14.38	90.93	1.21	54.83	54.72
G39	4.09	-5.90	94.47	0.88	46.86	46.70
G40	1.97	-6.06	78.32	0.44	30.56	30.44
Minimum	0.35	-19.00	40.98	0.08	7.33	7.09
Maximum	7.83	-0.98	94.47	1.70	63.15	63.03
Average	1.85	-6.66	74.87	0.41	26.26	25.90

All the values are expressed in epm.

Table 4. Classification of groundwater samples based on irrigation indices

Classification Index	Empirical formulae	Category	Range	Number of samples	Samples (%)	sample numbers
SAR (Richards, 1954)	$Na^+ / (\sqrt{Ca^{2+} + Mg^{2+}} / 2)$	Excellent	<10	40	100	1-40
		Good	10-18	0	--	--
		Doubtful	18-26	0	--	--
		Unsuitable	>26	0	--	--
Na (%) (Doneen, 1964).	$[(Na^+ + K^+) / (Ca^{2+} + Mg^{2+} + Na^+ + K^+)] * 100$	Excellent	0-20	18	45.0	1, 2, 3-10, 15, 17, 24-26, 28-29, 34
		Good	20-40	14	35.0	3, 12, 13, 16, 18-21, 27, 30, 31, 33, 36, 40
		Permissible	40-60	7	17.5	14, 23, 32, 35, 37-39
		Doubtful	60-80	1	2.5	22
		Unsuitable	>80			
RSC (Richards, 1954)	$(CO_3 + HCO_3) - (Ca + Mg)$	Good	<1.25	40	100	1-40
		Medium	1.25-2.5	0	--	--
		Bad	>2.5	0	--	--
MAR (Raghunath, 1987)	$Mg / (Ca + Mg) * 100$	Suitable	<50	1	2.5	30
		Unsuitable	>50	39	97.5	1-29, 31-40
KR (Kelly, 1951)	$Na^+ / (Ca^{2+} + Mg^{+2})$	Suitable	<1	38	95.0	--
		Unsuitable	>1	2	5.0	22, 38
SSP (Eaton, 1950)	$(Na^+) \times 100 / Ca^{2+} + Mg^{2+} + Na^+ + K^+$	Good	<20	18	45.0	1, 2, 4-11, 15, 17, 24-26, 28, 29, 34
		Permissible	20-40	15	37.5	3, 12-14, 16, 18-21, 27, 30, 31, 33, 36, 40
		Doubtful	40-80	7	17.5	22, 23, 32, 35, 37-39
		Unsuitable	>80	--	--	--

SAR ratio is used to measure the alkali/sodium hazard to the crop and, hence, considered to be an important parameter for determining the water suitability for irrigation because sodium concentration can reduce the soil permeability and soil structure (Todd, 1980). This index gives an idea about the proportion of sodium to calcium and magnesium ions in water. Generally, water having a low SAR value is good for irrigation (Karanth, 1987). SAR values ranges from 0.35 to 7.83 with an average 1.85 (Table 3). As per the Richards (1954) classification (Table 4), all the groundwater samples come under excellent water category for irrigation. The spatial variation map of SAR illustrated that, the Southern regions contain high concentration of sodium. The hotspots (sample numbers 20, 22, 23, 32, 37, 38 and 39) are identified in intense agricultural zone (Figure 5a).

Percent Na is an important ratio used to identify the soluble sodium content of the water and also used to

expose the sodium hazard. Sodium by the process of base-exchange replaces calcium in the soil which as result soil permeability reduced (Doneen, 1964). In the study area, the percent Na value ranges from 7.33 to 63.15 with an average 26.26 (Table 3). As per the Doneen classification (Table 4), 45%, 35 % and 17.5% groundwater samples fall in excellent, good and permissible class for irrigation, respectively. However, only one sample (number 22) is characterized as doubtful class of irrigation use. The downstream part of the study area is having intense agriculture, where, high value of Na(%) encountered (Figure 5b).

