

# Intra-annual variability in the heavy metal geochemistry of ground waters from the Deccan basaltic aquifers of India

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**Abstract** Geochemical baseline (geogenic+anthropogenic) and background (geogenic) levels of heavy metals in the ground waters from basaltic aquifers of Deccan Volcanic Province of India depicted intra-annual variability on spatial scale. Classified into ‘Group I’ (Fe > Mn > Zn > Pb) and ‘Group II’ (Mo > Ni > Cr > Cu), metals depicted contrasting enrichment and depletion patterns seasonally, attributable to geologic controls and water table fluctuations. While, fortification in Mo–Ni in post-monsoon (high water table) is on account of combined lithogenic+anthropogenic contributions, pre-monsoon augmentation in Fe–Mn (low water table) is entirely lithogenic. Positive values of Normalised Difference Dispersal Index, replicates the dominant role of soil/vadose zone as a chief supplier of metals to the groundwater during post-monsoon, while negative figures recommend host rock as a primary source of accretion of metals in pre-monsoon. Higher Ni/Cr ratios for wells in alluvial aquifer (fertile agriculture plain) than the basaltic and dyke aquifers, further suggest enhanced input of the elements (Mo, Ni > Cu) from soil and agriculture land use in post-monsoon season. Values of Ni/Cr ratio above unity for majority of the wells in post-monsoon and nearly 50 % wells in pre-monsoon suggest privileged weathering of olivine, followed by pyroxene > plagioclase feldspar (Ni/Cr <1) as a major cause of heavy metal load to the groundwater. Pearson correlation coefficients authenticate these inferences by means of elemental associations. The study

unveils multi-source derivation of heavy metals related to seasonal fluctuation in the water table conditions leading to range of heavy metals in the groundwater from the study area. The target hazard quotient (THQ) values of heavy metals closer to unity and above unity highlight the possible health risk hazard associated with the consumption of metal contaminated groundwater. The study thus highlights the importance of baseline geochemical mapping to assess the state of near surface environment as heavy metals are closely linked to human health.

**Keywords** Heavy metals · Groundwater · Intra-annual variability · Basaltic aquifers · Target hazard quotient

## Introduction

Amongst several pollutant groups, the heavy metals are kept under surveillance for their mobility and availability from the point of view of biogeochemical and eco-toxicological significance (Tume et al. 2008; Sharma and Subramaniam 2010; PuYang et al. 2015; Gupta et al. 2015). Heavy metals present in the form of free cations occur in miniature quantities dissolved in the water in concentrations less than 1 mg per liter (U.S.G.S. 1993). They are the most frequently analyzed among numerous pollutants occurring in water and sediments, as well as in the majority of organisms (Michalec et al. 2014). The heavy metals (Fe, Mn, Ni, Co, Zn, Cu, and Pb) have also been used as indicators to ascertain the degree of contamination and/or pollution (Engin et al. 2015). Accrual of some of these metals in aquatic environment has direct consequences on human health and ecosystem (Adomako et al. 2008; Gupta et al. 2015). Further, concerns about food safety have been raised because of heavy metal

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contamination of soils (Zhang et al. 2015). Their significance to human health and relation to plant growth have therefore prompted many workers to initiate studies on understanding their relative contributions from different sources and mechanisms of metal transport (Pawar and Nikumbh 1999; Alam et al. 2003; Rajmohan and Elango 2005; Kelepertzis 2014; Arinze et al. 2015; Shirke and Pawar 2015). Health risks to humans via dietary intake of fish were then assessed based on the target hazard quotient (THQ) and hazard index (PuYang et al. 2015) in China. Similarly, Gupta et al. (2015) have conducted studies along Gomati River in India by using THQ to determine quality of dietary intake of fish and water. Fernandez and Nayak (2015) have attempted to study the speciation of metals and their distribution in tropical estuarine mudflat sediments, to understand the depositional environment, post depositional processes, bioavailability of metals and their toxicity.

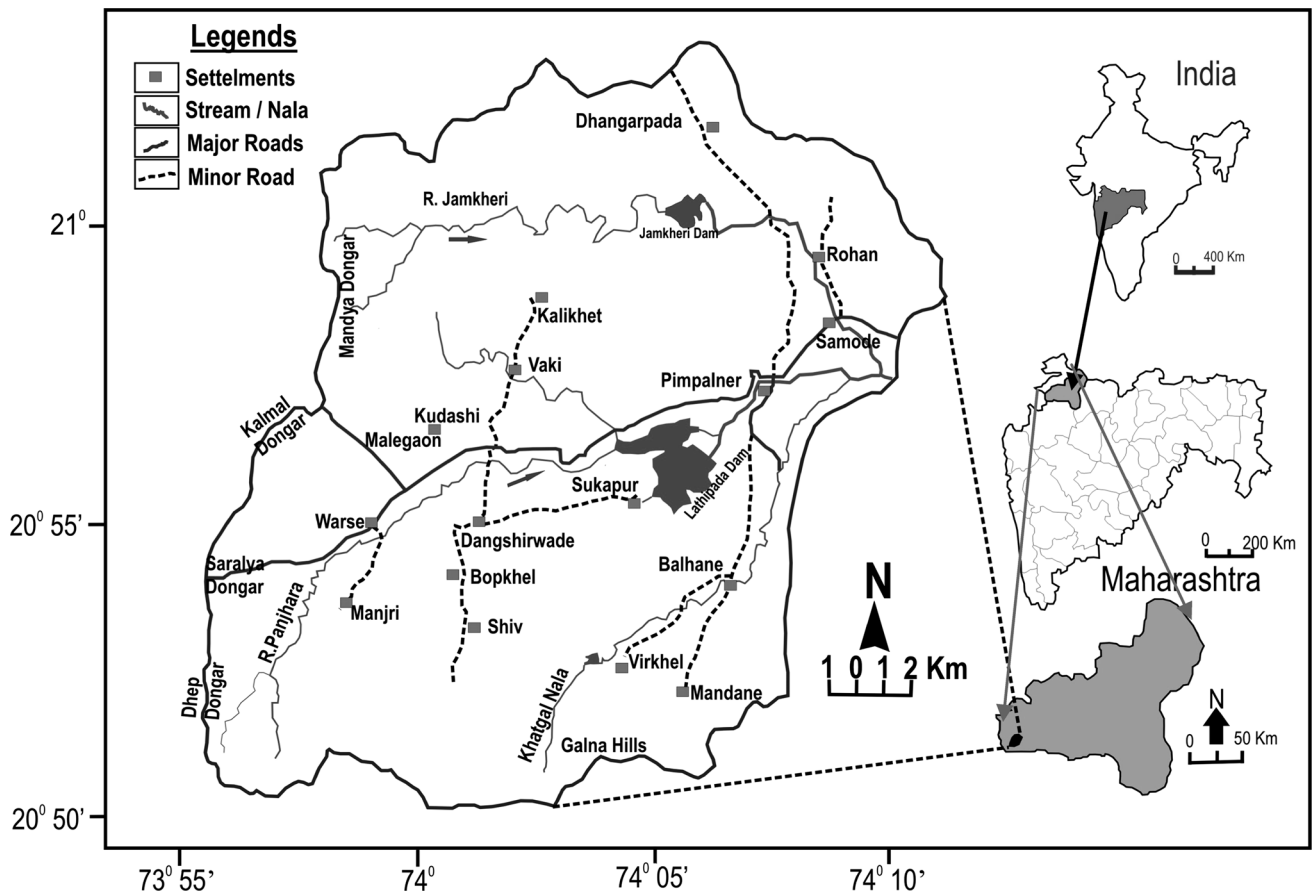
In aquatic environment heavy metal pollution can result from direct atmospheric deposition, weathering of rocks and through anthropogenic sources (Han et al. 2006; Challenger 2007; Suyash et al. 2008; Kelepertzis 2014; Tiwari et al. 2015). To discriminate between anthropogenic and natural sources, distinction of background and baseline values of toxic elements from anomalies is achieved through environmental geochemical mapping (Albanese et al. 2007; Galan et al. 2008; Yuan et al. 2014). While, background values point to sources of metals related exclusively to geogenic origin, the geochemical baseline (anthropogenic and geogenic inputs) is used to predict future trends in metals accumulations. The International Geological Correlation Program initiated IGCP Project 360 on Global Geochemical Baselines to assess the natural variations in the concentration of an element in the superficial environment (Galan et al. 2008). In the case of water resources in general and groundwater resources in particular, the geochemical mapping of background values is not attempted so far in many countries and India is no exception to this. However, in absence of any availability of regional level geochemical maps, using small area based isolated studies as a ready reference in identifying lithogenic/anthropogenic derivation of metals in the aquatic environment is imperative. Although for most anthropogenically derived metallic load, the soils are regarded as an ultimate sink, nonetheless the difficulty lies in the complex nature of the soils and their differing capacity for receiving and purifying metal pollutants (Fazeli et al. 1998; Wong et al. 2006; Krishna and Govil 2007; Yuan et al. 2014). Because, the metal retention capacity of the soils is largely dependant on the soil structure, humus content, calcareousness, pH, exchange capacity and water regime (Orlov 1992); lack of such a favorable soil structure for metal retention finally allows them to enter into the aqueous system. Though, heavy metals occur in minute

