


Geochemical evaluation of thermal springs in Odisha, India

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Received: 5 January 2017 / Accepted: 17 August 2017 / Published online: 28 August 2017
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Abstract The Indian state of Odisha has a number of thermal springs. These thermal springs are located at eight places (Attri, Tarabalo, Deulajhari, Magarmuhan, Bankhol, Badaberena, Taptapani and Boden) and belong to Mahanadi Geothermal Province, which is an Archean/Pre-Cambrian Geothermal Province. The thermal water discharging from these springs shows moderately acidic to moderately alkaline character (pH: 5.05–8.93) and the temperature ranges from 28 (Boden) to 58 °C (Tarabalo). Total dissolved solids (TDS) also shows a wide variation between 16.9 (Bankhol) and 595 mg/L (Deulajhari). A wide variation in the chemical characteristics of the thermal waters has been observed as they are located in different geological settings. Based on water chemistry, all the thermal springs can broadly be grouped into three water types: Na–Cl, Ca–HCO₃ and Na–HCO₃. The thermal spring water from Attri, Tarabalo and Deulajhari belongs to Na–Cl water type which is due to the circulation through granitic rocks. Higher concentrations of Cl and F in these thermal waters further suggest limited mixing and longer residence time as compared to the other areas where Ca–HCO₃ and Na–HCO₃ water types were found. Anion variation diagram clearly indicates that the thermal waters from Attri, Tarabalo and Deulajhari are fast ascending and fall in the mature water field; thus, their chemical signatures can be used to determine the reservoir temperature. However, in other areas, water chemistry is shaped by near-surface groundwater mixing processes and thus the chemical geothermometers may not be applicable to

determine the reservoir temperature. No appreciable temporal variations have been observed in the water chemistry of the thermal waters.

Keywords Thermal spring mixing · Hydrochemistry · Temporal and spatial variation of thermal waters

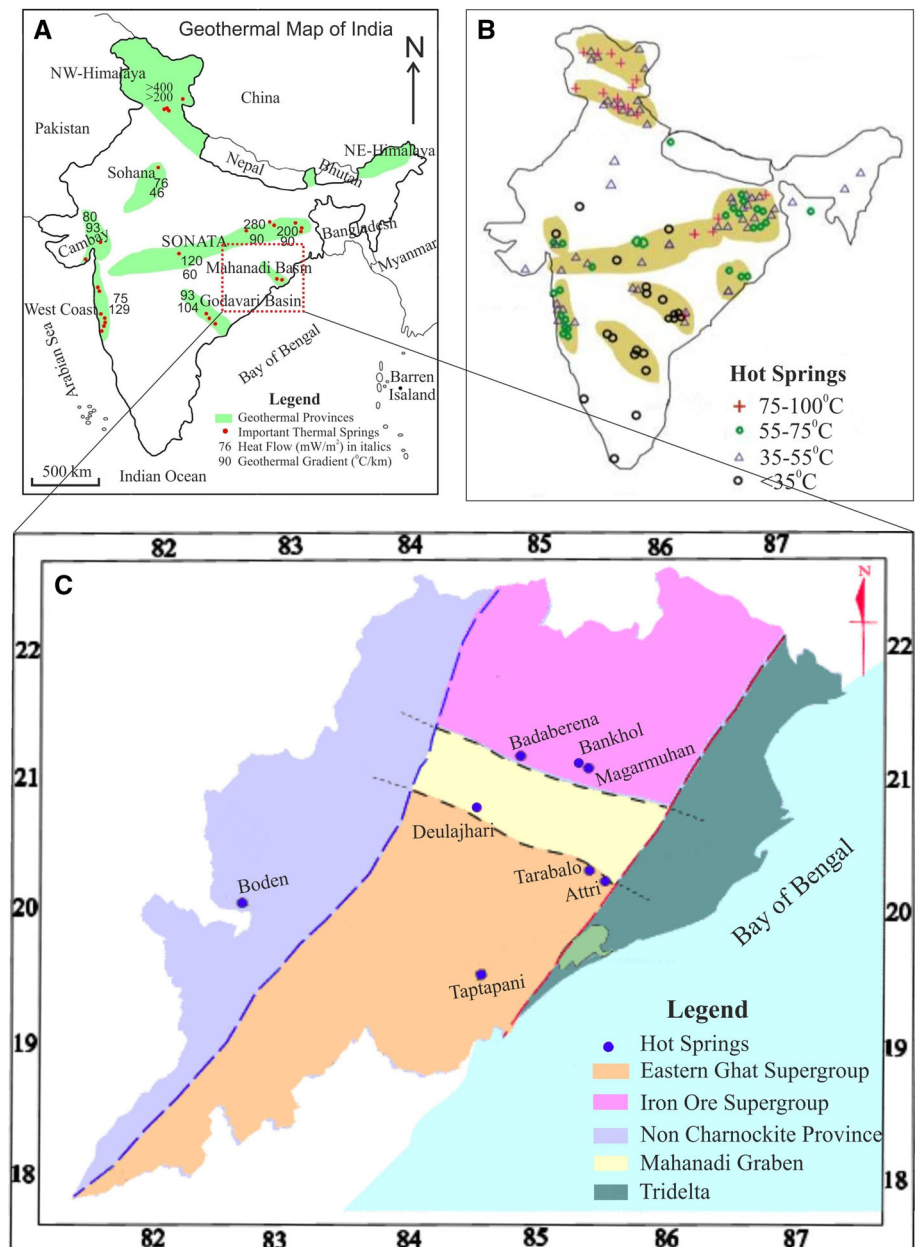
Introduction

The demand for energy is increasing exponentially over the time. To meet this increasing demand in an eco-friendly way, alternative energy resources are being developed and geothermal energy forms an important part of it. Existences of vast reservoirs of geothermal energy at depths are manifested on the surface in form of thermal springs. In India, there exist around 400 geothermal springs (Chandrasekharam 2000). These geothermal springs are distributed across the country and are grouped into 10 geothermal provinces, namely Himalayan Geothermal Province; Naga Lushai Geothermal Province; Andaman–Nicobar Islands Province; West Coast Geothermal Province; Cambay Graben Geothermal Province; Aravalli Province; Son–Narmada–Tapti (SONATA) Geothermal Province; Godavari Geothermal Province; Mahanadi Geothermal Province and South Indian Cratonic Province (Fig. 1a) (Thussu 2002; Shanker et al. 1991; Chandrasekharam and Chandrasekhar 2010a). Around 50% of the thermal springs are located in the Himalayan Geothermal Province alone (Craig et al. 2013). The source of heat and the surface water temperature varies widely and thus their geothermal potential. The surface water temperature ranges from >35 to 100 °C. Maximum surface water temperature (75–100 °C) is observed in Himalayan and SONATA Geothermal Provinces (Fig. 1b)