Generally, water with high concentration of CO_3 and HCO_3 has the tendency to cause the precipitation of calcium and magnesium as a result water in the soil become concentrated. It leads to relative proportion of sodium (Na^+) in the water and, as a result, sodium bicarbonate is increased (Sadashivaiah et al., 2008). When, RSC becomes too high, the CO_3 combines with

Ca and Mg to form solid material, which settles out of the water and ends with increase in SAR and % Na. Positive RSC shows that sodium built is possible in the soil. The RSC value ranges from -19.00 to -0.98 with an average value of -6.66 (Table 3). According to Richards (1954) classification, RSC value (<1.25) all groundwater samples are considered safe for irrigation (Table 4). The spatial extent map of RSC represented that few hotspots is observed at the North and Central regions of the study area with high RSC value (Figure 5c).

The MAR ratio indicates the excess amount of magnesium (Mg^{2+}) over calcium (Ca^{2+}) (Raghunath, 1987). Generally, the source of magnesium in groundwater is due to ion exchange of minerals from rocks and soils by water (Mukherjee et al., 2005). The high MAR (>50) results in increase soil alkalinity and affects the crop yield. In the study area, a wide range of MAR values are observed with ranges of 40.98 to 94.47 with an average value of 74.87 (Table 3). As per MAR classification, 97.5% samples are unsuitable for irrigation and only 2.5% (number 30) groundwater sample confirm their fitness for irrigation (Table 4). In the vicinity of agricultural areas of south and north regions, where, sample locations like 5, 14, 20, 35, 37, 38 and 39 comprises high MAR value (Figure 5d).

Kelley's ratio is used to measure the sodium concentration against calcium and magnesium. If ratio is >1 suggests the excessive concentration of sodium which leads to undesirable effects on soil properties and reducing soil permeability. Consequently, water with ratio (>1) is unsuitable and (<1) is supposed to be suitable for irrigation (Kelley, 1951). In this study, KR values ranges from 0.08 to 1.70 with an average 0.41 (Table 3). It is inferred that majority of the groundwater samples (i.e. 95 %) are suitable for irrigation, while 5 % (numbers 19 and 38) are unsuitable for irrigation (Table 4). It is observed that the south part where intense and prolonged agriculture taking place is one of the cause of high concentration of sodium; hence, samples restricted irrigation in downstream part (Figure 5e).

The SSP ratio is used to evaluate sodium hazard. Water with SSP greater than ($>60\%$) may result sodium accumulation; hence, soil physical properties will breakdown. Irrigation with high sodium content water may cause an accumulation of exchangeable sodium ion on soil colloids. Also, continues use of alkaline water for irrigation has adverse effects on soil physical properties and reduces the crop yield (Fipps, 2003). In general, when sodium content is high in irrigation water, sodium ion tends to be absorbed by clay particle, displacing magnesium and calcium ion. The exchange process in soil reduces the soil permeability and affects the internal drainage. The calculated values of SSP

varied from 7.09 to 63.03% with an average 25.90% (Table 3). SSP classification suggests that, 45% and 37% groundwater samples fall in good (<20) and permissible (20-40) categories. While, (17.5%), numbers (22, 23, 32, 35, 37, 38 and 39) groundwater samples are come under doubtful category (Table 4). The spatial variation map of SSP illustrated that, high value of SSP is observed in southern part, few patches at central parts of the study area (Figure 5f).

4.3 Multivariate Statistical Analysis

The multivariate statistical analysis was performed to reduce and organize the data with similar hydrochemical characteristics. Total 14 physicochemical parameters were considered for the formulation of Correlation Matrix (CM) and Principle Component Analysis (PCA) and their results are tabulated (Table 5 and 6).