quantities in water as compared to soils, their distribution is influenced by (a) nature of parent material, (b) climate and (c) their relative mobility depending on soil parameters such as mineralogy, texture and classification (Krishna and Govil 2007; Galan et al. 2008; Shirke and Pawar 2015). Metals enter the natural aqueous system through several sources: (a) weathering of rocks and soils directly exposed to surface and ground waters forming the largest natural source (Patino et al. 2003) and (b) the anthropogenic sources viz. urbanization, agriculture and industrialization (Pawar and Nikumbh 1999; Wong et al. 2006; Krishna and Govil 2007; Challenger 2007; Suyash et al. 2008; Suyash and Pawar 2010; Michalec et al. 2014; Tiwari et al. 2015; Arinze et al. 2015). Out of these two main contributing sources, to infer the background (geogenic) contributions (Albanese et al. 2007) from natural sources (rock weathering) requires studies initiated on aqueous system in pristine natural environment fairly unaffected by anthropogenic causes. In view of this, investigations were conducted in the headwater portion of the Panjhara River in the northern part of Deccan Volcanic Province (DVP) with the main aim of studying the (1) intra-annual distribution of geochemical baseline levels of ecotoxic heavy metals in the ground waters on spatio-temporal scale and (2) identifying their lithogenic and anthropogenic sources. As stated before, heavy metals persist in the environment, possess bio-accumulative nature and toxicity they are the serious cause of concern from human health point of view.

## The study area

The study area is in the northern part of the Deccan Volcanic Province (DVP) of India (Fig. 1). It is drained by Panjhara River, which is a tributary of E-W flowing Tapi, a major river of Central India that finally empties into and merges with Arabian Sea on the west coast of India. The river originates at an altitude of 760 m amsl in the E-W trending Galna hills of the Western Ghats mountain range. Quite a few tributary streams concoct the adjoining hills of Dhep Dongar in the West and Kalmal and Mandya Dongars in the northwest. Hilly and precipitous landscape with deciduous forest characterizes the source area of the river that merges into rolling hummocky background and gradually unwraps into broad and flat valley floor in the downstream. The headwater part of the basin covering an area of 434 km<sup>2</sup> was chosen for the baseline and background geochemical mapping of the eco-toxic heavy metals as it is untouched by industrialization and urbanization except elfin patches of agricultural activities.

The watershed is in the rain shadow zone of Western Ghats region with annual rainfall ranging from 300 to 862 mm (average 512 mm/year) and average precipitation

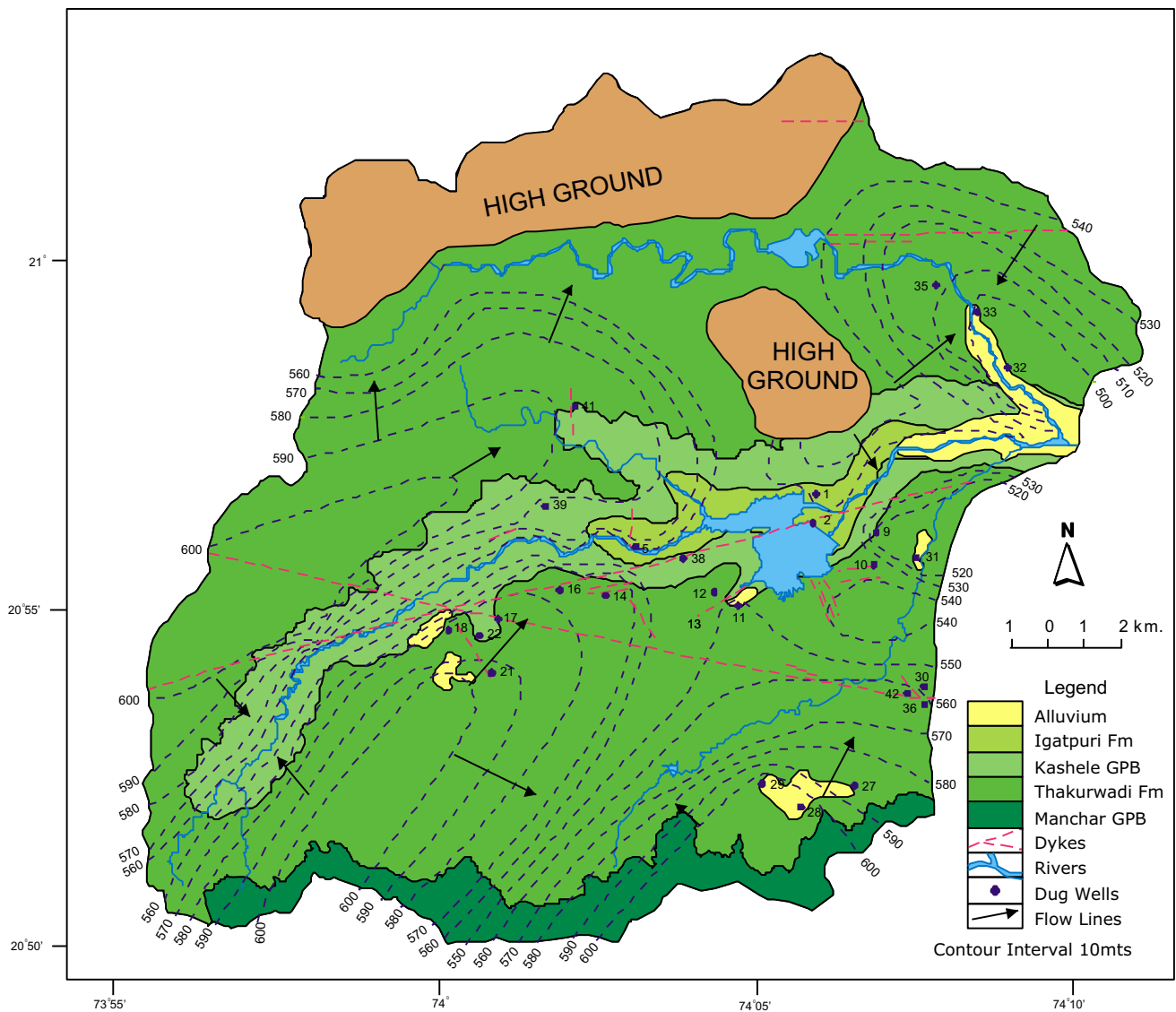


**Fig. 1** Location map of Panjhara basin, DVP, India

is nearly constant for over one decade. More than 90 % of the rainfall is confined to south-west monsoon season lasting for 4–5 months from June to October. Most of the rivers originate in the high rainfall Western Ghat’s region and flow towards semi-arid east, wherein to augment the needs of water numerous percolation tanks and irrigation dams have been constructed. Amongst them two medium sized irrigation dams (Latipada and Jamkheri) and several percolation tanks have been erected across the Panjhara and its tributaries that have amplified the groundwater as well as irrigation potential of the area. Agricultural land with varied cropping pattern is spread only along water-courses, while mountainous and hilly parts are under degraded forest wrap besides grasslands on hill slopes and rolling plains. Entire population of the area is dependant on surface and groundwater resources for both drinking and agricultural needs. Livestock population of the area also forms an important part of agricultural activity, thus emphasizing the necessity for evaluating the suitability of water for drinking purpose from heavy metals viewpoint.

**Geological and petrochemical characteristics**

The study area is typified by oldest and moderately weathered basaltic flows of Kalasubai subgroup of DVP (Fig. 2) embracing multi-aquifer system separated by thin tuffaceous red bole layers. On the basis of geochemical data, the Kalasubai subgroup has been divided into five different formations from base to top namely Jawahar, Neral, Igatpuri, Thakurwadi and Bhimashankar each separated by marker Giant Plagioclase Basalt (GPB) flows (Bean et al. 1986). The lava flows from the study area have been divided into Thakurwadi Formation (TF) underlain by Igatpuri Formation (IF) (Bean et al. 1986; Subbarao et al. 1994), separated by Kashele GPB flow. The uppermost part of the IF is exposed along Panjhara riverbed and remaining portion of the watershed is covered by entire TF. Thin section studies of basalts from these formations (samples of dug well sections DW-21, DW-22) show clinopyroxenes (both Ca-rich and Ca-poor), plagioclase feldspar, iron oxides (magnetite and



**Fig. 2** Geological and hydrogeological map of Panjhara basin, DVP, India

ilmenite) and small amount of olivine (2–2.5 %) divulging typical textures such as fine grained inter-granular to porphyritic and ophitic to sub-ophitic (Subbarao and Hooper 1988). Chemically, flows of IF express MgO content of 4.41–8.82 % and of TF between 3.51 and 11.86 %. While CaO % (8.36–10.85 %), Na<sub>2</sub>O is <3 % and Fe (total) is as high as 15 %, in both the formations variation in trace elements viz Cr, Cu, Ni and Zn is noticeable (Bean et al. 1986). The Ni and Cr in both the formations are abundant trace elements followed by Zn > Cu > Co (Subbarao and Hooper 1988). Mutually doleritic and gabbroic dykes unveil fine grained inter-granular to coarse-grained hypidiomorphic textures with ophitic and sub-ophitic characters infesting the flows (Sethna et al. 1996).

