Environ Sci Pollut Res (2014) 21:3880–3890
DOI 10.1007/s11356-013-2376-4

RESEARCH ARTICLE

Occurrence and distribution of selected heavy metals and boron in groundwater of the Gulf of Khambhat region, Gujarat, India

Devang Upadhyaya · Mayur D. Survaiya · Shaik Basha · Subir K. Mandal · R. B. Thorat · Soumya Haldar · Sangita Goel · Himal Dave · Krushnakant Baxi · Rohit H. Trivedi · Kalpana H. Mody

Received: 3 April 2013 / Accepted: 15 November 2013 / Published online: 29 November 2013

Abstract The concentration of selected heavy metals, like As, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn as well as B, was measured by inductively coupled plasma–optical emission spectrometry (ICP–OES) in groundwater samples from various locations in the Gulf of Khambhat (GoK), an inlet of the Arabian Sea in the state of Gujarat, India, during post-monsoon, winter, and pre-monsoon seasons in a year. Most heavy elements are characterized by low mobility under slightly alkaline and reducing conditions; concentrations in confined aquifers are smaller than the maximum permissible values for drinking water. The temporal changes indicate that a majority of metals is entering the aquifer during monsoon. Principle component analysis of the heavy metal data suggests that Co, Cu, Cd, and Zn are interrelated with each other and derived significantly from anthropogenic route, while input of Pb and Cr may be due to atmospheric deposition in the study area. Both weathering of rocks and anthropogenic input were found to be main sources of elements in the groundwater. The heavy metal levels in groundwaters of the GoK region in comparison with some of the European and Asian sites were higher; however, these metal levels were found to be comparable with few urban sites in the world.

Responsible editor: Vera Slaveykova

D. Upadhyaya · M. D. Survaiya · S. Basha (✉) · S. K. Mandal · R. B. Thorat · S. Haldar · S. Goel · H. Dave · K. Baxi · R. H. Trivedi · K. H. Mody
Discipline of Marine Biotechnology and Ecology, CSIR–Central Salt and Marine Chemicals Research Institute, G B Marg, Bhavnagar 364002, Gujarat, India
e-mail: sbasha@csmcri.org

Present Address:
S. Goel
Air Pollution Control Division, CSIR-National Environmental Engineering Research Institute (NEERI), Nehru Marg, Nagpu 440020, India

Keywords Heavy metal · Groundwater · Gulf of Khambhat · Principal component analysis

Introduction

Groundwater is a vital resource for sustaining the communities and economies of coastal regions across the world. In India, due to the scarcity of surface water in many regions, groundwater is becoming an important source of drinking water supply. However, the present status of groundwater resources of the country is a matter of serious concern as India has emerged as one of the largest users of groundwater in the world, drawing an estimated 210 billion cubic meters (BCM) of water per year, much higher than China's withdrawals of 105 BCM and the US's 100 BCM (Vijay Shankar et al. 2011).

Although groundwater has long been considered as a relatively pure natural resource stored in subsurface aquifers, its quality is under continuous threat from human influences. Changes in chemical quality of groundwater in coastal region generally occur through natural processes such as saline water intrusion, wind-driven sea spray and marine aerosols deposited on the topsoil, evaporation, and interaction with brines and sedimentary formations (Polemio et al. 2006). In addition, direct inputs of the variety of contaminants including toxic trace metals from industrial, agricultural, and municipal activities through groundwater abstraction and through artificial recharge are other major causes of water quality deterioration (Bouwer 1996; Moon et al. 1994; Lee et al. 2001; Vidal et al. 2000; Gerth and Forstner 2004; Srinivasamoorthy et al. 2011). Moreover, a recent study revealed that the anthropogenic activities induced by groundwater extraction could influence how and when earthquakes occur (Kristy et al. 2012).

Groundwater contamination by toxic elements is an important problem, especially in tropical countries like India, since it directly affects its ecological quality. The magnitude of hazards in groundwater depends on chemical composition, concentration of toxic elements, and the water-bearing formation and water pH. Health related studies have shown that excessive intake of toxic trace metals results in neurological and cardiovascular diseases as well as renal dysfunction (Jarup 2003; Mitchell et al. 2011). Therefore, the preliminary step toward assessment of health risks posed by metal pollution requires regular monitoring of water quality in terms of trace metal distribution, source identification, and assessing any temporal change.

The main objectives of this study, the first of its kind in the Gulf of Khambhat region, are to (1) establish the levels of metals in the groundwater and (2) ascertain and distinguish their sources using statistical methods. It is anticipated that the study would be helpful to evolve practical measures related to future groundwater pollution abatement programs, considering the trends of distribution of metals based on source identification.