4.3.1 Correlation Matrix (CM)

The correlation matrix is used to determine the degree of correlation among the various physicochemical parameters which influence groundwater quality in the study area. The correlation analysis involving statistical calculations and gives a measure of how well one parameter predicts the value of another parameter (Pearson, 1896; Kurumbein and Graybill, 1965). In water chemistry, CM is recognized as a common and useful statistical technique to know the positive and negative association of ions (Box et al., 1978; Chapman, 1996). A positive strong correlation can show the same sources of particular ions which can be natural or anthropogenic in origin; while, weak correlation indicates the sources of ions are independent from each other (Islam et al., 2017). The variables showing a correlation coefficient ($r>0.7$) are considered to be strong; where (r) values between (0.5-0.7) indicate a moderate correlation; while ($r < 0.3$) is weak correlation. Table 5 illustrated that a positive correlation of EC with TDS ($r = 1$), Cl ($r = 0.87$), Mg ($r = 0.75$), Na ($r = 0.77$), SO_4 ($r = 0.63$) and TH ($r = 0.70$) which indicate that the dissolution of salts increases the electrical process of weathering (Wagh et al., 2016a). In case of the study area, the inputs of Mg, Na, TDS, Cl, SO_4 , and NO_3 are influenced by rainfall and human induced activities. Also, the succeeding variables like TDS with TH ($r = 0.70$), SO_4 ($r = 0.63$), Mg ($r = 0.75$) and Na ($r = 0.77$) depicts strong association. Moreover, TH reveal a strong positive relationship with Mg ($r = 0.97$), SO_4 ($r = 0.66$), Na ($r = 0.50$) and Cl ($r = 0.77$). In addition, Mg with Cl ($r = 0.81$), HCO_3 ($r = 0.62$), Na ($r = 0.61$) and SO_4 ($r = 0.65$) shows positive correspondence. It is confirm that Na and Cl have a strong correlation ($r = 0.88$), Cl and SO_4 moderate correlation ($r = 0.59$), and CO_3 with HCO_3 ($r = 0.63$). As well, Ca, Mg, Na and Cl, EC, TH and TDS have confirmed the significant association with irrigation.