### Hydrogeological set up

Meager incidence of primary openings has imparted low porosity and permeability to basaltic flows in the area. Despite the fact that cavities, vesicles, flow contacts, lava pipes and tunnels can build up principal porosity in the basalt (Pawar and Shaikh 1995) the flows in the study area are relatively less to moderately porous. Conversely, jointing and fracturing by way of interconnectivity have conveyed sufficient secondary porosity and permeability to form suitable groundwater reservoirs at places (Pawar et al. 2008a, b). Further, the cooling features such as columnar joints serve as hydrologic discontinuities, which in turn function as pathways for rainwater that is chief agent of weathering. Resultant porosity is responsible for

restraining petite aquifers positioned usually in the fracture systems. From hydrogeological standpoint, Naik and Awasthi (2003) have divided the basaltic flows into two main units (1) lower massive component and (2) upper vesicular part. The massive section clutches trivial primary porosity or permeability and performs as an unyielding zone yet on account of jointing, fracturing and weathering, intermittently moderately porous rock structure is developed. On the other hand, defenseless to weathering, the vesicular entity with sufficient primary porosity helps in shaping good aquifers. Vesicular crust is the main water-bearing horizon in compound flows of TF in the study area (Pawar et al. 2008a). The flows of the two formations are plausibly weathered at the surface down to the depth of about 10–15 m depending upon local slope conditions. Underneath the weathered echelon, rock illustrates unpredictable degree of fracturing and jointing that goes on diminishing with depth. It is not easy to comprehend the geometry of fracture network due to ample variation in their densities, lengths and apertures (Tarits et al. 2006). In the well sections DW-12 and DW-41, it is seen that density of jointing and fracturing goes on waning with depth, as a consequence of this only shallow water table aquifers with limited thickness (not exceeding 15–20 m) subsist in the area. Being fractured rock with very low matrix permeability, the fluid flow in the basalt is often very heterogeneous and confined to few fractures, which is evident from some yielding bore wells placed very close to dry ones.

The well inventory data indicate that shape of all the dug wells is circular and they are fully or partly lined. While, the old wells are lined with stones, the concrete lining is observed in the case of new wells. Diameter of the dug wells varies from 4 to 8.5 m and the depth between 5.5 and 23 m. Wells in alluvial aquifer are deeper (av. depth = 13.28 m) than the basaltic aquifers (av. depth = 8.48 m). Depths of the bore wells vary from 70 m to nearly 100 m. Analysis of water level data indicates maximum fluctuation in alluvial aquifer (av. 8.55 m) and least in the dyke rock (3.5 m). They are indicative of topographic control in general and localized overexploitation in particular. The wells in the vicinity of Lathipada dam show less fluctuation in water table due to recharge from the dam. In general, the thickness of aquifers in dyke is minimum (<12 m), moderate in the case of basalts (5–15 m) and maximum for alluvium (up to 20 m). Pawar et al. (2008a) on the basis of electrical resistivity surveys have identified multiple aquifers in the area occurring at different depths viz. 30, 50 and 70 m, below this hard and compact rock structure without any joints and fractures prevails in the area. The bore wells in the area tap these aquifers.

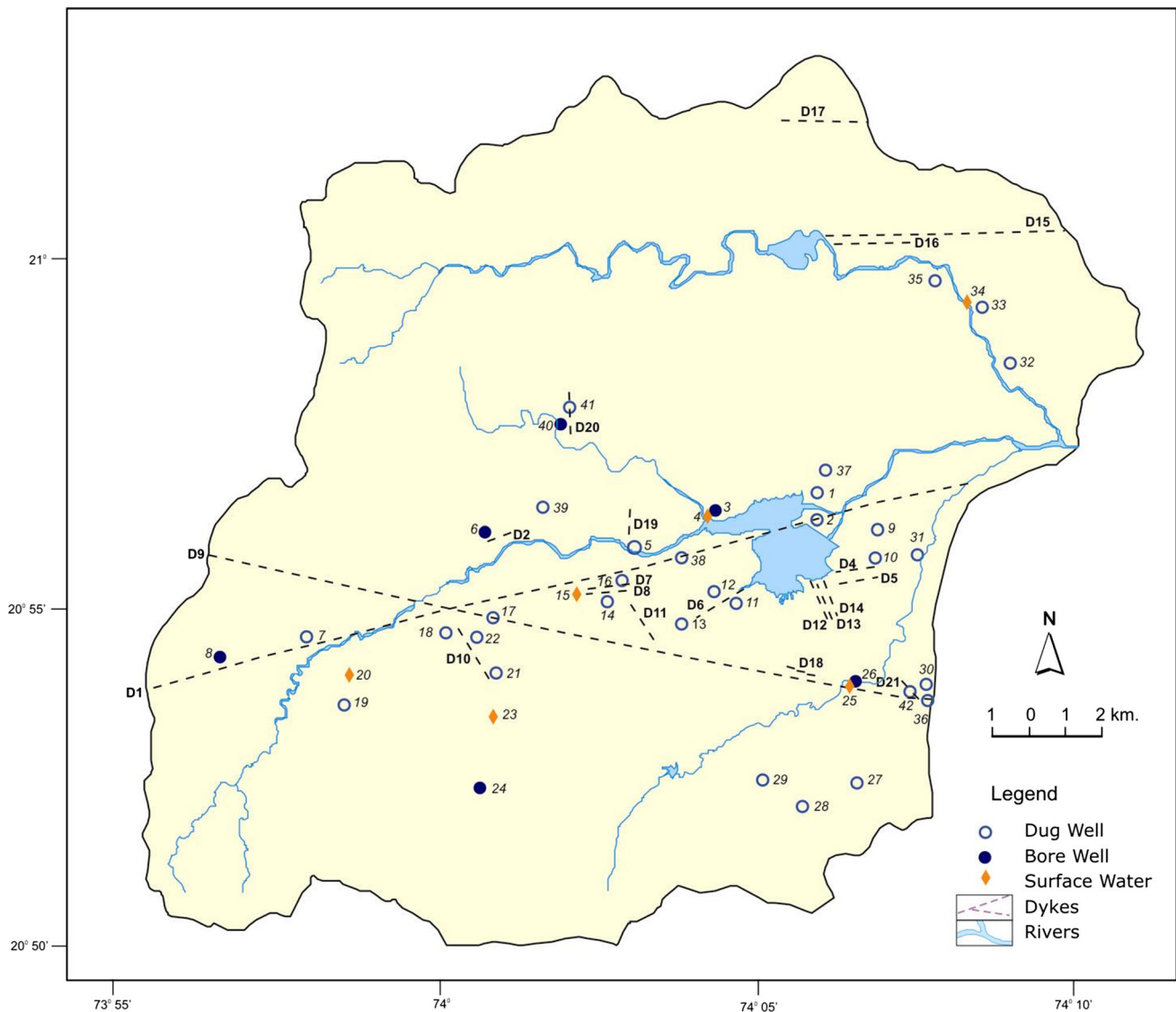
## Methodology

The watershed under review displays relatively less diversity in geological, hydrogeological and environmental conditions except a little modification by agricultural activity. This set up has provided opportunity to identify imprints of lithogenic factors on background and baseline heavy metal chemical composition of groundwater followed by anthropogenic sources.

### Sample locations and collection of water samples

In view of the above geological and hydrogeological conditions in the study area sampling wells were selected randomly (Fig. 3) based on type of lithology, aquifers, slope conditions and land use besides their availability and accessibility in the field for groundwater monitoring. Sampling locations covering post- and pre-monsoon seasons, (35 in post-monsoon and 37 in pre-monsoon) were established for groundwater monitoring. In pre-monsoon, the samples represented 29 dug wells (23 in post-monsoon), 7 bore wells (6 in post-monsoon), and 1 surface water sample (6 in post-monsoon) wrapping alluvial, basaltic, and dyke aquifers. Samples were collected as per standard methods (APHA 2005). Due care was taken to avoid contamination of samples during handling. One-liter capacity pre cleaned plastic containers were used for the collection of water samples. Groundwater samples were collected after the well was subjected to pumping for half an hour. In the case of bore wells fitted with hand pumps, samples were collected after hand pumping the bore well for a few minutes. Surface water samples were collected from flowing streams. The pH, electrical conductivity (EC), well depth, static water level, lithologs and aquifer type were recorded in the field. Suction-filtered (through 0.45  $\mu\text{m}$  membrane filter paper) samples were immediately acidified with high purity concentrated nitric acid to pH <2 to avoid Fe-oxide precipitation, to minimize absorption of metal on the container wall, to retard biological action, hydrolysis of chemical compounds and complexes, and reduction of volatile constituents and separately collected for analyses of heavy metals (De 1990). In all 72 samples representing post-monsoon (December, 2004) and pre-monsoon (May, 2005) were collected to find out the intra-annual trends (over 1 year period) in the heavy metal geochemistry of groundwater (Tables 1, 2). All the samples were stored in a refrigerator at 4 °C to prevent any change in volume before laboratory analyses (APHA 2005). The remaining unacidified portion of the sample was subjected for analyses of the major parameters including Ca, Mg, Na, K,  $\text{SO}_4$ , Cl,  $\text{HCO}_3$  in the laboratory and results obtained were published (Pawar et al. 2008a).