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Fig. 1 Map showing geothermal provinces of India and distribution of geothermal springs in Odisha. **a** Location of major geothermal provinces with heat flow values (Chandrasekharam and Chandrasekhar 2010a), **b** surface temperature of major geothermal springs (Krishnaswamy 1975), and **c** location of geothermal springs in the state of Odisha (Mahala et al. 2012)



(Krishnaswamy 1975). Three geothermal provinces (i.e., Himalayan Geothermal Province; Naga Lushai Geothermal Province; Andaman–Nicobar Islands Province) fall in the orogenic regions and are associated with the provinces of Tertiary magmatism and metamorphism. The remaining seven geothermal provinces fall in non-orogenic or the peninsular regions. Most of these peninsular geothermal provinces are associated with graben structure (Thussu 2002). Literature archive shows that a lot of studies have been done on non-orogenic geothermal provinces of India with regard to their surface water chemistry, reservoir temperature and evaluation of their geothermal potential except for the Mahanadi Geothermal Province which is still

one of the least studied as compared to the other geothermal provinces in India (Thussu 2002; Chandrasekharam and Chandrasekhar 2010a, b). The Mahanadi Geothermal province falls in the state of Odisha, and the thermal springs are manifested at eight locations, namely Attri, Tarabalo, Deulajhari, Magarmuhan, Bankhol, Badaberena, Taptapani and Boden. These springs belong to Archean/Pre-Cambrian Geothermal Province and the temperature of the surface water discharging from the thermal spring ranges from 28 to 58 °C. However, maximum temperature up to 85 °C has also been reported (Thussu 2002). In the case of Attri, Magarmuhan, Bankhol, Taptapani and Boden, the hot spring water discharges from a single spot,

whereas in Tarabalo, Deulajhari and Badaberena, hot water discharges from multiple spots. The rate of discharge recorded at Attri, Tarabalo, Taptapani and Deulajhari thermal springs is 2.1, 2.7, 2–7 and 2.1 l/s, respectively (Thussu 2002), while for other springs it is not known. Although Mahanadi Geothermal Province did not get the required attention in the past but now is considered to be a potential site for developing both wet and enhanced geothermal system (EGS) geothermal projects in the future (Chandrasekhar and Chandrasekhar 2010b).

Hydrogeochemistry of the spring water is a useful tool to decipher the reservoir temperature, mixing of the ascending water and the processes associated with it (Xilai et al. 2002; Bulbul 2015; Han et al. 2010; Chatterjee et al. 2017). The hydrogeochemistry of the thermal water mainly depends upon (1) the water type (i.e., the origin of water), (2) presence of structural lineaments, (3) mixing of ascending thermal water with the groundwater and (4) the rocks through which the thermal water interacts while it ascends. Studies have found that mixing of cold water with ascending thermal water modifies its chemical characters significantly (Han et al. 2010). The mixing may further be accelerated by groundwater exploitation near the faulted region (Bulbul 2015; Gokgoz and Akdagoglu 2016). However, in coastal regions, mixing of thermal water with seawater intruded through deeper faults may completely alter the chemical signatures of the thermal waters (Gemici and Feliz 2001). The origin of water/water type (connate, meteoric, and juvenile) has also an influence on the chemistry of the thermal waters. Thus, to draw any useful conclusion from the chemistry of thermal water, it is important to determine whether the water discharging from the thermal spring has preserved the chemical signatures of the geothermal reservoir or its chemical properties are modified by various processes (such as mixing with the groundwater, interaction with wall rock). It is also important to determine whether the chemistry of the thermal water changes seasonally. In the case of a prominent seasonal change in thermal water chemistry and extensive mixing, the inference drawn based on thermal water chemistry may not be very useful. A study has thus been undertaken with the following objectives: (1) to understand the water chemistry of the thermal springs located in different geological settings, (2) to determine the suitability of thermal spring waters to calculate reservoir temperature using chemical geothermometers, and (3) to determine whether the chemistry of thermal water varies due to seasonal changes in shallow groundwater chemistry.

Study area

The study area lies in the state of Odisha with a total area of about 155,842 Sq.km and located along the east coast of India within latitudes 17°48'–22°34'N and longitude 81°24'–

87°29'E. Geographically, the territory can be divided into four distinct regions: the Northern Plateau, the Central River Basin, the Eastern Ghats Hill Ranges and the Coastal Plains. The rocks of the state are mainly of Pre-Cambrian age with some Phanerozoic rocks, represented by the Gondwana Supergroup and minor patches of Tertiary and Quaternary formations (Chowdhury et al. 2011). The thermal springs manifested at eight locations are located in three different geological settings: Attri, Tarabalo, Deulajhari and Taptapani lie within Eastern Ghats Supergroup; Magarmuhan, Bankhol and Badaberena lie within Iron Ore Supergroup (IOSG); and Boden lies within Vindhyan Supergroup (Fig. 1c). The Mahanadi and Godavari Rift divides the Eastern Ghat Belt (EGB) into the northern, central and the southern segments (Sarkar and Nanda 1998) of which the northern segment and part of central segment lie within the state of Odisha. In Odisha sector, EGB is broadly divided into Khondalite Group, Charnockite Group and Migmatite Group, which from east to west lies in the sequence of Eastern Khondalite Zone, Central Migmatite Zone, Western Khondalite Zone, Western Charnockite Zone and Westernmost Transition Zone (Ramakrishnan 1987). The rock types encountered at Attri, Tarabalo, Deulajhari and Taptapani are Laterite, Khondalite, Charnockite and Augen gneiss (granitic), while at Magarmuhan and Bankhol mostly quartzite of IOSG is found (Mahala et al. 2012). The aerial photograph reveals the presence of NW–SE and NE–SW fractures/lineaments at Attri and Tarabalo (Thussu 2002). Deulajhari is located close to a NNE–SSW trending shear zone, and the thermal spring is located along banks of Mahanadi River which flows along a NW–SE fault in the area. One fracture trending NW–SE to WNW–ESE runs parallel to the Mahanadi lineament and passes very close to the Deulajhari thermal spring (Thussu 2002). A schematic geological profile illustrating the flow patterns of thermal springs located at the boundary of Gondwana Graben is shown in Fig. 2, and the generalized stratigraphic succession of the study area is given in Table 1. The state of Odisha has tropical climate characterized by high temperature, high humidity and medium-to-high rainfall. The annual rainfall varies from 1008 to 1988 mm with an average of 1481 mm across the state (Patra et al. 2012). The wind flow pattern developed in the upper atmosphere during the summer monsoon makes the state favorable for good rainfall (Mohapatra and Mohanty 2006). Rainfall data from the year 1871–2006 show that most of the rainfall occurs during the months of June, July, August and September (Patra et al. 2012).