Study area

The Gulf of Khambhat (GoK; formerly known as the Gulf of Cambay) is an inlet of the Arabian Sea on the western shell of India between the Saurashtra peninsula and mainland Gujarat. It has a width of 80 km at the mouth and funnels down to 25 km over the longitudinal reach of 140 km. Entire banks surrounding the GoK are bordered with large tidal flats nested into numerous tidal creeks. The tidal amplitude in the GoK remains the largest of the Indian coast, with spring tidal ranges of around 9 m and resulting in strong currents. Due to strong flood and ebb tidal currents, the water remains always turbid with high bed and suspended sediment loads. Thick coastal sediments occupied the entire northern gulf and eastern part of southern gulf. The GoK has been an important center of trade since ancient times; its ports connect central India to the maritime trade routes of the Indian Ocean. Many offshore oil, gas, and chemical terminals exist, and new installations are planned between Hazira and Dahej on the eastern part of the gulf. The surrounding area along the GoK consists of seven districts of Gujarat state including Ahmedabad, Anand, Bhavnagar, Kheda,Vadodara, Bharuch, and Surat. Bhavnagar district bears Deccan Traps, while alluvium covers most part of the remaining districts. The hydrogeology of the GoK region is a typical alluvial area with moderate to high salinity and shallow water tables. As the shallow and unconfined aquifers are alluvium with fine clay having silty sand at the top, the movement of groundwater is very slow and prone to very shallow water levels especially in monsoon and prone to water logging. In addition, to the high tide covers coastal area, the groundwater very quickly turns saline even in monsoon. The groundwater availability is in critical stage mainly because it is saline in major part of the study area.

The climate of the study area varies from arid through semi and tropical type. Summer commences in March and extends up to May. The southwest monsoon brings rain during June to September, and the mean annual rainfall varies from 300 to 1,100 mm. The summer temperature and winter temperature vary from 37 to 43 °C and 10 to 18 °C, respectively.

Government of Gujarat has formulated an ambitious project to develop a fresh water reservoir, namely the Gulf of Khambhat development project (also known as Kalpasar project), by constructing a dam between Kalatalav, located on the western shores of the Gulf in Bhavnagar district and Aladar located on the eastern shores of the Gulf in Bharuch district. The dam can store about 10,000 million cubic meters (Mm^3) fresh water from the rivers (Narmada, Dhadhar, Mahi, Sabarmati, and few of Saurashtra) flowing into the gulf, which otherwise, was getting discharged into the GoK. After completion, this will be the world's largest manmade freshwater reservoir in the gulf for meeting the demand of irrigation, domestic, and industrial water supply. The present study covers the surrounding region of GoK from Gopnath on the western side to Hazira on the eastern side. Total 11 sampling stations for groundwater were fixed, out of which, five stations fall within the Gulf of Khambhat development project area while remaining six falls in the downstream of the project (Fig. 1).

Materials and methods

All the chemicals/reagents were of analytical grade. Ultra pure water was used throughout the analysis. All glassware were properly washed with soap, rinsed with water, soaked in 10 % HNO_3 overnight, and then rinsed with distilled water before use. Calibration standards were prepared by dilution from 1,000 mg/L certified standard solution of each metal with good linearity.

Groundwater samples were obtained from shallow wells/handpumps/dug wells (<30 m) that tap the unconfined alluvial/fracture aquifer of the gulf region covering three seasons (post-monsoon, winter, and pre-monsoon. Prior to the groundwater sampling, the data on the groundwater level was collected from the concerned authority. The depth of these bore wells vary between 20 and 30 m in the study area. Groundwater samples in triplicate were collected after pumping the water for about 10 min from the hand pumps/wells and allowed the water table to recover. During this period, the pH and temperature of the water stabilized and samples were collected in 1-L double cap, polypropylene bottles. All samples were vacuum filtered through 0.45 μm membrane filters, whereupon samples for heavy metal and boron analysis by ICP-OES (Perkin Elmer, Waltham, MA; Optima 2000 DV) were acidified with concentrated nitric acid