**Fig. 3** Locations of surface and groundwater samples, Panjhara basin, DVP, India

### Analyses of water samples and quality control

The refrigerated acidified water samples 100 mL each were subjected for nitric acid digestion (since it is acceptable matrix in flame AAS) on hot plate (150 °C) by adopting the standard procedure (APHA 2005). After complete digestion evidenced by clear solution the samples were filtered through Whatman-42 filter paper. By transferring the filtrate to 100 mL conical flask and spiking it with known concentrations of standard (standard addition method) the volume was made to mark and mixed thoroughly and subjected for heavy and trace element detection on AAS. Using Varian, AA-220 double beam atomic absorption spectrophotometer the heavy metal analysis was performed. The recommended standard working conditions of the instrument varied from 0.01 to 2 ppm (mg/L) for Zn

at 231.0 nm wavelength to 0.2–100 ppm in the case of Mo at 313.3 nm wavelength. The lower limit of working range was about ten times the defined detection limit of the metal (Varian 1989). The standard detection limits in ppm (mg/L) are cadmium 0.002, chromium 0.02, copper 0.01, iron 0.02, manganese 0.01, lead 0.05, nickel 0.02, zinc 0.005 and molybdenum 0.1 (APHA 2005). The determinations were done by direct aspiration of sample into the air-acetylene flame for all metals except Mo, where the nitrous oxide-acetylene flame was used. The Merck standards (minimum three) were also used for the calibration of the elements analyzed and the reproducibility of the instrument was 90–95 %. In order to ensure the baseline stability blank was analyzed between the sample and standard reading. Along with every batch of ten samples a black digest containing only acid and standard solution was analyzed.

**Table 1** Trace element data for the ground waters from the Upper Panjhara Basin, DVP, India (post monsoon—2004)

Sr. No.	pH	EC	Pb	Cu	Mn	Cr	Fe	Zn	Ni	Cd	Mo
DW1	7.1	290	58	630	543	531	312	346	880	25	1390
DW2	7.2	273	38	560	28	ND	322	187	786	15	430
BW3	7.65	631	31	190	91	180	343	235	534	ND	1070
SW4	7.35	404	21	309	34	ND	217	123	654	2	830
DW5	7.35	397	31	320	99	687	248	194	635	ND	750
BW6	7.4	339	24	ND	175	129	197	288	684	ND	800
DW7	7.56	198	15	ND	242	310	205	334	607	ND	330
BW8	7.6	149	15	680	ND	255	111	562	552	ND	460
DW9	7.28	496	10	ND	139	83	180	ND	611	ND	930
DW10	7.55	329	16	72	1	104	174	89	605	ND	1230
DW11	7.68	244	59	207	316	550	256	149	624	57	680
DW12	7.62	337	12	58	64	249	285	132	648	ND	970
DW13	7.55	380	17	ND	39	163	118	186	635	28	920
DW14	7.9	146	40	ND	ND	182	296	241	587	16	590
SW15	7.8	330	80	ND	92	167	205	205	621	ND	870
DW16	7.78	387	20	21	88	142	207	156	588	ND	710
DW17	7.6	408	40	ND	61	154	165	268	641	ND	950
DW18	7.66	329	ND	42	60	196	99	199	675	ND	940
BW19	7.5	411	ND	ND	73	97	234	189	607	ND	710
SW20	7.78	236	30	335	55	267	338	236	647	29	800
DW21	7.3	408	ND	401	329	547	211	338	817	89	1100
DW22	7.55	291	47	ND	23	217	246	144	484	ND	700
SW23	7.8	257	58	ND	79	129	158	236	649	ND	540
BW24	7.55	267	80	ND	15	253	206	447	684	ND	700
BW25	7.5	417	70	ND	38	31	103	206	409	ND	990
SW26	7.95	344	20	ND	69	ND	228	199	53	ND	610
DW27	7.86	374	ND	ND	75	228	160	87	658	ND	880
DW28	7.75	360	ND	21	49	64	114	291	63	ND	710
DW29	7	305	70	17	122	142	131	ND	628	ND	850
DW30	7.76	511	ND	ND	10	60	233	256	631	ND	1540
DW31	7.62	507	10	288	337	54	130	490	718	ND	1080
DW32	7.6	681	48	ND	82	34	ND	135	543	ND	1340
DW33	7.6	729	14	ND	108	56	104	119	564	ND	1060
SW34	8.1	257	ND	ND	97	172	90	79	538	ND	410
DW35	7.95	270	ND	ND	60	230	268	160	643	ND	620
Avg	7.59	362.6	38	259.4	111.9	208.2	202.8	268	597.2	32.63	842.6
Min	7	146	10	17	1	31	90	79	53	2	330
Max	8.1	729	80	680	513	687	343	1490	880	89	1540
Std. Devi	0.24	132.6	34.436	222.2	116.8	161.3	73.27	246.4	159.8	27.75	278.5
Variance	0.06	17590	1185.8	49351	13652	26031	5368	60689	25545	770	77578

All values of the elements are in ppb

DW dug well, BW bore well, SW surface water, ND not detectable

The data obtained was corrected for known concentration of standard added and results were reported in ppb (µg/L).

The chemical data was subjected for statistical analysis such as min. max. average, standard deviation and

variance. The Pearson correlation coefficients were calculated using MS-Excel for appraising possible metallic associations and relating them with geochemical processes.

**Table 2** Trace element data for the ground waters from the Upper Panjhara Basin DVP, India (pre monsoon—2005)

Sr. No	pH	EC	Pb	Cu	Mn	Cr	Fe	Zn	Ni	Cd	Mo
DW1	8.04	268	63	277	200	334	747	318	216	30	70
DW2	8.33	212	71	8	136	310	752	292	263	66	41
BW3	8.06	650	69	856	135	298	679	284	255	88	299
DW5	8.22	375	69	4	577	228	652	278	224	83	52
BW6	8.29	453	50	ND	509	133	724	555	147	53	56
DW7	8.41	213	75	ND	333	223	689	313	238	59	48
BW8	8.32	140	56	ND	327	113	619	187	203	72	51
DW9	8.21	427	97	11	387	70	769	235	243	37	70
DW10	8.34	251	69	ND	228	208	629	267	199	85	32
DW11	7.92	539	65	ND	480	206	710	251	232	37	53
DW12	8.16	276	68	1	254	156	606	137	176	90	50
DW13	8.13	356	58	ND	554	4	613	355	274	48	52
DW14	8.41	144	46	11	240	197	606	317	153	48	56
DW16	8.06	331	89	23	462	251	687	270	144	25	43
DW17	8.19	307	50	ND	617	181	715	309	25	60	63
DW18	8.13	286	50	ND	560	112	529	309	65	49	76
BW19	8.34	250	61	ND	429	167	709	305	47	38	50
DW21	8	355	51	171	215	161	678	274	77	63	84
DW22	8.2	323	35	334	602	290	702	285	31	80	87
BW24	8.18	254	37	ND	508	88	454	324	253	24	72
BW25	8.09	444	52	ND	277	244	593	298	213	ND	68
DW27	8.27	325	27	ND	280	219	643	275	252	67	76
DW28	8.2	310	42	6	137	184	590	343	146	52	93
DW29	8.22	295	40	ND	272	22	699	252	218	12	79
DW30	8.25	510	38	ND	269	195	629	218	154	16	85
DW31	8.19	500	22	186	280	117	618	195	182	56	90
DW32	7.88	654	16	ND	226	106	653	256	177	40	80
DW33	7.92	647	50	ND	187	225	719	80	181	469	89
SW34	8.12	387	54	59	78	251	670	286	202	319	95
DW35	8.11	289	55	29	241	189	621	275	194	ND	91
DW36	8.3	376	36	ND	324	163	415	295	167	27	93
DW37	8.23	308	43	1	380	142	553	306	266	510	88
DW38	8.15	329	35	106	409	123	655	251	387	44	104
DW39	8.05	448	29	ND	359	174	703	178	352	61	96
BW40	8.47	236	36	318	ND	ND	167	282	358	62	105
DW41	7.95	163	40	158	300	217	669	282	387	67	97
DW42	8	508	30	657	342	324	644	297	391	42	102
Avg	8.17	355	54	169.26	336.5	184.3	635.41	276.6	207.9	85.11	79.35
Min	7.88	140	16	1	78	4	167	80	25	12	32
Max	8.47	654	97	856	617	334	769	555	391	510	299
Std.Devi	0.14	134.15	20.16	237.43	144.54	78.47	109	72.78	93.13	112.48	42.24
Varian.	0.02	17997	496.51	56371	20891	6157.3	11881	5296.5	8673	12651	1784.2

All values of the elements are in ppb

DW dug well, BW bore well, SW surface water, ND not detectable



### Application of THQ

The consumption of heavy metal containing water is likely to pose risk to human health. The THQ offers an indication of risk level due to pollutant exposure and has been used by many researchers. It was first established by U.S. Environmental Protection Agency (1989) and later on applied for judging the quality of beverages by Hague et al. (2008); seafood by Storelli (2008), Petroczi and Naughton (2009) and for water, sediment and fish by Gupta et al. (2015) and PuYang et al. (2015). The THQ is expressed (U.S. EPA 1989) as follows:

$$THQ = \frac{(E_{Fr} \times ED_{tot} \times SFI \times MCS_{inorg})}{(RfD \times BWa \times ATn)} \times 10^{-3}$$

where  $E_{Fr}$  is exposure frequency (considered as 365 days/year);  $ED_{tot}$  is the exposure duration (70 years life expectancy),  $SFI$  is the mass of selected dietary ingested (av. water consumption as per Indian Standards (IS 1993) is 5 L/person/day),  $MCS_{inorg}$  is the concentration of metal in water (ppb),  $RfD$  is the oral reference dose (mg/L based on WHO (1971)/IS (1993) drinking water standards),  $BWa$  is the average body weight (55.9 kg for adult) and  $ATn$  is the average exposure time for non-carcinogens (365 days/year  $\times ED_{tot}$ ).