Sampling and methodology

To investigate the water chemistry of the thermal springs, water samples were collected directly from the springs following the standard scientific protocol (APHA 1995).

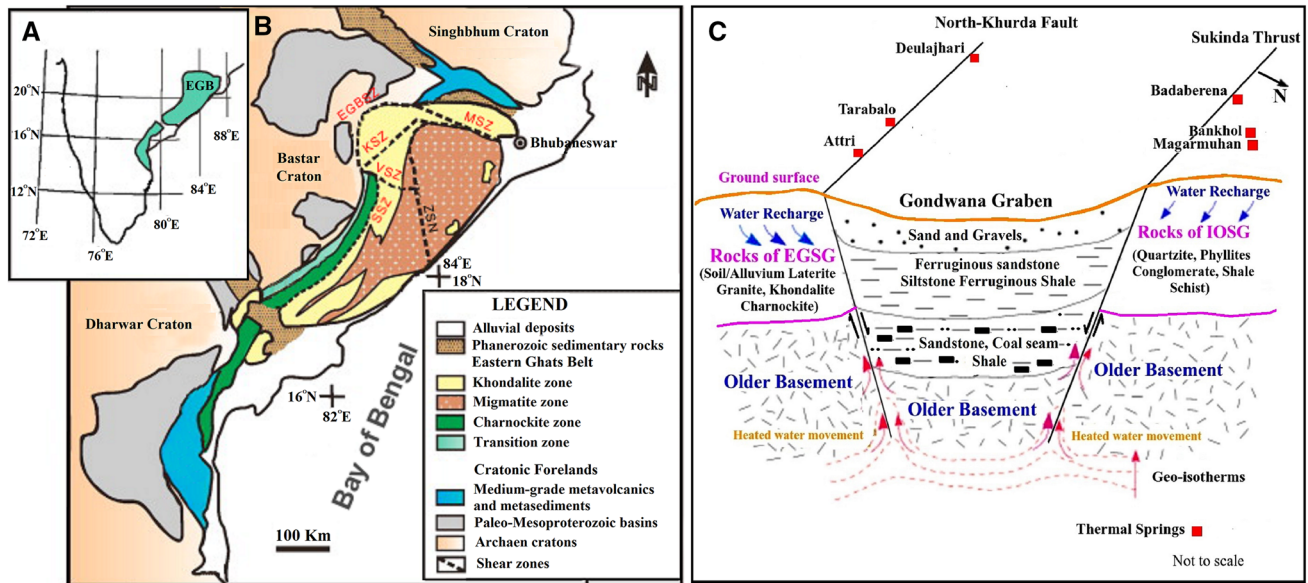


Fig. 2 Map showing **a** location of Eastern Ghat Belt (EGB) in India, **b** litho-tectonics units of EGB and adjacent cratons. Abbreviations used are *MSZ* Mahanadi Shear Zone, *VSZ* Vamshadhara Shear Zone, *NSZ* Nagavalli Shear Zone, *SSZ* Sileru Shear Zone, *KSZ* Koraput–Sonepur Shear Zone, and *EGBSZ* Eastern Ghats Boundary Shear Zone

(Dasgupta et al. 2013), and **c** conceptual model with schematic geological profile and the flow pattern (Mahala et al. 2012; Sastri et al. 1981). *EGSG* Eastern Ghat Supergroup, *IOSG* Iron Ore Supergroup

Table 1 Geological succession of study area and its adjacent areas (Chowdhury et al. 2011)

Age	East India Craton & Singhbhum–Gangpur Mobile Belt	Eastern Ghats Belt	
Palaeo Proterozoic	Upper Bonai Group/Simplipal Group/ Singhbhum Group/Gangpur Group/ Dhanjori Group/Bonai Lava/ Dangoaposi Lava/Dhanjori Lava	Migmatite Group	
Proterozoic	Granophyre (Mayurbhanj Granite) Newer Dolerite Gabbro, norite, anorthosite	EASTERN GHATS SUPERGROUP	
Archaean	Chhotanagpur Gneissic Complex		
	Ultramafics of Sukinda-Nuasahi Granitic Complex		
	Bonai Granitic Complex		Charnockite Group
	Lower Bonai Group		Khondalite Group
	Gorumahisani-Badampahar Group		
	Singhbhum Granite/Nilgiri Granite		
	Older Metamorphic Tonalitic Gneiss		
Older Metamorphic Group			

Water samples were collected from the thermal springs during the pre-monsoon, monsoon and post-monsoon seasons. In the areas where hot springs occur in clusters, a number of samples were collected randomly to represent the entire area. Additionally, shallow surface water samples were collected from the areas near to the thermal springs. Each sample collection site was georeferenced using a Garmin Global Positioning System (GPSMAP-76S) instrument. Water samples from all locations include the collection of: (1) filtered samples (0.45 μm cellulose nitrate filter) for analyses of major anions and (2) acidified (with 5 mL 14 M ultrapure HNO_3/L) samples for major cation and trace element analyses. Samples were tightly sealed and stored at a low temperature until further analyses. Parameters like pH, temperature, electrical conductivity (EC) and total dissolved solids (TDS) were measured in the field. The pH value was measured with a portable pH meter (Orion 261S) using a combination electrode (pH C2401-7). EC and TDS were measured by a conductivity meter (Orion 250A+) with an operating range between 0 and 500 mS/cm. Alkalinity was measured by titration method using auto-titrator model Titrino Plus; fluoride and chloride were measured by ion analyzer with combination electrode Orion ionplus and sulfate concentrations were measured by UV-visible spectrophotometer. Analyses of cations were done with inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Results and discussion