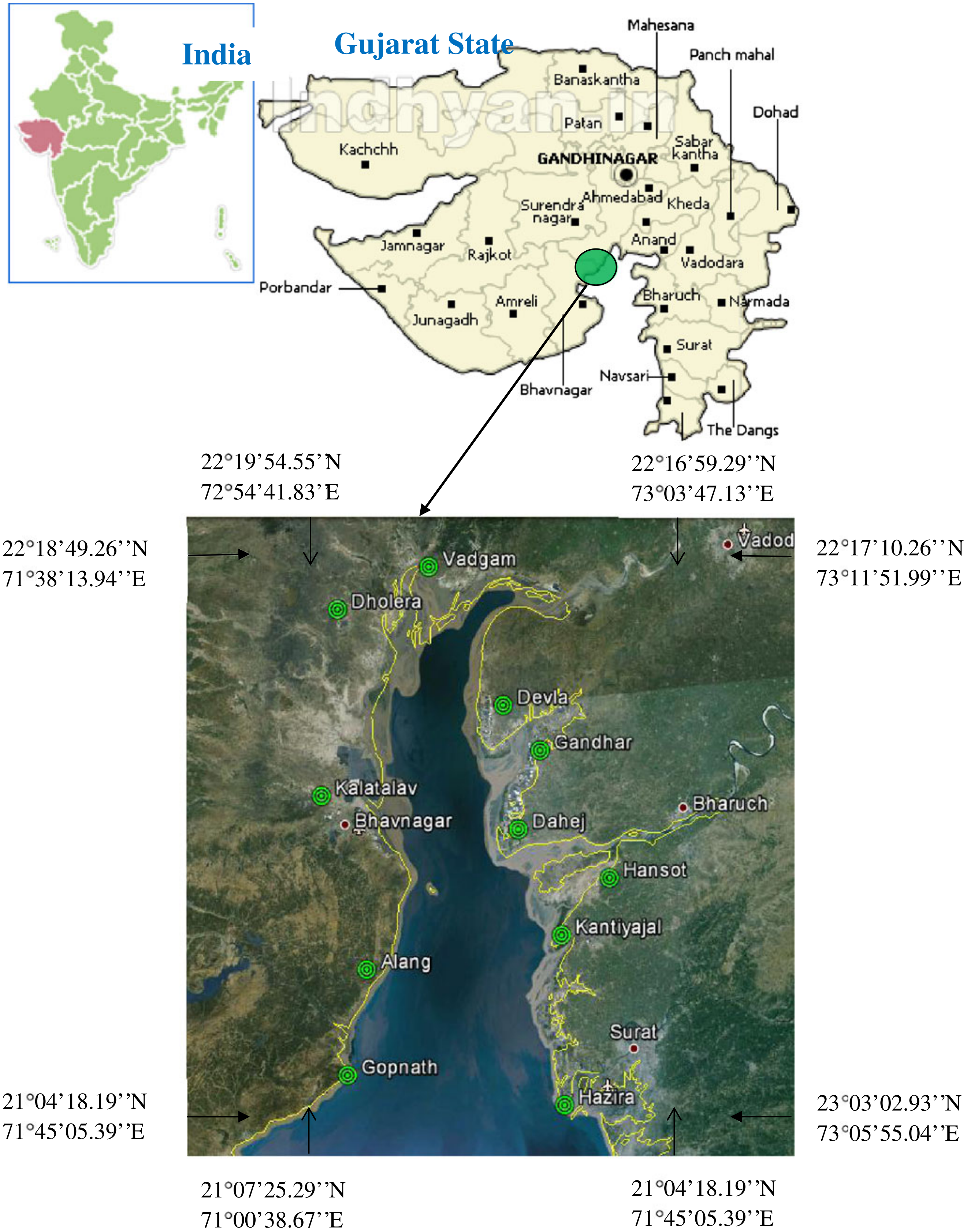

Fig. 1 Map of the Gulf of Khambhat region showing the location of groundwater sampling sites

to a pH of 2. All samples were stored in the insulated container containing ice and delivered on the same day to the laboratory and kept at 4 °C until further analysis.

Sample batches were regularly interspersed with standards and blanks, and all data were corrected for instrument drift. The results of three replicate analyses indicated that the precision of metal measurements was generally better than 5 %. For the purpose of constructing all plots and statistic calculation, data below analytical detection limits were set to a value of half of the detection limit.

Results and discussion

pH and TDS in groundwater

The pH of groundwater is very important, as it may affect the solubility and toxicity of metals in aquatic system (Efe et al. 2005). The pH of water samples from all stations in the GoK region ranged from 7.23±0.15 to 8.43±0.21, 7.4±0.15 to 8.70±0.21, and 7.64±0.22 to 8.19±0.22 during pre-monsoon, post-monsoon, and winter seasons, respectively (Table 1). In general, the distribution of pH indicates that the groundwater in the area is slightly alkaline in nature and did not show any specific trend within the region. However, the western part of the gulf region showed an increase in pH values during post-monsoon season. The pH of all the groundwater samples in the Kalpasar region are within the WHO prescribed limit of 7–9.2 for drinking water. The values are also below the permissible limit of Indian standard (first revision) IS-10500:1991 for drinking water—specification, i.e., (6.5 to 8.5) except during post-monsoon period (BIS Bureau of Indian Standards 1991). The water is suitable for drinking except in the localized area where the presence of other elements makes the water not fit for drinking.

Total dissolved solids (TDS) is a valuable indicator of the groundwater quality, and a TDS value less than 300 mg/L can be considered as excellent for drinking purpose (WHO 2011). As per the Indian standards, the desired limit is 500 mg/L and permissible limit in the absence of alternate source is 2,000 mg/L (BIS Bureau of Indian Standards 1991). The distribution of TDS values for all the three seasons clearly showed that the Kalpasar region falls above the prescribed limit except at Gandhar during post-monsoon and winter seasons. During pre-monsoon, values ranged from 1,267±503 to 7,941±864 mg/L, while it varied from 276±46 to 4,323±352 and 250±34 to 3,220±742 mg/L during post-monsoon and winter seasons (Table 1). Relatively high TDS values during pre-monsoon were found in the entire region. Similar results were obtained for groundwaters of the Arkavathi and Gadilam river basins of India (Venugopal 1998; Aravindan 1999). Low TDS values during post-monsoon and winter seasons as compared to pre-monsoon season due to unconfined aquifer system and prevailing high rainfall (Langmuir 1997).