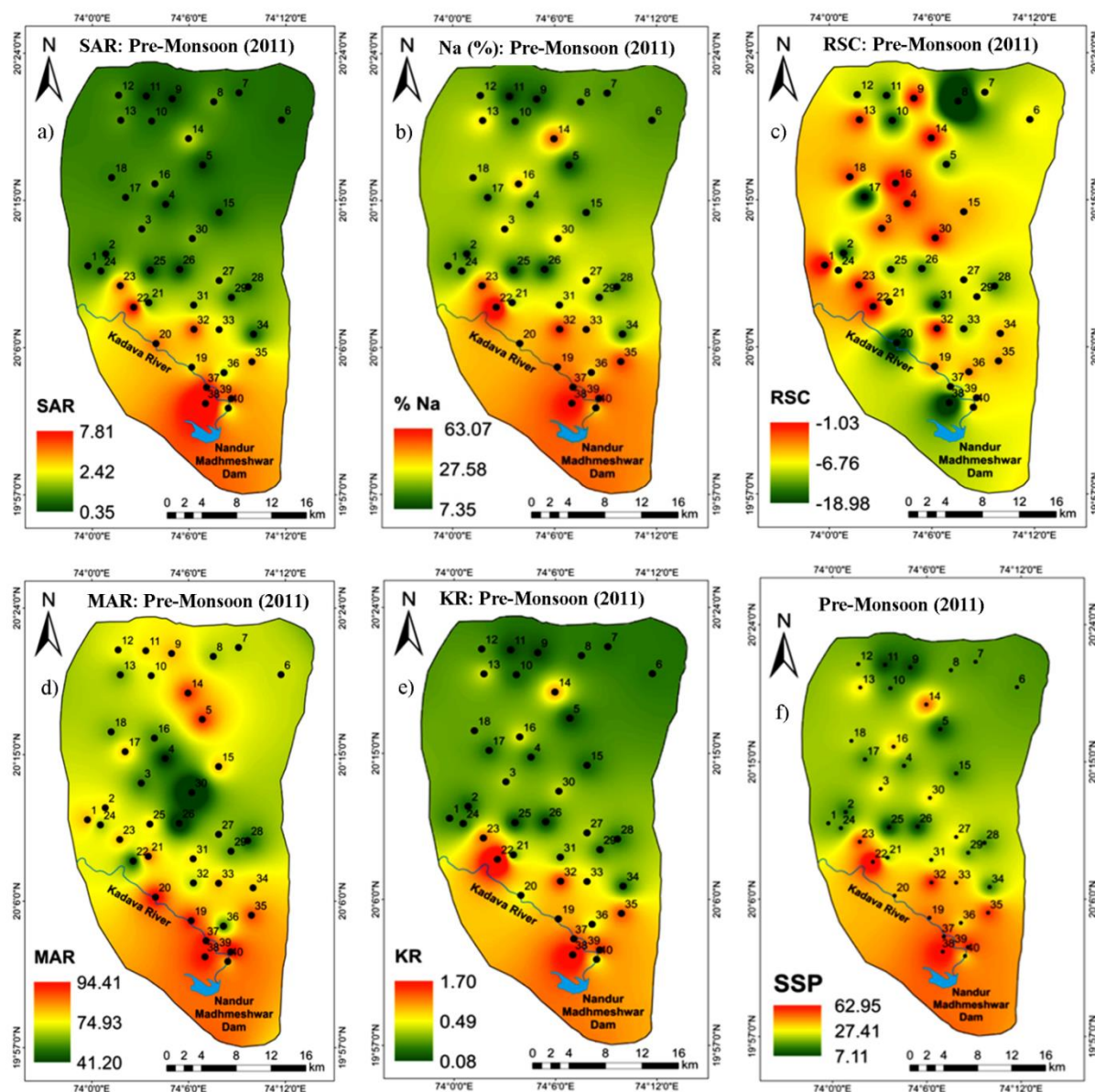


Figure 5. Spatial distribution of a) SAR, b) Na(%), c)RSC, d) MH, e) KR and f) SSP

Table 5. Correlation matrix

Parameters	pH	EC	TDS	TH	Ca	Mg	Na	K	Cl	F	CO ₃	HCO ₃	SO ₄	NO ₃
pH	1													
EC	-0.16	1												
TDS	-0.16	1.00	1											
TH	-0.30	0.70	0.70	1										
Ca	-0.35	0.09	0.09	0.46	1									
Mg	-0.22	0.75	0.75	0.96	0.20	1								
Na	0.12	0.77	0.77	0.50	-0.19	0.61	1							
K	0.23	0.00	0.00	-0.08	-0.03	-0.08	0.16	1						
Cl	-0.08	0.87	0.87	0.77	0.12	0.81	0.88	0.13	1					
F	0.09	0.12	0.12	-0.08	-0.38	0.03	0.24	0.36	0.12	1				
CO ₃	-0.20	0.16	0.16	0.45	0.16	0.44	0.19	-0.15	0.12	-0.17	1			
HCO ₃	-0.25	0.41	0.41	0.60	0.15	0.62	0.40	0.05	0.40	0.00	0.65	1		
SO ₄	-0.20	0.63	0.63	0.66	0.25	0.65	0.37	-0.22	0.59	0.01	0.01	0.05	1	
NO ₃	-0.29	0.32	0.32	0.16	-0.08	0.20	0.17	-0.08	0.20	-0.04	0.00	0.01	0.23	1

Bold values indicates significant correlations among physicochemical parameters.