The thermal spring water samples collected from the study area show moderately acidic to moderately alkaline characteristics. During the pre-monsoon season, pH values range from 5.1 to 8.8 (mean 7.5), while for monsoon and post-monsoon seasons, the value ranges from 5.9 to 8.6 (mean 7.2) and 6.7 to 8.9 (mean 7.8), respectively. The pH does not show any season-specific trend. In some sample, higher pH value has been observed during post-monsoon, while in other samples higher pH values have been observed either during pre-monsoon or monsoon season. The temperatures of discharging thermal water do not show any significant temporal variation, and the temperature varies within a range of 1–4 $^{\circ}\text{C}$ for all the thermal springs. However, a significant spatial variation in the temperature of discharging thermal water has been observed, and the minimum temperature of 28 $^{\circ}\text{C}$ at Boden and maximum temperature of 58 $^{\circ}\text{C}$ at Tarabalo thermal spring have been observed. TDS values do not show much variation and remain same in all the seasons except for Tarabalo, where lower TDS values have been observed during monsoon season. However, a wide spatial variation in TDS values has been observed and it ranges from 16.9 (Bankhol) to

595 mg/L (Deulajhari). It is interesting to note that the major ion concentration also does not show much temporal variation, whereas a significant spatial variation has been observed in their concentrations. Sodium (Na) and chloride (Cl) are the dominant ions in the hot spring water discharging from Attri, Tarabalo and Deulajhari locations, whereas at other locations, bicarbonate (HCO_3) is the most dominant species present in the thermal discharge. The concentration of Na and Cl ranges from 1.33 to 239.2 and 0.98–289 mg/L, respectively. Calcium (Ca), magnesium (Mg) and potassium (K) are present in much lesser concentrations, and their concentration varies between 0.15 and 65.45, <0.1–22.9 and 0.42–7.48 mg/L, respectively. The concentrations of HCO_3 range between 9.4 and 306.6 mg/L. Higher HCO_3 concentrations have been observed specifically in those locations where lower Cl concentration has been registered (Fig. 3). Sulfate (SO_4) concentration ranges between 4.35 and 130 mg/L which is much lower than HCO_3 and Cl concentrations. Among all the thermal springs, higher sulfate concentration has been observed at Attri, Tarabalo, and Deulajhari. In addition to major ions, lithium (Li) concentrations were also measured in the thermal water sample. The concentration of Li remains low in all the samples and ranges between <0.1 and 0.26 mg/L. The low Li/Na ratio indicates that the water is of shallow origin and had a limited interaction with the wall rock (White 1957). For better understanding of the temporal and spatial variation in the chemistry of the thermal waters, time series data of rainfall and surface temperature for different locations of study area have been obtained from Tropical Rainfall Measuring Mission (TRMM, 3B43) (Huffman et al. 2007) and European Centre for Medium-Range Weather Forecasts (ECMWF) (Dee et al. 2011), respectively. The plot of monthly average maximum temperature and monthly rainfall is shown in Fig. 4a, b. Despite significant seasonal changes in the surface temperature and rainfall, the hydrochemical characteristic of the thermal water remains the same. This can only happen when there is no appreciable seasonal change in supply and mixing of shallow water with the thermal water. The absence of a prominent seasonal variation in water chemistry of the thermal waters indicates that the thermal water sample can be collected in any season during the year and may be used to decipher the subsurface properties of the reservoir based on the chemical signature. However, it is important to note that the water from every single thermal spring cannot be used to determine the reservoir temperature or interpret other important subsurface parameters that depend upon the chemistry of the thermal water, until it fulfills some primary requirements. Anion variation diagram helps in determining the samples that can be used to determine the reservoir temperature using a cation geothermometer (Giggenbach 1988). The