### Results

#### Spatio-temporal trends in the heavy metals

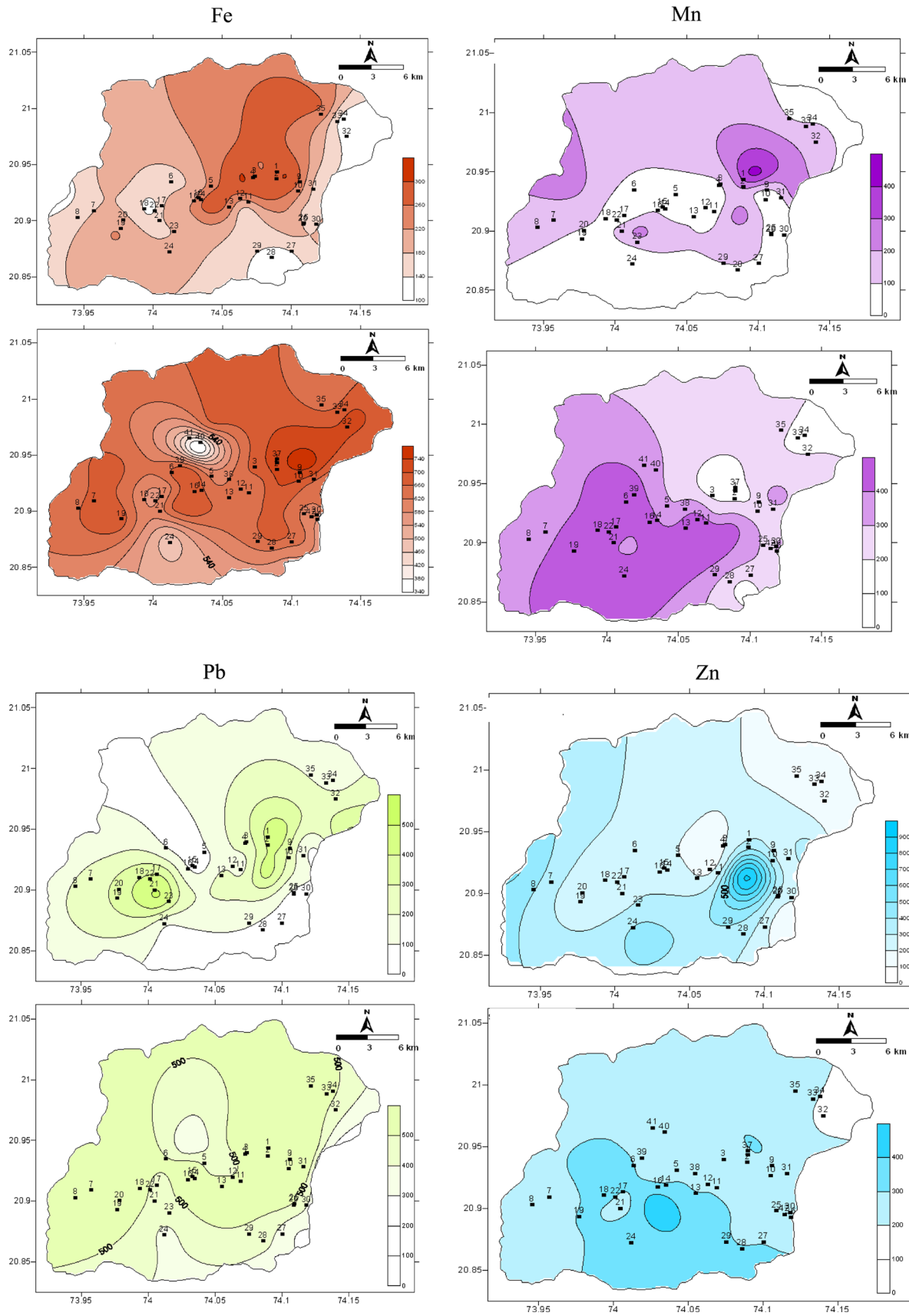
The concentrations of heavy metals in the ground waters from Upper Panjhara basin depicted with the help of isoline plots, show remarkable intra-annual variations on spatial scale (Figs. 4, 5) in spite of nearly uniform geological conditions in the area. Although alluvium is present in patches, it has local basaltic provenance and has possibly inherited many metals from weathering of basalt. Based on their intra-annual variability the heavy metals in the Panjhara basin have been grouped into (1) Group I: represented by Fe, Mn, Pb, Zn and Cd and (2) Group II: signifying Mo, Ni, Cu and Cr. The order of abundance of Group I elements in the groundwater is  $Fe > Mn > Zn > Pb$  and that of Group II elements is  $Mo > Ni > Cr > Cu$  (Tables 1, 2). In general, the concentrations of Group I elements are lower in post-monsoon season when water table is high (av. depth = 3.83 m) and higher in pre-monsoon season. In contrast, the Group II (Mo, Ni, Cu and Cr) depicts higher values in post-monsoon season and lower in pre-monsoon (av. water table depth = 8.23 m). These changes in the temporal behavior of the metals can be attributed to the water table fluctuations related to rainfall recharge inducing changes in redox conditions (Edmunds et al. 2002).

Temporal pattern of the elements depicting higher Mo and Ni values in post-monsoon is on account of recharge from monsoon rainfall indicating collective input of elements from lithogenic + anthropogenic factors respectively from higher elevation non agricultural areas (TF flows) and fertile soil zone in the alluvial plains covered by patches of agriculture along water courses. During rainy season due to ‘rinse-out’ effect caused by dissolution and precipitation of soil salts (Smoulders et al. 2004), there is remarkable increase in concentrations of the above elements in the groundwater. The propensity of remaining metallic elements depicting higher concentrations in pre-monsoon is accountable predominantly to rock-water interaction due to higher residence time at moderately deeper depth (IF flows) as rainwater recharge ceases. This is particularly true for low lying discharge areas along the course of main rivers wherein the plots depict higher concentrations.

On the spatial scale Group I (Fe and Mn) isoline pattern reflects the control of groundwater flow on the variations of elements (Fig. 4), with Pb and Zn demonstrating less differences (Tables 2, 3). It is seen from the figure that Fe concentrations increase in the downstream direction with a ‘concentration high’ in low lying area in post-monsoon that expands in pre-monsoon depicting several anomalies spread over entire area. Similarly, Mn also shows small anomalies downstream around dam that disappears in pre-monsoon. However, in the upstream part of dam, expanded Mn anomalies are visible in pre-monsoon. Amongst Group II elements, greater inconsistency in Cu is conspicuous. This necessitates local anthropogenic causative sources of Cu (fungicides and micronutrients) in the groundwater, in addition to the lithogenic inputs (Pawar and Nikumbh 1999). The Ni and Mo (Fig. 4) values though comparable and widely distributed over larger area, enrichment is confined to the alluvial areas with irrigated agriculture. Relatively lower background concentrations of these elements in non-agricultural parts of the basin in upper reaches put forward the view that their input is predominantly from lithological sources such as weathering of olivine, pyroxene and plagioclase feldspar (Subbarao et al. 1994). Elevated values of Group II elements (Ni and Mo) in the central and eastern parts of the area near the confluence of Panjhara and Jamkheri rivers divulge additions possibly from agricultural sources (Pawar et al. 2008a). This high concentration area expands during post-monsoon season indicating likely contribution of both the elements from fertilizer-remains in the soil zone (Pawar and Nikumbh 1999).