Heavy metal and boron levels in groundwater

Table 2 provides mean metal concentrations in groundwater samples, along with other relevant statistical distribution parameters. High mean concentrations were found for Zn during all the three seasons followed by Cu, Cr, and B during pre-monsoon, post-monsoon, and winter seasons, respectively.

Table 1 Groundwater sampling locations with coordinates in the Gulf of Khambhat region and seasonal variation of pH and TDS

Location	GPS	Sampling station details	Pre-monsoon		Post-monsoon		Winter	
			pH	TDS	pH	TDS	pH	TDS
Gopnath	N 21° 12.600' E 72° 06.225'	Groundwater wells	8.15±0.07	3,550±212	7.9±0.42	1,433.5±547	7.51±0.12	1,314±829
Alang	N 21° 26.027' E 72° 11.968'	Groundwater wells	7.7±0.15	1,406±331	8±0.28	614.5±59	8.02±0.16	658.5±3.5
Dholera	N 22° 14.987' E 72° 11.523'	Hot water spring	7.4±0.11	3,450±1237	7.4±0.15	4,323±352	7.78±0.17	1,779.2±193
Vadgam	N 22° 19.624' E 72° 25.418'	Groundwater wells	7.56±0.32	1,396.6±504	7.62±0.07	1,411±455	7.8±0.14	1,240±327
Devla	N 21° 59.751' E 72° 34.471'	Bore wells	7.23±0.15	7,941±864	8.1±0.2	3,227±1,840	7.64±0.22	2,700±1,213
Gandhar	N 21° 53.171' E 72° 39.460'	Well water	8.1±0.13	1,600±269	8.7±0.21	276±46	8.01±0.11	250±34
Dahej	N 21° 41.132' E 72° 35.577'	Groundwater well/bore well/hand pump	8.0±0.14	3,000±521	8.4±0.22	2,250±429	7.88±0.18	3,220±742
Hansot	N 21° 34.802' E 72° 48.738'	Groundwater well/bore well/hand pump	7.7±0.17	2,000±775	8.23±0.05	1,120±663	8.05±0.25	1,264±595
Hazira	N 21° 05.727' E 72° 38.340'	Bore well/hand pump	8.43±0.21	1,267±503	8.26±0.15	725±271	8.19±0.22	788±246

Table 2 Seasonal variation of trace element concentrations (micrograms per liter) and statistical parametrs at all sampling sites in the Gulf of Khambhat region

Parameter	Heavy metals and Boron									
	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	B
Post-monsoon season										
Min	BDL	BDL	BDL	BDL	BDL	BDL	0.93	BDL	4.33	BDL
Max	BDL	11.80	7.03	10.43	18.00	10.01	8.00	15.00	79.5	6.20
Mean	–	2.12	1.19	3.05	5.22	1.11	3.49	3.67	32.09	1.77
Median	–	0.97	0.53	1.15	3.70	0.00	3.33	2.05	29.0	0.00
SD	–	3.68	2.22	3.90	5.49	3.33	2.36	4.51	23.66	2.64
SE	–	1.23	0.74	1.30	1.83	1.11	0.79	1.50	7.89	0.88
Kurt	–	8.35	8.38	0.58	3.74	9.00	0.50	6.27	1.31	−0.84
Skew	–	2.85	2.86	1.45	1.82	3.00	0.96	2.40	1.17	1.06
Winter season										
Min	BDL	0.36	0.1	0.85	0.85	BDL	1.5	2.85	6.8	2.75
Max	4.35	7.35	0.77	16.55	27.40	8.96	3.80	6.87	124.0	12.65
Mean	1.68	2.18	0.34	6.10	15.95	2.59	2.69	4.14	52.64	7.73
Median	0.90	0.50	0.24	1.67	16.80	2.00	2.86	3.67	21.80	7.35
SD	1.70	2.58	0.23	6.44	8.29	2.52	0.73	1.20	49.49	3.57
SE	0.57	0.86	0.08	2.15	2.76	0.84	0.24	0.40	16.50	1.19
Kurt	−1.27	1.96	0.23	−0.97	0.18	6.79	−0.42	4.81	−1.61	−1.43
Skew	0.68	1.79	1.10	1.02	−0.66	2.41	−0.10	1.98	0.80	−0.07
Pre-monsoon season										
Min	BDL	0.085	0.22	0.2	0.8	BDL	0.167	0.45	3.05	2.2
Max	6.50	5.15	3.77	26.00	5.50	15.33	5.30	4.95	39.43	30.30
Mean	3.14	2.02	1.46	10.00	3.97	3.17	2.43	2.23	13.05	11.35
Median	2.65	0.40	0.75	8.10	3.00	1.70	1.77	1.75	6.67	4.90
SD	2.34	2.21	1.32	8.77	2.87	4.83	1.71	1.67	11.95	10.28
SE	0.78	0.74	0.44	2.92	0.96	1.61	0.57	0.56	3.98	3.43
Kurt	−1.40	−1.56	−0.39	−0.10	−0.64	6.36	−0.70	−1.25	4.04	0.01
Skew	0.21	0.80	1.02	0.76	0.81	2.42	0.46	0.50	2.07	1.15

The concentrations of Cd, Co, Ni, and Pb displayed relatively high values during the post-monsoon season while As, Cr, and Mn showed high concentrations pre-monsoon season (Fig. 2).