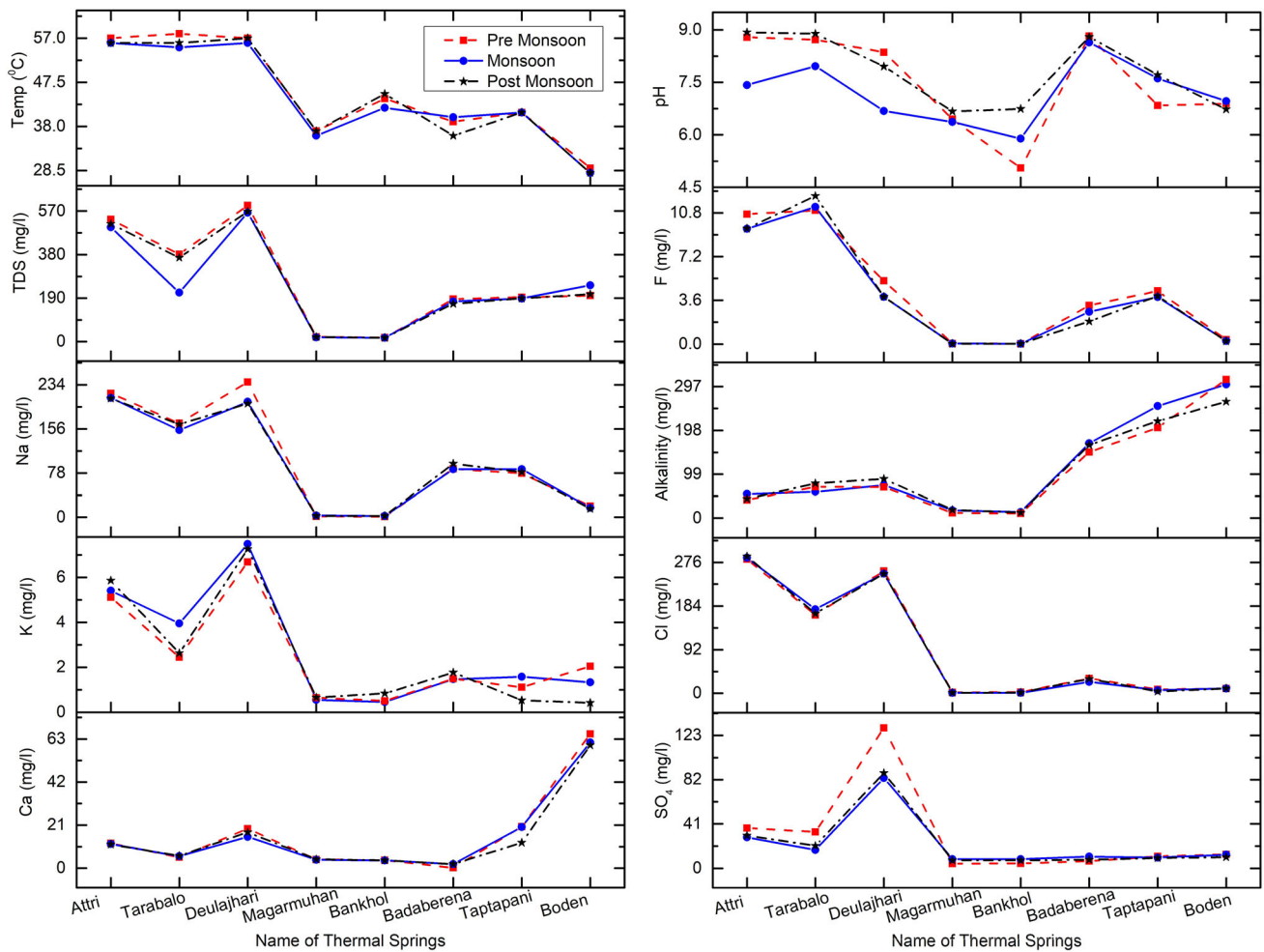


Fig. 3 Temporal and spatial variation of temperature, TDS, pH, major ions and fluoride present in thermal waters

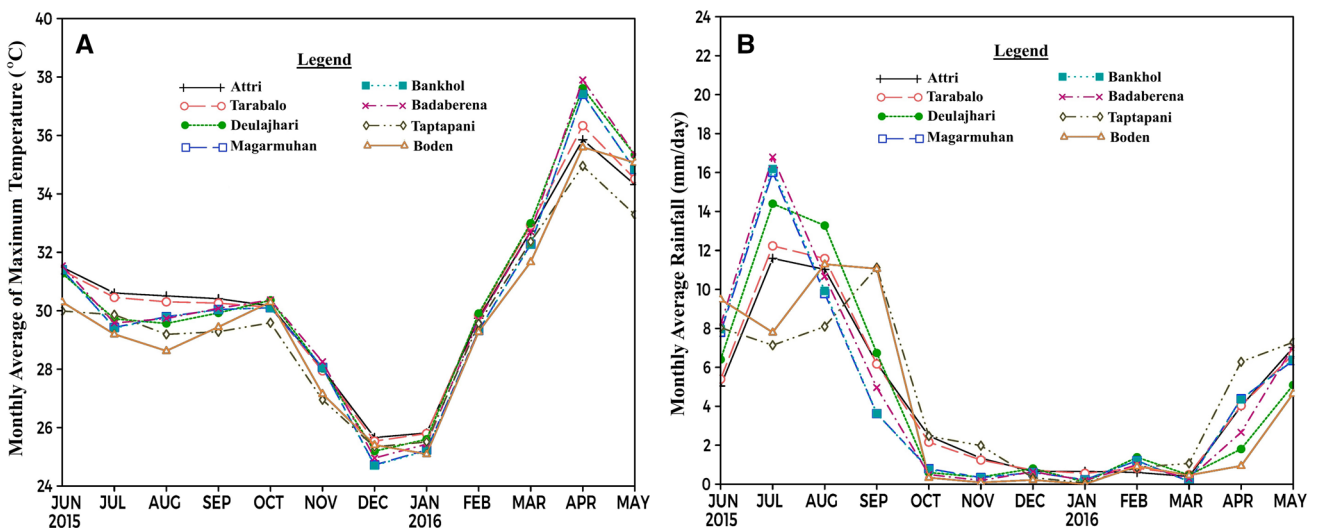
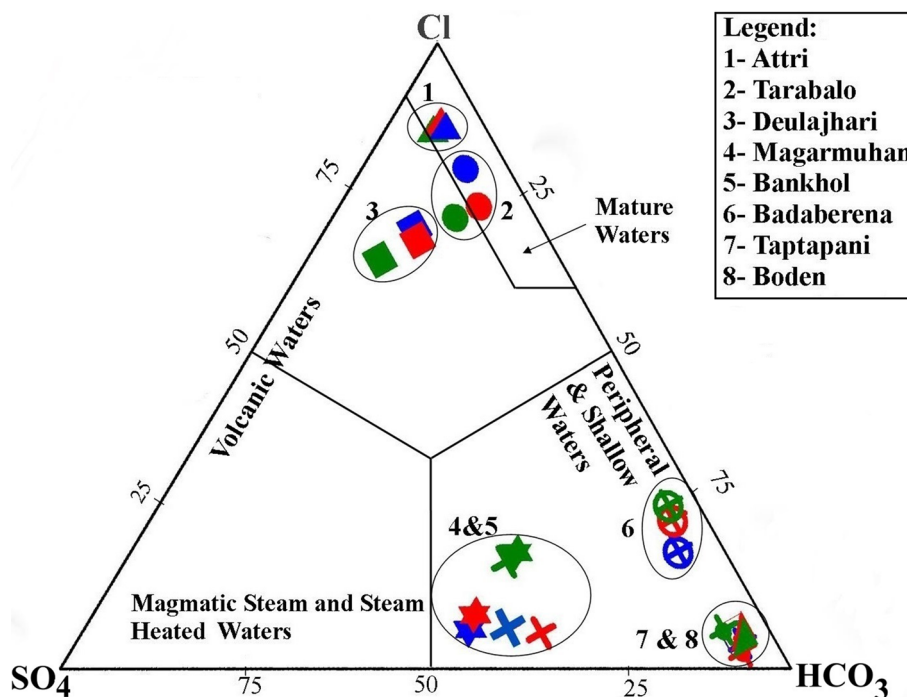


Fig. 4 Variability of climatological parameters of the study area during the study period. **a** Monthly average maximum surface temperature at geothermal spring locations during June 2015 to May

2016, **b** monthly average rainfall in the location of geothermal springs during June 2015 to May 2016