4.3.2 Principal Component Analysis (PCA)

It is important to relate the association of different physicochemical parameters and their possible sources of contamination due to complexities of the local hydrogeological conditions and hydrochemical processes that occurs in aquifers which are complicated to explain. Thus, in order to identify the most influencing physicochemical parameters on groundwater quality, R-mode factor analysis using SPSS 22.0v was applied to the hydrochemical data to classify the different groups based on inherent qualities of parameters. R-mode factor analysis examines the relationship among variables by analyzing a matrix of simple correlation coefficients for all pairs of variables considered (Saager and Singlair, 1974). Factor analysis is performed with Kaiser Varimax rotation to differentiate the factors without changing the data structure which helps to reduce the contribution of less significant parameters affecting water quality (Mertler and Vannatta, 2005). Table 6 summarizes the rotated component matrix of five factors with Eigenvalues, % of Variance and Cumulative % of each factor. It is seemed that first factor (Factor 1) accounts for 42.46 % of the total variance and is positively loaded with EC (0.926), TDS (0.926), TH (0.768), Mg (0.821), Na (0.818), Cl (0.944) and SO₄ (0.764). The Na and Cl show the highest PC loadings due to their high solubility behavior (Rao, 2014). The high loading of TDS (0.926)

is controlled by the Cl, Mg, Na, and SO₄ ions; whereas, TH (0.768) is influenced by the correspondence of Mg, Cl and SO₄ which indicate the permanent type of water hardness which has been confirmed by a high positive loading with TDS. The high loading of Na over Ca represents the ion exchange process between Ca and Na ion (Drever, 1988). Also, positive loadings of Mg, Na, Cl and SO₄ supported that groundwater is significantly influenced by anthropogenic inputs. The Factor 2 shows CO₃ (0.886) and HCO₃ (0.862) with 15.46% of total variance suggesting groundwater is recharged with fresh water and CO₂ dissolution during precipitation and infiltrated water reacts with soil CO₂ forming H₂CO₃. The water with high alkalinity is caused by long-term irrigation practices (Rao, 2014). Therefore, factor 2 is considered to be alkalinity controlled. The third factor (Factor 3) shows high loadings of calcium (0.931) and TH (0.409) with 10.94% of the total variance suggesting a diminutive amount of calcite minerals dissolution. However, Factor 4 is dominated by high loadings of potassium (0.884) and fluoride (0.696) with 8.02% of the total variance owed to the application of fertilizers and agrochemicals in agriculture to increase crop productivity, hence, reflecting anthropogenic origin. The fifth factor (Factor 5) is influenced by nitrate positive loading (0.791) exemplifying the leaching of agricultural and animal wastes, fertilizers and pesticides in the aquifer which turn to increase the concentration of nitrate in the study area.

Table 6. Principal Component Analysis

Parameters	Factors				
	1	2	3	4	5
pH	-.013	-.226	-.419	.058	-.754
EC	.926	.110	-.031	.051	.173
TDS	.926	.110	-.031	.051	.173
TH	.768	.402	.409	-.082	.087
Ca	.092	.075	.931	-.103	.013
Mg	.821	.421	.156	-.058	.092
Na	.818	.196	-.328	.203	-.093
K	-.010	-.023	.095	.884	-.180
Cl	.944	.116	.038	.145	-.010
F	.111	-.086	-.337	.696	.089
CO ₃	.084	.886	.036	-.197	.018
HCO ₃	.315	.862	.078	.119	.048
SO ₄	.764	-.217	.255	-.235	.154
NO ₃	.235	-.088	-.208	-.066	.791
Eigenvalues	5.945	2.165	1.532	1.124	1.003
Variance (%)	42.462	15.465	10.945	8.029	7.163
Cumulative %	42.462	57.928	68.872	76.901	84.064

Bold values indicate the high positive loading.