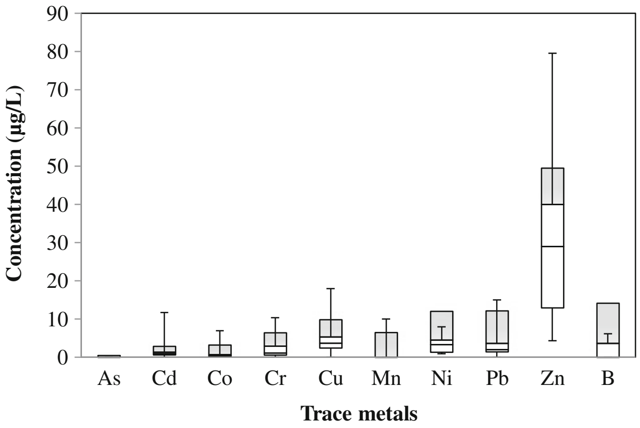

Fig. 2 Box–whisker plot showing the distribution of metals and boron (microgram per liter) in the groundwater during post-monsoon season

Though average levels of Cd in the GoK region was low (2.09 µg/L), concentrations of 7.35 and 11.80 µg/L were detected at some stations which gave cause for concern since cadmium has been reported to be carcinogenic and endocrine disrupter (Kjellström 1986). Generally, Zn is used as an anti-corrosion agent where it is coated on iron pipelines to protect them against corrosion, and these galvanized pipelines are used during the construction of the boreholes. High levels of Zn in the groundwater of the study region may be attributed to corrosion of pump parts. Even though the Zn levels at all the stations were less than the WHO (2011), IS (BIS Bureau of Indian Standards 1991), and USEPA (2012) guideline limits, the slightly high concentration of this metal is alarming and should pose concern to the groundwater users.

Concentration of As was below detectable level (BDL) during post-monsoon season while it ranged from BDL to 6.5 µg/L and BDL to 4.35 µg/L during pre-monsoon and winter seasons, respectively (Figs. 3 and 4). In general, As in natural waters is usually related with sedimentary rocks of marine origin, mineral deposits, fossil fuels, agricultural use, and irrigation practices (Hunt and Howard 1994). It also forms water-soluble complexes with Al, Fe, Ca, and Mg through adsorption (Ganje and Rains 1982). However, the slightly higher As levels in some of the groundwater stations of the GoK region could be from marine sediments, fossil fuels, agriculture, and irrigation practices.

The decreasing trend of average metal levels was as follows: Zn>Cu>Pb>Ni>Cr>Cd>B>Co>Mn>As, Zn>Cu>B>Cr>Pb>Ni>Mn>Cd>As>Co, and Zn>B>Cr>Cu>Mn>As>Ni>Pb>Cd>Co for pre-, post-monsoon, and winter season, respectively. Boron is often cited as contamination tracer and usually occurs as a non-ionized form as H_3BO_3 in soils at $pH<8.5$, but above this pH, it exists as an anion, $B(OH)_4$ (Miller and Donahue 1995). Waters having boron concentrations below 200 μg/L are considered as "uncontaminated" (Rabiet et al. 2005). In the present study, B concentrations were lower than 20 μg/L which is less than the IS limits in most of the stations (95 %). In addition, since the pH was less than 8.5 for many samples, it is more likely that B would be in the non-ionized than the ionized state.

A comparison of the mean and median values evidenced almost randomized distribution of Mn, B, Cr, Cd, Co during pre-monsoon, Cr, Cd, and Zn during post-monsoon, and Cd, Mn, Zn, and B during winter season, suggesting large dispersion around the mean metal levels. The substantial differences in the symmetry parameters in the case of Cr, Cu, Mn, Pb, and Zn indicated a non-normal distribution, thus supporting a possibility of random infiltration of the metals from some anthropogenic source. Large standard deviations in the case of Zn, Cu, Cr, and Pb levels revealed their randomly fluctuating concentration levels in the groundwater.

Before evolving a judgment on the observed distribution of metal levels regarding their probable origin, the metal data was first examined on the basis of linear correlation between metal pairs in terms of significant positive correlation coefficient, $r>0.80$, at $p<0.001$. The correlation matrix of the heavy metals is given in Table 3 for pre-, post-monsoon, and winter seasons. Instead of eliminating metal concentrations below detection limits of some groundwater samples, a value corresponding to half of the detection limit of the metal was considered to that sample. Strong positive correlations were observed for Co–Cd, Pb–Cd, Co–Ni, and Ni–Cd during post-monsoon season, indicating the existence of a common source/origin of these metals in the groundwater. In the winter and pre-monsoon seasons, a strong association between Cr–As and Cu–Cd pairs suggests mixed sources. The correlations provided the primary evidence for a mutual concentration dependence of the metals in the groundwaters of the GoK region.