Fig. 5 Anion variation diagram showing distributions of thermal water samples into different water fields (Color code: *Green* pre-monsoon season, *Blue* monsoon season, and *Red* post-monsoon season)



plotting of collected thermal water samples into anion variation diagram clearly shows that the water samples fall into two fields: Cl and HCO₃ field (Fig. 5). The water samples belonging to Attri, Tarabalo and Deulajhari fall in and around the chloride/mature field and thus are considered as fast ascending waters with limited shallow surface mixing. Such type of thermal waters can be used to determine the reservoir temperature with a higher accuracy. The other thermal water falls in the HCO₃ field which indicates the dominant influence of peripheral and shallow water in controlling the chemistry of the thermal waters. The SO₄ field of the plot suggests mixing of volcanic gas with the thermal water (Singh et al. 2014). However, in the present study, none of the thermal spring water falls in SO₄ field. This indicates that the subsurface geothermal reservoir is not emanating any gases. The HCO₃:Cl ratio which indicates the degree of mixing of shallow water with ascending thermal water is given in Table 2. The physical and chemical parameters of shallow surface water samples collected from the surrounding areas of thermal springs are given in Table 3. The value of the HCO₃:Cl ratio remains less than unity for thermal springs belonging to Attri, Tarabalo and Deulajhari. This further supports that there is little or no mixing of the ascending thermal waters with the shallow surface water. In the case of all other thermal springs, the HCO₃:Cl ratio is more than 1, which indicates that the thermal water composition is modified by the secondary processes. In the case of Taptapani and Boden, the HCO₃:Cl ratio is even above 20 which signifies severe mixing of shallow surface water in these thermal spring

Table 2 Degree of mixing of thermal water with shallow ground-water as determined by HCO₃:Cl ratio

Location	HCO ₃ :Cl ratio		
	Pre-monsoon	Monsoon	Post-monsoon
Attri	0.13	0.16	0.14
Tarabalo	0.40	0.30	0.44
Deulajhari	0.26	0.29	0.34
Magarmuhan	5.23	15.58	18.98
Bankhol	4.89	14.34	10.41
Badaberena	4.58	6.86	5.16
Taptapani	24.33	38.80	57.17
Boden	31.03	30.15	25.62

water. It is thus clear that the chemical geothermometers can be applied only to the thermal spring waters belonging to Attri, Tarabalo and Deulajhari locations.

The major ion composition of the thermal spring water samples (Table 4) was plotted in the Piper diagram using AquaChem 2012.1 software which is widely used in bringing out chemical relationships among the water samples and also to infer about their subsurface interaction with the surrounding rock (Piper 1944). The diagram consists of two triangles for plotting cations and anions. The values plotted in these triangles are projected so as to form a single point in a diamond-shaped field from which inferences are drawn. The plot clearly distinguishes the collected thermal water samples into three water types (Na–Cl type, Ca–HCO₃ type and Na–HCO₃ type). The

Table 3 Physico-chemical parameters of shallow surface water samples

Location	pH	TDS (mg/L)	EC ($\mu\text{s}/\text{cm}$)	F (mg/L)	Cl (mg/L)	Alkalinity (mg/L)	K (mg/L)	Mg (mg/L)	Na (mg/L)	Ca (mg/L)	SO ₄ (mg/L)
Attri	7.93	108.3	219.9	0.27	31.90	67.9	8.73	2.22	18.85	17.51	7.10
Tarabalo	8.54	266.4	542.6	0.79	73.70	173.6	13.9	10.50	59.15	23.86	15.3
Bankhol	6.97	14.76	29.1	0.05	1.02	12.0	0.26	0.54	1.58	3.20	3.20
Badaberena	6.65	417	849.5	0.73	18.80	308	17.6	16.50	43.22	40.41	8.80
Taptapani	7.69	134	274	0.19	12.30	87.3	4.37	4.94	13.49	23.83	6.60
Boden	7.90	607	1239	0.79	41.50	434	1.66	24.28	62.41	103.8	36.9

thermal water samples from Attri, Tarabalo and Deulajhari fall in Field-II and are characterized as Na–Cl water type (Fig. 6). Such water type generally reflects the mixing of seawater with the ascending thermal waters (Gemici and Feliz 2001). The contribution from the sea not only causes an increase in Na and Cl concentrations but also results in higher TDS values. The value of TDS as high as 35,000 mg/L has been reported in the case of Na–Cl water where sea water mixing controlled the chemistry of thermal water (Gemici and Feliz 2001). However, in the present study maximum TDS value of 595 mg/L is registered. Such TDS value indicates that the Na and Cl concentrations are not contributed by seawater mixing but from some other sources. Chloride is considered as a good tracer in geothermal systems due to its conservative behavior (Michard 1990; Alcicek et al. 2016; Bulbul 2015); thus, the concentration of major ions from Attri, Tarabalo and Deulajhari was plotted against Cl (Fig. 7). A strong correlation of Cl with Na ($R^2 = 0.77$) and good correlation with K and Ca ($R^2 = 0.57$ and 0.51 , respectively) clearly establish that the rock–water interaction is a dominant mechanism for controlling the concentrations of these ions in the system (Alcicek et al. 2016). The geophysical studies conducted in the area show the existence of a vertically faulted margin along with the presence of granite and syenite at the deeper level (Nayak et al. 1998). The water in a granitic terrain when circulates deeper through various structural lineaments (i.e., faults, shear zone) picks up Na and Cl ions (Chandrasekharam and Antu 1995; Savage et al. 1987; Hem 1985). Similar circulation through the fault intersecting the granitic rocks in the study area accounts for higher concentrations of Na and Cl in thermal waters. Further, low concentrations of calcium along with higher concentrations of fluoride have also been observed in the thermal waters. Due to lower calcium concentrations, the water does not reach the solubility product of fluorite (Ozsvath 2008; Chae et al. 2007; Farooqi et al. 2007) and thus results in higher fluoride concentrations (3.88–12.2 mg/L) in thermal waters collected from Attri, Tarabalo and Deulajhari. However, at other locations, the average fluoride concentrations are lower. The long

residence time of the thermal water is one of the prime factors that contribute to higher fluoride concentration into the thermal waters (Hudak and Sanmanee 2003; Kim and Jeong 2005). In a granitic terrain, if the water resides for a prolonged period, the fluoride concentrations in the groundwater enrich continuously even after the groundwater reaches in equilibrium state with respect to fluorite (CaF_2), mainly due to the removal of Ca by precipitation of calcite (CaCO_3) (Kim and Jeong 2005; Chae et al. 2007). Higher fluoride concentrations are not uncommon in the geothermal waters and are reported from several geothermally active areas, such as the East African Rift Valley, New Zealand, France, Iceland, China, and parts of the western USA (Ozsvath 2008). Continuous discharge of higher fluoride-containing water from the geothermal spring of Attri, Tarabalo and Deulajhari may contaminate the local groundwater. The fluoride concentration higher than 1.5 mg/L in drinking water poses severe health risks to the population living the nearby areas (World Health Organisation (WHO) 2011; Centers for Disease Control and Prevention (CDCP) 1999).