4.4 Hydrochemical evolution

To recognize the hydrochemical evolution within study area, then it is important to know local geology and mineralogical composition of rocks, agricultural inputs, dissolution, precipitation climate condition, etc., influence the groundwater chemistry. In general, during groundwater recharge within aquifer, it reacts with soil, rock-water interactions, types of weathering like silicate or carbonate and significant anthropogenic inputs may alter groundwater composition in the area (Todd, 1980). The scatter plot of EC vs. TDS (Figure 6a) represents good correlation which indicate EC is attributed from dissolution of salts and inorganic pollution load in the water. Scatter plot of Mg vs Na (Figure 6b) represent that weak correlation which confirm that magnesium concentration is increasing due to silicate weathering. The Na/Cl ratio (Figure 6c) is used to identify the salinity mechanism in semi-arid and arid environment (Sarin et al., 1989). The halite maintains the ratio to 1 by releasing Na and Cl ions (Hounslow, 1995). The groundwater ratio of Na/Cl indicates good correlation, if higher value of Na/Cl ratio then the possible source of Na is silicate weathering and; if ratio less than 1 confirm the possibility of ion exchanges of Na with Ca and Mg in clay particles (Tiwari and Singh, 2014).

Cl vs Ca+Mg ratio (Figure 6d) indicates moderate correlation confirmed that the salinity is increased due to chloride is associated with increased contents of Ca + Mg. Na/Cl vs Cl (Figure 6e) illustrated weak correlation due to ion exchange process in groundwater which is adsorb sodium into aquifer in exchange for Ca + Mg (Raju et al., 2016). The plot of Ca+Mg vs $\text{HCO}_3 + \text{SO}_4$ (Figure 6e) is used to represent the ion exchange and different weathering processes. 1:1 equiline ratio is maintained by the dissolution of calcite, dolomite and gypsum (Cerling et al., 1989). The significant contribution from silicate weathering and required demand $\text{HCO}_3 + \text{SO}_4$ is balanced by alkalis Na+K (Datta et al., 1996). The plot showing positive correlations ($r^2 = 0.9$) indicating ion exchange process is dominant in the groundwater. The ionic concentrations in meq/l are falling above the equiline indicating both carbonate and silicate weathering. Such a plot also shows that HCO_3 is in excess of Ca+Mg possibly pointing to the process of ion exchange reaction (Rajmohan and Elango, 2004). The ratio of Ca+Mg/ HCO_3 (Figure 6f) shows weak correlation. This ratio is significantly used to know the origin of Ca and

Mg. If the ratio is less than 0.5 may be due to the depletion of Ca and Mg or weathering minerals like pyroxenes and amphiboles (Sami, 1992). It indicates that alkaline elements (Ca and Mg) may be derived from silicate and carbonate minerals (Mahato et al., 2016). The scatter plot of Cl vs TZ^+ (Figure 6g) represents positive correlation ($r^2 = 0.91$) which suggest chloride is enriched due to agricultural waste, excessive use of chemical fertilizers, irrigation water runoff, percolation and leaching of waste, etc. The scatter plot of Na+K vs $\text{Cl} + \text{SO}_4$ (Figure 6h) depicted that there is increase of alkali elements due to presence of sodium sulphate, potassium sulphate, sodium chloride and potassium chloride in soil system (Bhardwaj et al., 2010). The plot of $\text{HCO}_3 + \text{SO}_4$ vs Ca+Mg indicates that carbonate and silicate weathering is the dominant process (Datta et al., 1996). It is confirm that silicate weathering is the main process followed by carbonate weathering and ion exchange process which are affecting the groundwater quality of the study area (Figure 6i). The plot of total cations (TZ^+) vs Ca+Mg illustrated that many of the groundwater samples fall below the equiline and which reflecting high concentration of sodium and potassium with increasing dissolved solids (Figure 6j).