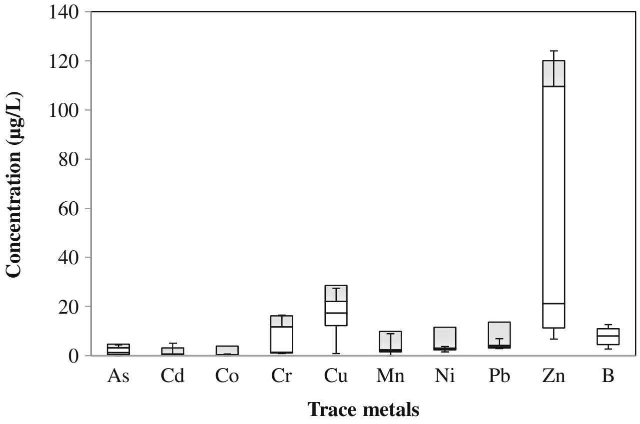

Fig. 3 Box–whisker plot showing the distribution of metals and boron (microgam per liter) in the groundwater during winter season

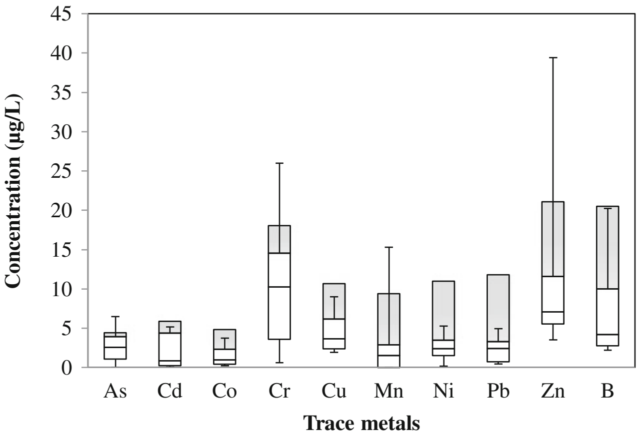

Fig. 4 Box–whisker plot showing the distribution of metals and boron (microgram per liter) in the groundwater during pre-monsoon season

As individual metal concentrations were higher several folds in comparison to the background levels in uncontaminated groundwater sampled from far-off locations, it was inferred that industrial wastes were affecting the water table in the area. The recorded higher Cd and Cr levels were a good pointer toward dyes and intermediates as well as tanning industry effluents since chromium compounds are used in large bulk in the industry. Currently more than 200 dyes and intermediate units are operative in the area from which water samples were taken for analysis. Moreover, the GoK has the largest concentration of chemical industries. Soil disturbance during residential development and inputs from septic systems are hypothesized to mobilize Cd and Cr from soils to groundwater (Koshle et al. 2008).

Average concentrations of trace metals in the groundwater of the GoK region in comparison with the worldwide reported levels from different areas showed that most of the present trace element levels were comparatively higher than coastal regions like Sweden (Augustsson et al., 2009), Mediterranean catchment in France (Potot et al. 2012) except for B and Shenzhen, China except for As, Co, Mn, and Pb (Table 4) (Chen et al. 2007). The mean As concentration estimated in the present study was found to be higher than recorded from Bangladesh (Bhuiyana et al. 2010), Hong Kong (Leung and Jiao 2006), Mexico (Lopez et al. 2002), Switzerland (Kilchmann et al. 2004), and France (Potot et al. 2012). Mean levels of Cd, Co, and Cr were higher than European, South American, and US groundwaters (Augustsson et al. 2009; Kilchmann et al. 2004; Potot et al. 2012; Lopez et al. 2002; Shand and Edmunds 2008; Newcomba and Rimstidt 2002). However, B levels pertaining to the present study were found to be lower than those reported for most of the regions including Krishna Delta, India (Mondal et al. 2010).

Present Zn levels in the groundwater were found to be comparable with those reported from Shenzhen, China (Chen et al. 2007) and Hong Kong (Leung and Jiao 2006) but higher than those reported from Bangladesh (Bhuiyana et al. 2010), Sweden (Augustsson et al. 2009), Switzerland (Kilchmann et al. 2004), France (Potot et al. 2012), and European groundwaters (Shand and Edmunds 2008). Mean

Table 3 Pearson's correlation matrix among elements in the studied groundwater samples during various seasons