In Bankhol and Magarmuhan, the discharging thermal water falls in Field-I and thus belongs to Ca–HCO₃ water type (Fig. 6). The water from these thermal springs is poorly mineralized and has TDS values ranging between 16.9 and 20.9 mg/L. Shorter resident time in the subsurface coupled with heavy mixing with the shallow groundwater may cause the lowering of the TDS content (Bulbul 2015). However, studies have also established that vapors generated from the deep-seated high-temperature geothermal reservoir may get condensed at shallower depth and gives rise to thermal waters with lower TDS values (Glassley 2015). Such a condition is very unlikely in the study area as the temperature of the discharge water is quite low (36–45 °C). The outlet temperatures are very close to the average annual air temperature, suggesting that these waters do not circulate deeper and confine mainly to the shallow aquifers (Brombach et al. 2000).

The thermal waters discharging from Badaberena and Taptapani thermal spring belongs to Field-VI and is of Na–

Table 4 Physico-chemical parameters of water samples from the thermal springs

Locations	Atri		Tarabalo		Deulajhari		Magarmuhan		Bankhol		Badaberena		Taptapani		Boden	
	PtM	M	PtM	M	PtM	M	PtM	M	PtM	M	PtM	M	PtM	M	PtM	M
Temperature (°C)	57	56	58	55	56	56	57	56	57	56	57	56	57	56	57	56
pH	8.79	7.42	8.93	8.72	7.96	8.89	8.36	6.68	7.95	6.67	6.67	6.67	6.67	6.67	6.67	6.67
TDS (mg/L)	534	499	514	381	214	367	595	563	568	20.9	18.8	20.4	17.6	17.0	16.9	186
EC (µs/cm)	1089	1018	1047	777	437	749	1212	1149	1159	42.6	37.3	40.6	35.0	33.7	34.4	379
Cl (mg/L)	283	286	289	165	177	168	258	252	252	1.80	1.13	1.00	2.21	0.98	1.22	31.3
Alkalinity(mg/L)	41.2	54.2	43.7	70.3	59.1	78.1	70.2	74.3	88.5	11.8	17.6	18.9	10.8	14.1	12.7	149
SO4 (mg/L)	37.2	28.7	30.2	33.7	17.1	20.9	130	83.6	88.4	4.35	8.55	7.46	4.60	8.55	7.46	6.59
F (mg/L)	10.7	9.50	9.51	11.0	11.3	12.2	5.20	3.88	3.89	0.06	0.05	0.04	0.03	0.04	0.03	3.18
Na (mg/L)	219	211	210	166	154	164	239	204	201	1.61	3.02	2.71	1.33	2.49	2.60	85.4
Ca (mg/L)	12.1	11.8	11.6	5.29	5.83	5.91	19.2	15.3	17.5	4.19	4.04	4.34	3.89	3.76	3.78	0.15
Mg (mg/L)	0.03	bdl	0.03	0.04	0.07	bdl	0.04	0.05	0.04	0.74	1.24	1.35	0.58	1.15	1.19	0.06
K (mg/L)	5.11	5.41	5.86	2.45	3.95	2.63	6.68	7.48	7.26	0.65	0.55	0.66	0.51	0.46	0.84	1.49
Li (mg/L)	0.07	0.08	0.08	0.05	0.06	0.06	0.24	0.23	0.26	bdl	bdl	bdl	bdl	bdl	bdl	0.02

PtM Pre-monsoon, M monsoon, PoM post-monsoon, bdl below detection limit. Detection limit 0.01 mg/L for Mg and Li

Fig. 6 Piper diagram showing chemistry of the thermal spring water

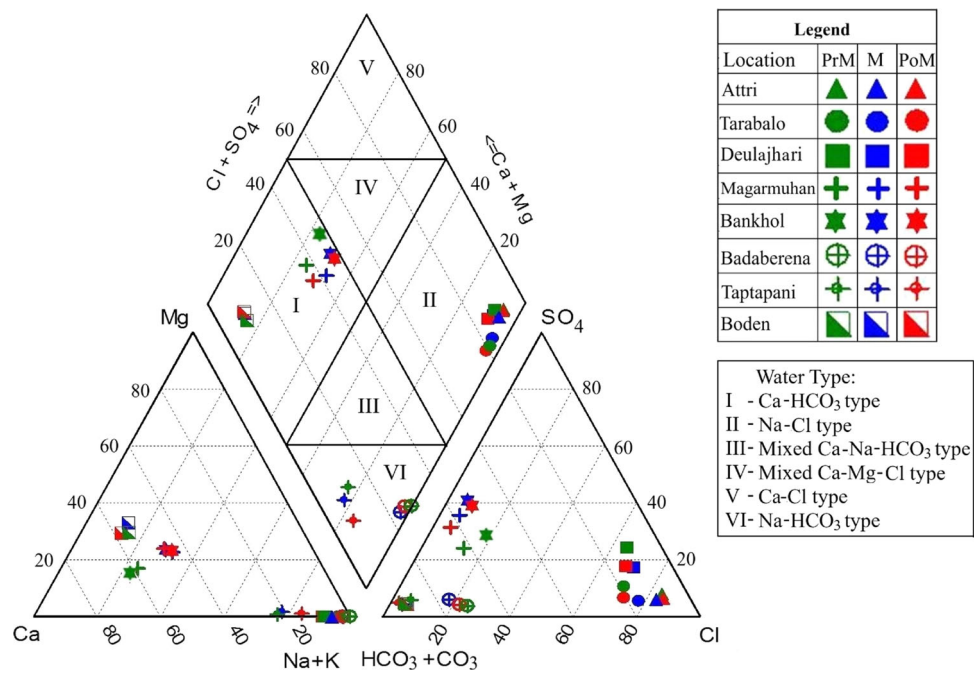
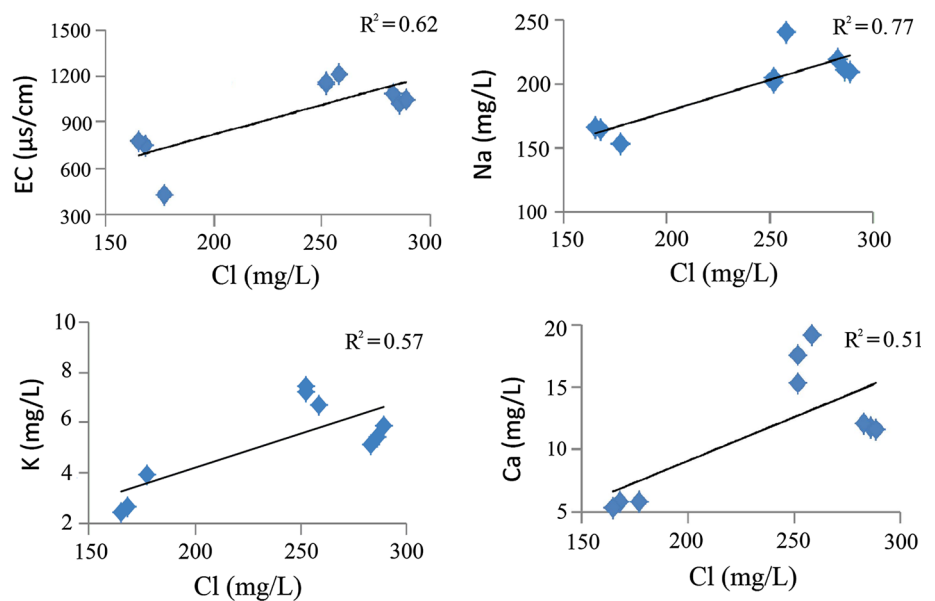