Also, total cations (TZ^+) vs Na + K plot (Figure 6k) shows sodium and potassium have positive correlation with total cations particularly at higher concentration. It is illustrated that silicate weathering is dominant process which controls the groundwater chemistry. Scatter plot of Cl vs Ca/Mg (Figure 6L) shows moderate correlation ($r^2 = 0.59$) which confirm that salinity is increased due to chloride associated with increase in Ca + Mg and decrease in Na/Cl may be from ion exchange process which adsorbs sodium onto aquifer in calcium and magnesium exchange (Raju et al., 2016). The logarithmic bivariate plot of Mg/Na vs Ca/Na is used to know the type of weathering (Figure 6m). The higher solubility of sodium than calcium which increases the sodium concentration, therefore Ca/Na ratio is expected to low which infers the silicate weathering as dominant geochemical process followed by carbonate weathering due to presence of lime kankar in the area (Zhu et al., 2014). The plot of (Ca+Mg)-($\text{HCO}_3 + \text{SO}_4$) vs (Na+K)-Cl (Figure 6n) confirms cation exchange process. The samples falling close to zero are not affected by ion exchange while those falling on slope line -1 will exchange Na, Ca and Mg ions (Jankowski et al., 1998, Kortatsi, 2006).

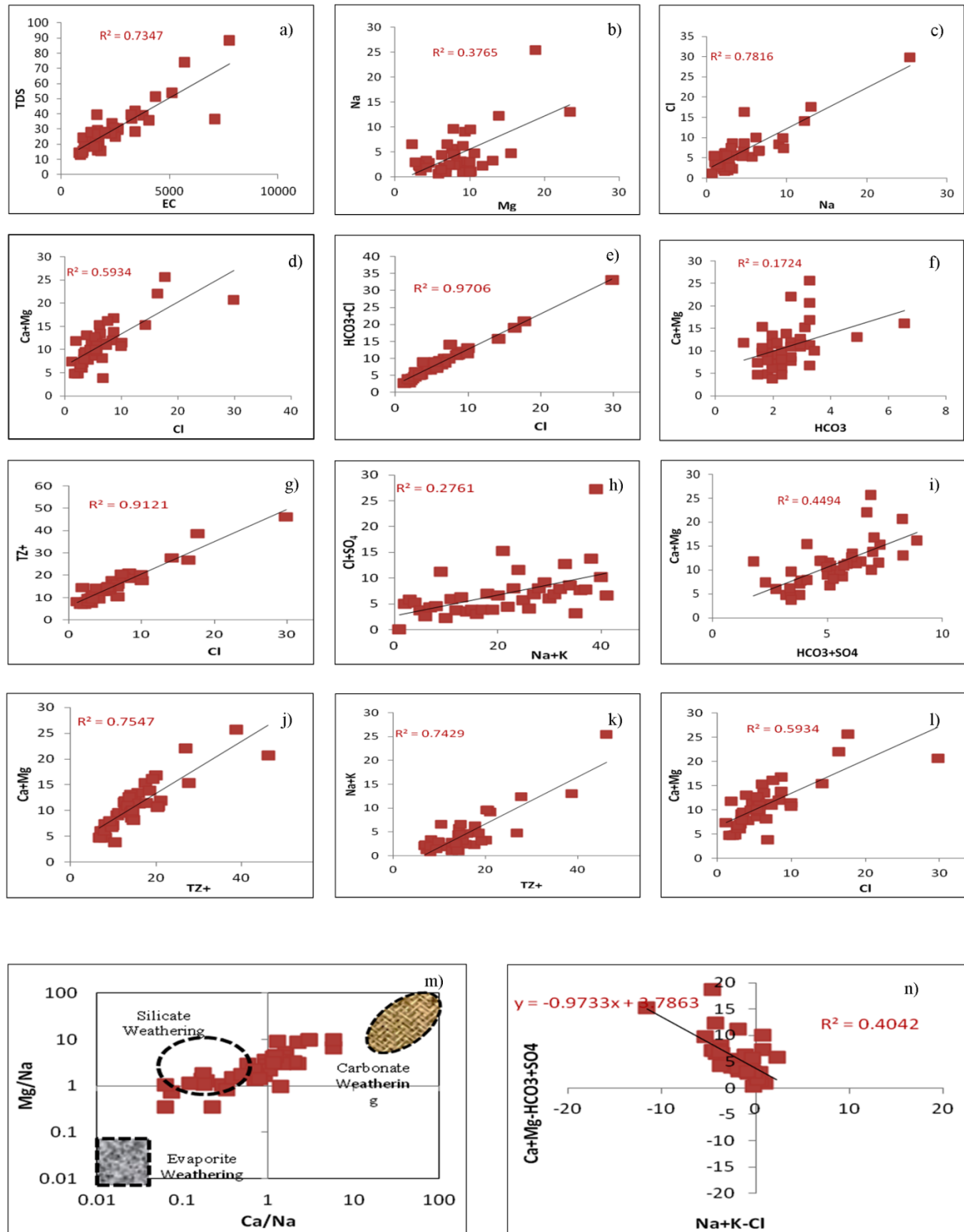


Figure 6. Scatter Plots of a) EC vs TDS, b) Mg vs Na, c) Na vs Cl, d) Cl vs Ca + Mg, e) Cl vs HCO₃ + Cl, f) HCO₃ vs Ca + Mg, g) Cl vs TZ⁺, h) Na + K vs Cl + SO₄, i) HCO₃ + SO₄ vs Ca + Mg, j) TZ⁺ vs Ca + Mg, k) TZ⁺ vs Na + K, l) Cl vs Ca+Mg, m) Ca/Na vs Mg /Na and n) Na+K-Cl vs Ca+Mg-HCO₃+SO₄

5 CONCLUSIONS

In Kadava river basin, the integration of hydrochemical categorization and multivariate statistical analysis were applied to explicate the influence of geogenic and anthropogenic factors on groundwater quality and its suitability performed. Hydrochemical analysis confirmed that groundwater is alkaline and hard in nature; thus, restricted for drinking. As per WHO drinking standards, 75% groundwater samples beyond the PL of EC; such elevated EC is due to salt dissolution and inorganic pollution load in the groundwater. According to BIS, TDS (27.5%), TH (27.5%), Mg (45%), Na (15%), Cl (2.5%), NO₃ (52.5%) and F (2.5%) samples exceed