	As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	B
Post-monsoon season										
As	1.0									
Cd	–	1.000								
Co	–	0.991**	1.000							
Cr	–	−0.102	−0.084	1.000						
Cu	–	0.543*	0.481*	−0.061	1.000					
Mn	–	0.539**	0.548**	−0.203	0.258	1.000				
Ni	–	0.838**	0.832**	0.245	0.493*	0.395	1.000			
Pb	–	0.959**	0.956**	0.056	0.601**	0.579**	0.882**	1.000		
Zn	–	0.200	0.151	0.045	0.371	0.179	0.146	0.193	1.000	
B	–	0.156	0.198	0.177	0.393	0.276	0.174	0.367	−0.06	1.000
Winter season										
As	1.000									
Cd	0.055	1.00								
Co	−0.08	−0.131	1.000							
Cr	0.883**	0.233	0.033	1.000						
Cu	0.663**	−0.103	0.181	−0.443	1.000					
Mn	−0.146	−0.263	−0.099	−0.373	0.122	1.000				
Ni	0.19	−0.143	0.446	0.077	0.088	0.154	1.000			
Pb	−0.489*	−0.275	0.245	−0.501*	0.176	0.217	0.017	1.000		
Zn	−0.527*	−0.193	0.146	−0.399	0.403	−0.111	−0.065	0.642**	1.000	
B	0.734**	−0.301	−0.104	−0.772**	0.383	0.256	−0.345	0.376	0.475*	1.000
Pre-monsoon season										
As	1.000									
Cd	−0.271	1.000								
Co	−0.028	−0.129	1.000							
Cr	−0.634**	0.590**	−0.177	1.000						
Cu	−0.175	0.836**	−0.261	0.628**	1.000					
Mn	0.561**	−0.360	0.22	−0.392	−0.059	1.000				
Ni	−0.121	0.545*	−0.063	0.332	0.328	−0.469*	1.000			
Pb	0.406	0.407	−0.111	0.081	0.551**	0.413	0.378	1.000		
Zn	0.226	−0.273	0.192	−0.467*	−0.283	−0.037	0.119	−0.115	1.000	
B	0.610**	−0.445*	−0.010	−0.652**	−0.402	0.479*	−0.608**	−0.125	0.303	1.000

*Correlation is significant at the 0.05 level

**Correlation is significant at the 0.01 level

Table 4 Comparison of average levels (micrograms per liter) of heavy metals and boron in groundwater d with international water quality standards and other studies around the world

Parameter		As	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn	B
BIS (Bureau of Indian Standards) (1991))		50	10	–	50	1,000	2,000	20	10	5,000	5,000
WHO (2011)		10	3	–	50	2,000	100	70	10	3,000	2,400
USEPA (2012)		–	5	–	100	–	50	100	15	5,000	–
Union) (1998))		–	5	–	50	–	50	50	50	100	–
Japan (MHLW Ministry of Health and in Japan 2004)		–	10	–	50	–	10-50	10	50	–	–
Present study	Coastal region	2.41	2.11	1.0	6.38	8.38	2.29	2.87	3.35	32.59	6.95
Pesarlanka, Krishna Delta, India (Mondal et al. 2010)	Island	114.3	1.62	9.07		11.5	444.2	7.35	26.21	453.5	254.9
Cuttack, India (Das 2003)	Urban area	–	–	14.3	6.67	3.33	41.6	6.67	28	53.3	–
Golaghat district, Assam, India (Boarh and Misra 2010)	Rural area	32.81	15.9		249.9	33.45	124.2	19.65		858.9	
Hattar, North West Frontier Province of Pakistan (Manzoor et al. 2006)	Industrial area	–	20	80	220		40	80	260	180	–
Shenzhen, South China (Chen et al. 2007)	coastal area	5.11	0.055	1.6	0.86	0.865	889	2.25	5.04	31.67	–
North western Bangladesh (Bhuiyana et al. 2010)	Coal mine area	<0.028	–	<0.072	<0.072	<0.027	0.026	<0.1	0.07	0.29	–
Mid-Levels, Hong Kong (Leung and Jiao 2006)	Natural slope	0.42	0.07	0.02	0.54	0.14	2.72	–	0.54	40.83	18.84
El Oro, Mexico (Lopez et al. 2002)	Volcanic area	2.22	0.054	0.26		1.64	1.33	–	0.355	54.54	15.06
Baltic coast of Sweden (Augustsson et al. 2009)	coastal area	–	0.013	–	1.15	1.85	–	1.81	0.695	4.38	–
Carbonate rocks of Alpine aquifer (Kilchmann et al. 2004)	–	<0.5	<0.2	<0.2	–	0.3	–	–	0.4	0.9	8
Lower Var Valley, Alluvial groundwater (Potot et al. 2012)	Mediterranean catchment	0.66	0.016	0.17	–	0.67	–	–	0.032	6.67	26.75
Chaco Province, Argentina (Blanes et al. 2011)	Watershed area	–	–	–	–	90		10	20	1,530	–
Sohag, Egypt (Komy 1993)	Banks of the Nile river	–	0.37	1.41	–	5.0	508	3.1	10.2	119	–
Lagos, Nigeria (Awofolu 2006)	Residential area		20			140–1,390	10–180	20–110	30	40–430	
European groundwater (Shand and Edmunds 2008)	–	0.5	<0.05	0.08	–	1.2	–	–	0.39	11.5	34.2
US groundwaters (Newcomba and Rimstidt 2002)	–	13.9	–	4.3	4.4	70.6	–	11.5	2.6	264.8	–

Pb levels estimated in the present study were higher in comparison with the levels reported from Bangladesh (Bhuiyana et al. 2010), Hong Kong (Leung and Jiao 2006), Mexico (Lopez et al. 2002), Sweden (Augustsson et al. 2009), Switzerland (Kilchmann et al. 2004), France (Potot et al. 2012), European (Shand and Edmunds 2008), and US groundwaters but comparable to those found in Shenzhen, China (Chen et al. 2007). In conclusion, the trace element levels in groundwaters of the GoK region in comparison with some of European and Asian sites were higher; however, these trace element levels were found to be comparable with few urban sites in the world. Nonetheless, the estimated elemental levels in the present study were lower than those reported for regions like Pakistan, Nigeria, India, and USA.