Fig. 7 Relationship of chloride (Cl) with EC, Na, Ca and K for Attri, Tarabalo and Deulajhari thermal spring during all three seasons



HCO₃ type (Fig. 6). In general, except Attri, Tarabalo and Deulajhari, all other thermal spring water shows Na/Ca-HCO₃ type characteristics which are a typical indicator of shallow groundwater. This suggests prominent mixing of shallow cold water which is believed to have been circulated within the alluvium or sedimentary formations with the ascending hot spring water (Singh et al. 2014). Higher concentrations of various ions have been observed in thermal waters from Attri, Tarabalo and Deulajhari, while, their concentrations remain very low for the mixed water type, especially those showing HCO₃ characteristics (i.e., shallow groundwater). The near-surface water presumably

has no residence time in the reservoir and only short or no contact with the wall rock, whereas the conditions for water in the deep reservoir are just opposite and thus they have considerably higher dissolved solid concentrations. The solute concentration of the thermal water tends to be directly related to the degree of mixing (Hem 1985). In the case of an extensive mixing with the near-surface water, the thermal water may nearly become as dilute as near-surface water. Mostly the near-surface water (i.e., shallow groundwater) has slightly higher ionic concentrations than the streams which typically contains ≈ 200 mg/L of dissolved salts (Hem 1985). Thus, it can be concluded that the

thermal water of mixed water type (i.e., HCO₃ water type) has undergone thorough mixing with shallow surface water. The difference in water chemistry of different thermal springs of the study area may also be due to the interaction with rocks of varied mineralogy, as the interaction of thermal water with the wall rock is another key factor that modifies the chemical characteristics of thermal water (Wen et al. 2012). It is also important to note that the thermal water from all the springs, irrespective of their water types, does not show a prominent seasonal variation and the concentration of most of the ions remains same throughout the year. Such behavior of thermal water has great implications, as the water from these thermal springs can be sampled any time during the year and generated data can be used for interpreting the subsurface parameters (i.e., reservoir temperature).

Conclusions

The thermal springs in the state of Odisha are clustered at eight places. The pH values of the thermal spring water have significant temporal and spatial variation showing moderately acidic (5.05) to moderately alkaline (8.93) character. The temperature of the thermal water ranges from 28 (Boden) to 58 °C (Tarabalo). Major ion concentrations and TDS in the thermal waters do not show much temporal variation, but significant spatial variation has been observed and the TDS concentration ranges from 16.9 (Bankhol) to 595 mg/L (Deulajhari). The absence of a significant seasonal variation in thermal water chemistry indicates that the water samples from these springs can be collected anytime during the year and can be used to determine various subsurface parameters (especially reservoir temperature) based on their chemical signatures. Anion variation diagram shows that the thermal waters from Attri, Tarabalo and Deulajhari fall in the chloride/mature water field; thus, chemical geothermometers can be applied to determine the reservoir temperature. The remaining thermal water samples fall in the immature water field, indicating that either the water has not been equilibrated with the geothermal reservoir or there is an extensive mixing of ascending thermal water with the shallow groundwater. Thus, the chemical geothermometers, if applied to these thermal waters, may not give the correct reservoir temperature. The plotting of thermal water samples into piper diagram further conforms that there is no appreciable seasonal change in the water chemistry of the thermal waters. The water samples from Attri, Tarabalo and Deulajhari fall in Na–Cl field of the piper diagram which indicates a deeper circulation through the granite rocks. However, the samples from other thermal springs fall in Na/Ca–HCO₃ field indicating that the

thermal water chemistry is shaped mainly by shallow water mixing processes. Further, higher fluoride concentration in thermal waters discharging from Attri, Tarabalo and Deulajhari springs poses a severe threat to local groundwater contamination.

Acknowledgements The authors are thankful to the Ministry of Earth Sciences (MoES), Govt. of India for providing the financial support through Bay of Bengal Coastal Observatory (BoBCO). Horthing V. Zimik gratefully acknowledges the financial support received from the Council of Scientific & Industrial Research (CSIR), India through the research fellowship (award number 09/1059(008)/2014-EMR-I). Indian Institute of Technology Bhubaneswar is specially thanked for providing necessary laboratory facility to carry out this research work. TRMM 3B43 monthly precipitation data used in this study are freely available at <https://giovanni.sci.gsfc.nasa.gov/giovanni/>. ECMWF surface temperature data are freely available at <http://apps.ecmwf.int/datasets/data/interim-full-daily/levtype=sfc/>. The authors thank the anonymous reviewer for the valuable suggestions and comments which helped improve the quality of the original manuscript.

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