the permissible limit (PL); hence, unfit for drinking. It is observed that the inputs of TDS, Cl, SO₄, Mg, Na and NO₃ are controlled by precipitation and agricultural activities. High content of nitrate owed to excessive use of nitrogen complex fertilizers in agriculture. TH is associated with Mg, Cl and SO₄ attributing permanent type of water hardness. The positive loading of CO₃ and pH advocate that aquifers are recharged through rain water which influences the alkalinity of water. The correlation between Ca+Mg vs. Na+K are weak, suggesting addition of Ca and Mg ions in groundwater sourced from the weathering of silicate-rich basalts in the area. Ca/Mg ratio suggests that salinity increased due to Cl is associated with increase in Ca+Mg and decrease in Na/Cl may be from ion exchange process. The Cl vs HCO₃+Cl ratio exhibits salinization due to agricultural inputs. The spatial distribution map reveals that south part of the study area is mostly affected due to the percolation and leaching of contaminants into aquifer. In context of irrigation suitability, SAR and RSC results proved that all groundwater samples are suitable for irrigation. MAR ratio implies that 97.5% samples are unfit for irrigation due to (MAR >50). Moreover, SSP ratio shows that 37.5% and 17.5 samples fall in permissible and doubtful category; only, 45% samples are fall in good category of water for irrigation. KR ratio depicts wide suitability in 95% samples and only 5% samples come under unsuitable category. In nutshell, the results corroborates that geogenic processes viz., ion exchange, silicate weathering, evaporation and anthropogenic inputs are the dominant factors influencing the groundwater composition. The outcomes of the study may help to local authorities to develop compressive water management plans to improve groundwater quality in semiarid environment of basaltic terrain.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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ABBREVIATIONS

APHA: American Public Health Association; **BIS:** Bureau of Indian Standards; **CGWB:** Central Groundwater Board; **GSI:** Geological Survey of India; **UNEP:** United Nations Environmental Programm.

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