#### Heavy metals drift along groundwater flow lines

Though certain trace and heavy metals illustrate systematic enrichment on temporal scale, their slightly disorganized



**Fig. 4** Spatio-temporal variations in the Group I heavy metals in the ground waters (post-monsoon—2004 and pre-monsoon—2005 respectively) of Panjhara basin, DVP, India

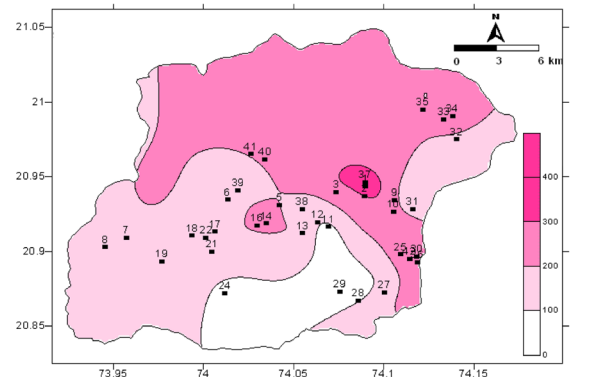
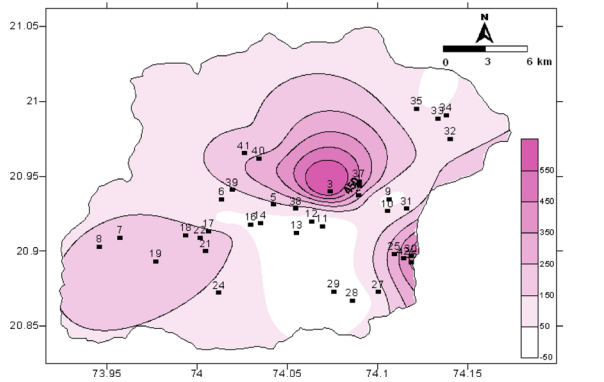
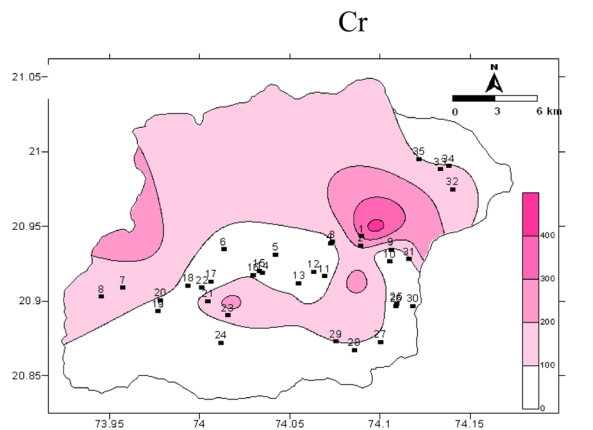
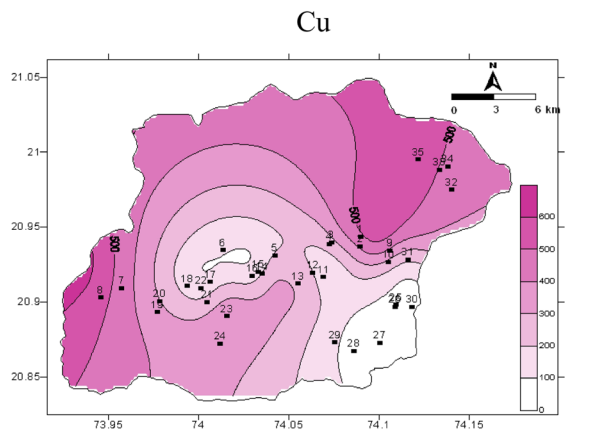
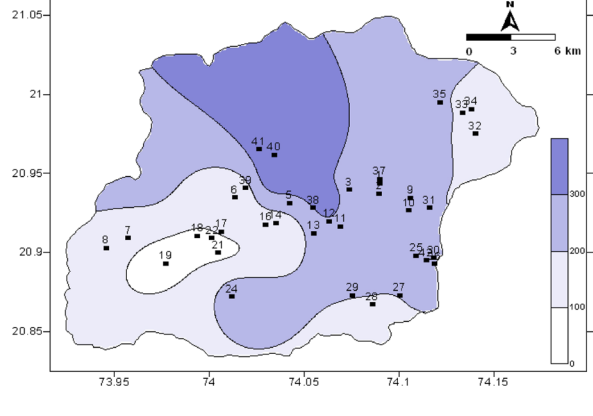
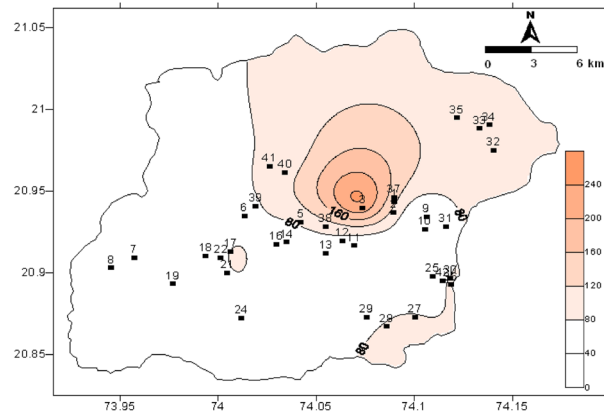
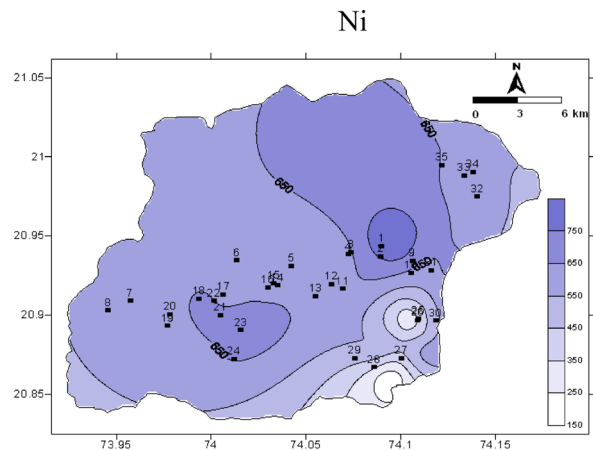
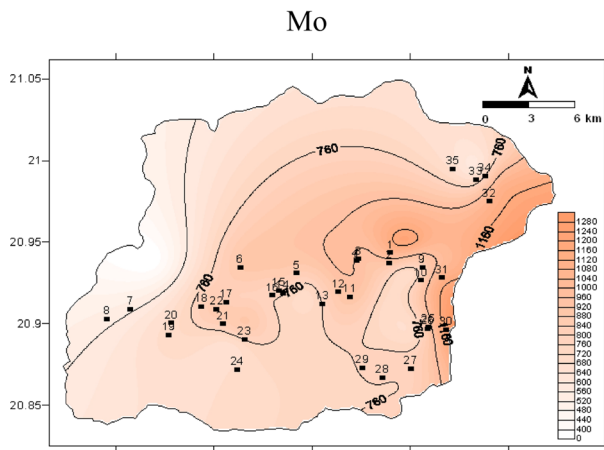
pattern along groundwater flow lines is apparent (Fig. 6). Several authors have related orderly elemental variations with distance along flow lines (Larocque and Rasmussen 1998; Edmunds et al. 2002; Rajmohan and Elango 2005). As compared to these studies the trends in heavy metal concentrations along three different chosen sections passing through wells 18–17–16–14–12 followed by 10–9–2 and 35–33–32 (Fig. 6) are slightly inconsistent possibly indicating complex groundwater flow patterns, heterogeneity in the rock structure and source composition (Ghosh 1983). This is because, in a fractured rock like basalt with very low matrix permeability, the fluid flow is often very heterogeneous and confined to few fractures, causing random variations in metal elements. Further, the source heterogeneity in DVP is manifested by quartz normative flows, under-saturated basalts and olivine tholeiites. Chemically, quartz normative flows show relatively higher Cu and under-saturated basalts depict elevated Zn, Cr, Ni, Pb and Co, besides olivine tholeiites enriched in Cr, Ni and Co (Ghosh 1983). Therefore, variations in trace elements along groundwater flow in the area can be attributed to uneven distribution and abundance of tholeiites and olivine tholeiites in the area, as silica under saturated varieties are absent. Further, two contrasting patterns can be easily discerned from Fig. 6, (1) post-monsoon season depicting enrichment of groundwater with Mo and Ni and (2) pre-monsoon season showing increase in Fe and Mn. Changes in Cr and Zn are negligible. This pattern suggests that primarily Mo and Ni are contributed by twin sources (1) high altitude TF flows with picritic horizons (Subbarao and Hooper 1988) and (2) flushing of metals to phreatic zone from the soil/vadose stratum by rainwater recharge during post-monsoon season (Pawar and Nikumbh 1999). It is possible that shallow circulation of groundwater due to rising water table (post-monsoon = av. 3.83 m and pre-monsoon = 8.23 m) induced suitable (oxidizing?) conditions that are probably responsible for higher concentrations of Mo and Ni (Kafri et al. 2002). Moreover, Mo has relatively higher geochemical mobility under ambient earth surface environment wherein the predominant state is  $\text{Mo}^{6+}$ , which forms soluble molybdate anions in water (Hem 1991). However, this process would close in summer distinguished by (1) relatively deeper circulation of water swayed possibly through reducing environment and (2) break in the supply of oxygen by nonattendance of rainwater recharge, thereby diminishing the contribution of these elements to the groundwater (Pawar and Nikumbh 1999). In contrast, these conditions are more suitable for Fe

and Mn that amplify during summer probably as a result of higher residence time and moderate rock-water interaction involving pyroxenes and opaque minerals and less abundant olivine in IF flows, thus revealing predominantly geogenic input. The dissolved heavy metals in water are sensitive to pH values (Drever 1982). They are also controlled by their adsorption on manganese and iron oxy-hydroxides (Das and Krishnaswami 2007). It is therefore possible that with increase in pH (av. 8.17) in pre-monsoon season, the surface negative charge of manganese and iron oxy-hydroxides is also amplified, thereby allowing sequestration of metals on Fe-oxy-hydroxides and thus lowering the concentrations of associated Group I heavy metals (Pawar and Nikumbh 1999; Das and Krishnaswami 2007).