Principal component analysis

Factor analysis, using varimax normalized rotation, was employed to interpret and translate the complex dataset into a more simple form in which the original variables are replaced by factors (Gotelli and Ellison 2004). The factors are produced through an eigenvalue analysis of the correlation matrix, generated using average values of three seasons. Table 5 summarized the principal component analysis (PCA) results after removal of elements with poor reproducibility and high bias, and with a number of non-detects exceeding 25 %, as well as after removal of strong outliers. The number of significant factors, to understand the underlying data structure, was

Table 5 Varimax rotated factors matrix for the metal and boron concentrations in groundwater for all three seasons

Element	Component			
	PC1	PC2	PC3	PC4
As			0.777	
Cd	0.786			
Co	0.733			
Cr				0.605
Cu	0.837			
Mn		0.863		
Ni		0.704		
Pb				0.754
Zn	0.939			
B		0.818	0.175	
%age of total variance	31.72	20.61	11.26	9.17
Cumulative percentage of total variance	31.72	52.33	63.59	72.76
Eigen Values	3.85	1.92	1.22	1.06

established by considering only those with an eigenvalue >1.0 and the factor loading higher than 0.65.

Following this rule, three independent factors were extracted, which explained 91.1 % of the total variance. Component 1 (PC1) reveals 31.72 % of the total variances are positively loaded with Co, Cu, Cd, and Zn. Components in PC1 are derived from mixed sources such as municipal sewage, metallurgical industries, and infiltration of landfill leachate to the surrounding aquifers (Bhuiyana et al. 2010). Factor 2 (PC2) contributed 20.6 % to the total variance and was characterized by high loadings of Mn, Ni, and B. Low levels of Mn and Ni can end up in soils or water through weathering of minerals and generally varies (BDL, 15.33 μg/L for Mn and 0.17–8.0 μg/L for Ni). These variations may be attributed to the difference of distances between wells and catchments area. This was supported by high values of the coefficient of variation (data not shown), indicating that the distance and pathway of the recharge water to the aquifer was considerably influenced by the weathering process of rocks (Bacquart et al. 2012). The third factor (PC3) had a moderate loading for As and minor loading for B with 11.26 % of the total variance. Contamination of heavy metal pollution around industrial region is often accompanied by contamination with As considering the fact that these elements usually accompany nonferrous minerals (Tighe et al. 2005). These metalloids can be derived from both natural and anthropogenic sources and can dissolve in river water or groundwater or food chain through plants and animals (Mandal and Suzuki 2002).

The relatively high and minor weights for B on PC2 and PC3, respectively, indicate that this component was representative of B release due to mineral weathering or dissolution of evaporite deposits (Gemici et al. 2008). In general, boron is very soluble and tends to concentrate in environments where there is limited circulation of water, evaporites, and brines of marine origin (Vengosh et al. 1992). However, a detailed study is required to establish the affinity between B^{3+} and Cl^{-} and SO_4^{2-} ions (the two most important ion representatives of the salinization processes) in the groundwaters of the GoK region. Factor 4 (PC4) accounts for 9.17 % of the total variance and comprises of Cr and Pb. The occurrence of these metals in groundwater may be attributed to precipitation and deposition of airborne aerosols, from dust transported via atmosphere including automobiles and damaged computer accessories and paints (Hem 1991; Baptista et al. 2007).

Conclusions

Trace metal concentrations in groundwater of the GoK region provides a unique data set of substantial interest as it has severe environmental implications due to proposed world's biggest manmade freshwater reservoir namely Kalpasar. Comparison with international and Indian standards for water quality evidenced that trace metal levels were below the recommended safe limits. The results of the PCA allowed the reduction of the original data matrix to four important PCs explaining 91.1 % of the total variance, sufficient to give a good idea of data structure. The PCA suggested that the groundwater chemistry in the study area is principally influenced by weathering of minerals, anthropogenic pollutants, and atmospheric deposition. The detection of toxic metals such as Cd and Pb in some samples is of great concern to the health of people that utilize the water for drinking purposes. It is anticipated that the results of the present study would assist the decision makers in formulating a groundwater management plan including industrial pollution abatement to be executed.

Acknowledgments A part of this work was carried out by the financial support from Narmada, Water Resources, Water Supply and Kalpasar Department, Government of Gujarat, Gandhinagar through a consultancy project. The authors wish to express their sincere gratitude to Professor Bhavanath Jha, Discipline Coordinator of Marine Biotechnology and Ecology for constructive comments and suggestions throughout the work. Thanks are due to Mr Kalpesh Vakhani and Mr Vinod Yadav for the sampling work.

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