Spatial and temporal trends of heavy metals (Fig. 6) along groundwater flow could well explain accretion of these constituents possibly derived from diffuse soil sources and sediment disturbance by runoff (Zhou et al. 2007). High concentrations of these elements in post-monsoon suggest contribution from both geogenic and anthropogenic sources as Mo is potential micronutrient used for enhanced crop productivity (Orlov 1992) and has an ability to get enriched in the soil zone due to its strong affinity for near surface earth environment (Hem 1991). Similarly, besides rock, supplementary Ni and Pb can come from agrochemicals (as impurities) and electroplating activity (Liu et al. 2011). Relatively constant or almost stable concentrations of other elements except Fe and Mn specify their geochemical stability under prevailing environmental conditions (Edmunds et al. 2002). Background Cr concentrations are higher on account of its abundance as a trace constituent in basaltic rocks containing plenteous olivine in the picritic horizons of basalt (Bean et al. 1986; Subbarao et al. 1994). Cr is present generally as oxy-anion ( $\text{CrO}_3$ ) and pattern of its occurrence and spatial distribution reflects its natural background concentration in basaltic aquifer under available redox environment (Edmunds et al. 2002). Ni although geochemically related to Mg-olivine (picritic basalt) dominant lithology (Bean et al. 1986), enhances in winter pointing to additional source from soil zone altered by agricultural activity.

#### Depth integrated deviations in the heavy metals

Though the difference in the depth of bore (av. 50–100 m) and dug wells (5.5–23 m) is remarkable, depth integrated sampling was not possible during the present study. However, to get some idea about depth related variations, the waters collected from different sources indicating different depths such as surface, dug and bore wells have been compared (Fig. 7). It is seen from the figure that there is no noticeable change in the ionic concentration of



**Fig. 5** Spatio-temporal variations in the Group II heavy metals in the ground waters (post-monsoon—2004 and pre-monsoon—2005 respectively) of Panjhara basin, DVP, India

surface waters, shallow dug and deeper bore wells of Group I elements, demonstrating dominance of single source contribution evidently lithology. Remaining Group II elements show greater disparity in elemental values, which is indicative of their multiple source origin with respect to water types. This is to say that the surface and shallow ground waters tapped by dug wells depicting higher concentrations of the heavy metals at-least in winter season reflect combined participation of dominantly lithological and in part the anthropogenic sources.

As against this, the pre-monsoon trends reflect not as much of dissimilarity in the elemental values of dug as well as bore wells suggesting contribution predominantly from geogenic sources.

**Discussion**

**Elucidation of heavy metal eccentricity**

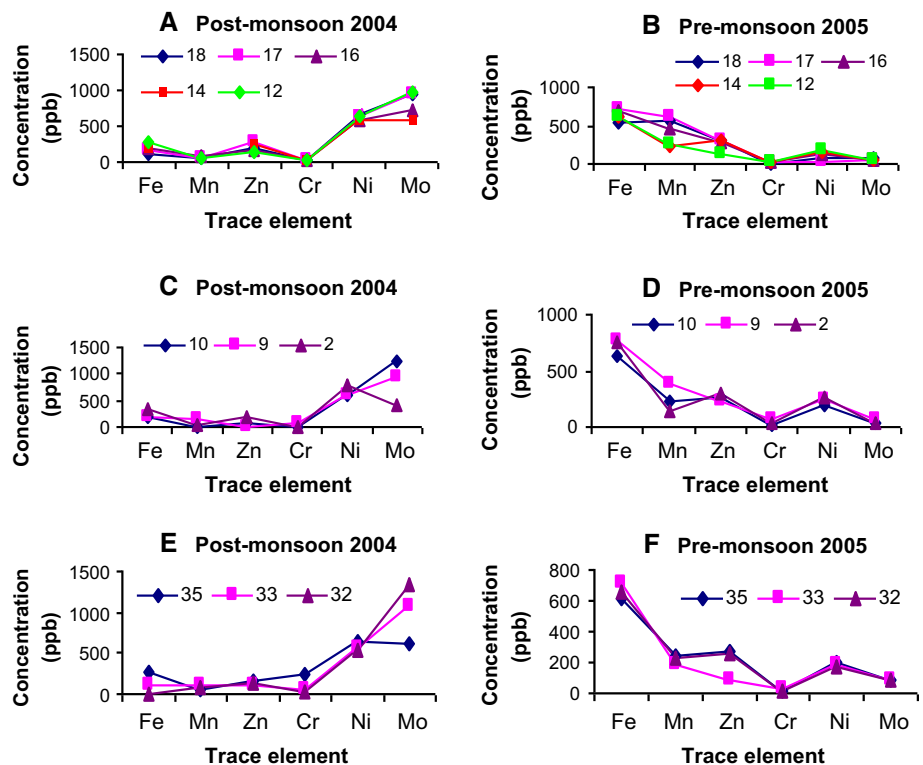
Two possible sources of heavy metals in the ground waters from Panjhara basin have been inferred on the basis of their spatio-temporal, depth-wise and groundwater flow related variations. These are (1) lithogenic contributions from

**Table 3** Comparison of heavy metal ratios for the rocks, minerals, fertilizers, animal wastes and the waters

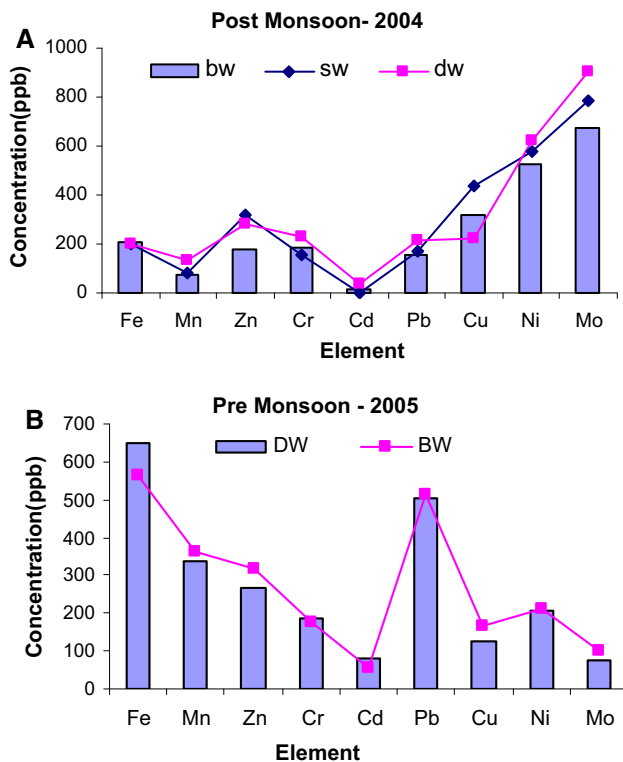
Source type	Ni/Cr	Ni/Cu	Ni/Zn
Rock (basalt)	0.55–0.59 (av. 0.57)*	0.74–1.28 (av. 1.14)	0.72–1.55 (av. 1.14)
Thakurwadi formation	0.79	1.28	1.55
Igatpuri formation	0.55	0.74	0.72
Olivine	5.62–115	–	–
Pyroxene	0.55–0.59 (av. 0.57)*	0.3–2.37 (av. 1.34)	0.49–0.76 (av. 0.63)
Plagioclase	0.67–1.15	–	–
Fertilizer	0.24–0.33 (av. 0.29)	0.24–2 (av. 0.56)	0.05–0.125 (av. 0.09)
Animal waste	0.63–1.81 (av. 1.22)	0.51–0.61 (av. 1.12)	0.15–0.31 (av. 0.23)
Surface water	0.8–4.28	3.42–4.93	0.71–3.74
Ground water	0.5–2.61	1.21–2.03	0.75–2

\* Indicate values for tholeiitic basalt

**Fig. 6 a–f** Trace element concentration in the wells along groundwater flow lines from the study area







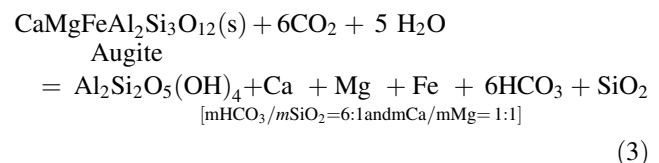
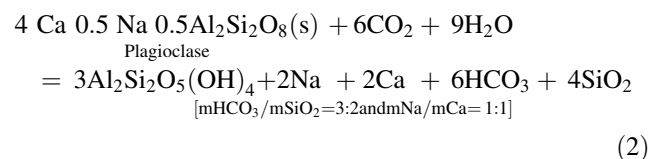
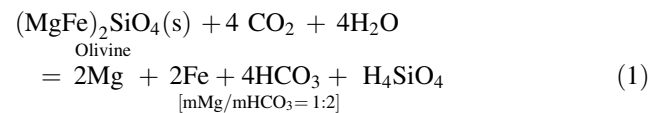
**Fig. 7** a, b Depth wise variations in trace element concentration in ground waters from the Upper Panjhara basin, DVP, India

weathering of basaltic rocks in the study area and (2) anthropogenic link with the discontinuous patches of agricultural activity as the area is devoid of industrialization and urbanization.

#### Lithogenic contributions

Geological factors control the distribution of heavy metals, as most of them are direct derivatives of local bedrock composition and hence, it is important to know the geochemical characteristics of rock (Koljonen 1992). The basaltic lithology in the area forms shallow weathered and fractured basaltic aquifers; therefore the sources of heavy metals could be related to their distribution and concentration in the aquifer media (Salonen and Neimi 2007). Because the study area is dominantly under basaltic rock formation, (with minor spread of alluvium and a few doleritic dykes), plausibly metal concentrations are likely to show systematic variations depending upon hydrogeological and geomorphological factors in the study area. However, most of the metals illustrate incoherent behavior that needs explanation based on lithological factors as the anthropogenic influences in the area are least. It is pointed out (Mysen and Kushiro 1976) that the trace and heavy metal content of the basalt depends on a number of factors for instance (1) proportion of crystalline mineral phases,

(2) participating phases making liquids and crystals, (3) composition of mantle source, (4) effects of degree of partial and fractional melting, (5) partition coefficients, (6) wall rock alteration and volatile transfer. Further, the quartz normative basaltic flows in the DVP contain relatively higher Cu; the under-saturated variety portrays higher Zn, Cr, Ni, Pb and Co, whilst the olivine tholeiites are more enriched in Cr, Ni and Co than others (Ghosh 1983). The Panjhara basin is typified by both quartz normative as well as olivine tholeiitic basaltic flows of both TF and IF, comprised of plagioclase feldspars, pyroxenes, olivine and opaque minerals, which are potential sources of heavy metals. Atypical patterns of metallic elements in the groundwater therefore could be the result of (1) differential weathering of silicate minerals in the basalt, (2) sulphide-oxidation reactions with sulphide minerals in basalt and (3) reductive dissolution of metal hydroxides (Robertson and Blows 1995). The silicate mineral dissolution reactions of primary minerals resulting from lithological divergence in the area (Pawar et al. 2008a) are typically incongruent type (except congruent dissolution of olivine) and can be summarized as follows:

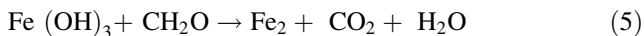
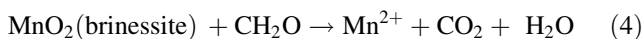


Rainwater charged by CO<sub>2</sub> in the atmosphere, permeates through soil zone and invigorates the basaltic aquifers in the area, which is the source of protons in the above reactions. These rock-water interaction processes unshackle not only the base cations (Ca, Mg, Na, K) but also the associated heavy metals with them such as Zn, Cr, Ni, Pb, Cu and Co besides bicarbonate along with concurrent increase in pH (Rabemanana et al. 2005). In the above reactions, privileged dissolution of certain minerals, their sequence of weathering, modal proportion of different mineral phases and spatial variability in mobilization can lead to differences in the release of metallic ions, thus causing inconsistent patterns (Pawar et al. 2008a).

The basaltic lithology holds nearly 13–15 % Fe–Ti oxide minerals (Sen 1986). The oxidation of ferrous sulphide occurring as accessory mineral (Sen 1986) and



reductive dissolution of Fe–Ti oxides (Robertson and Blows 1995) occurring as opaques in basaltic rocks could be responsible for releasing metals such as Fe, Mn and associated metals into the aquifer. Additionally, hydrous manganese and iron oxides occurring as coatings around silicate grains are ubiquitous in soils and alluvial sediments in the study area. The hydrous iron oxides are often amorphous, whereas Mn generally occurs as poorly crystalline birnessite or todorokite (Drever 1982). Since, these hydrous Fe–Mn oxides have extremely high adsorption capacity and affinity for heavy metals, many metals like Cu, Pb, Zn, Cr, Ni etc. that are released along with other cations from several mineral components are largely adsorbed by these oxide phases (Das and Krishnaswami 2007). Due to seasonally variable redox conditions, reductive dissolution of these metal oxides or hydroxides is expected to release the heavy metals in the surface and ground waters as follows:



Thus, ferric iron hydroxide and manganese oxide reduction not only releases Fe and Mn to the groundwater, but also metals co-precipitated or adsorbed onto these metal oxides. This could be the reason for some of the metals (Zn and Pb) to depict complimentary trends to Fe and Mn. For example, at pH values above 7 aqueous complexes of zinc begin to portion to particulate zinc as a result of sorption onto iron oxy-oxide (Challenger 2007). Further, the soils in the area are rich in montmorillonite type clay mineral (Pawar et al. 2008a), which is considered to be very effective in removing the metals from the water. In spite of these natural controls, some of the metals have been found to be occurring in higher concentrations in the groundwater as compared to drinking water standards.

#### *Mineral dissolution*

Compositionally, lithological divergence in Panjhara basin is evidently epitomized by varying abundances of heavy elements in two formations TF and IF. The order of abundance of the trace elements in IF is  $\text{Cr} > \text{Ni} > \text{Zn} > \text{Cu} > \text{Co}$  with concentrations in the range of  $106\text{--}240 > 70\text{--}182 > 94\text{--}142 > 45\text{--}224 > 40\text{--}49$  ppm respectively. This sequence remains same in TF except for the fact that their values are on much higher side ( $105\text{--}821 > 65\text{--}484 > 96\text{--}143 > 70\text{--}223 > 37\text{--}58$  ppm) due to higher MgO (8.36 and 10.85 %) content (Subbarao and Hooper 1988; Khadri et al. 1989). Therefore, privileged abundance of heavy metals in the groundwater points to their origin from weathering of mafic phases in the basalt namely olivine and clinopyroxenes (Subbarao and Hooper

1988). Higher concentrations of trace elements recount to greater modal abundance of olivine occasionally attaining 25–30 % proportion (Khadri et al. 1989). Higher values of Ni/Cr (0.79), Ni/Cu (1.28) and Ni/Zn (1.55) for TF than IF (Table 3) supports above observation. Further, the Ni/Cr ratio of pyroxene (0.55–0.59) and plagioclase feldspar (0.67–1.15) is low as compared to olivine (5.62–115). Compared to these values the Ni/Cr ratio for majority of the wells in post-monsoon and >50 % in pre-monsoon are above unity suggesting advantaged weathering of olivine, which could be major supplier of heavy metal load to the waters. This is because the silicate tetrahedra in olivine are linked through chemical bonding of single oxygen with divalent Mg, grading it as nesosilicate, which is weak structure and relatively less stable for chemical attack by water (Hem 1991). On the other hand, pyroxene with double oxygen ions in tetrahedra form long chain inosilicate structure (strong) and plagioclase feldspar amid three oxygen ions in tetrahedra shared with other tetrahedra shape tectosilicate configuration (stronger) appear to be supplementary in role due to relatively higher stability. This inference confirms the findings (based on major element data) of Pawar et al. (2008a) indicating olivine > augite > plagioclase feldspar as the sequence of mineral weathering in the Panjhara basin. It is therefore proposed that heavy metal intra-annual variability in the groundwaters is mainly the result of selective dissolution of mineral constituents in the basalt and their sequence of weathering. Needless to say high proportion of bonding between divalent cations and oxygen in nesosilicate structure of olivine followed by inosilicate configuration of pyroxene outline preferred zones of weaknesses that are easily disrupted by water as compared to silicon-oxygen or aluminum-oxygen bonds in tectosilicate makeup of plagioclase feldspar in the basalt (Hem 1991). Thus, weak structure and relatively less stability for chemical attack by water have possibly favored selective dissolution of olivine followed by pyroxene and plagioclase to release heavy metals in the groundwater, which is reflected in incoherent pattern.

#### *Anthropogenic input*

The heavy metals can also be derived from multitude of anthropogenic emissions in the environment (Challenger 2007). Though, mining and smelting, fossil fuel burning, municipal waste incineration, industrialization (Adomako et al. 2008; Suyash et al. 2008; Suyash and Pawar 2010) are important anthropogenic sources, none of these activities are prevalent in the study area. However, the basin is a part of tribal belt of central India; wherein agricultural practices followed by the local population are more traditional, yet

some agricultural sources of heavy metals could be envisaged in the area. Use of commercial fertilizers and pesticides, animal waste and waste water discharges has potential to contaminate the water resources (Challenger 2007). Therefore, in order to find out agricultural bustle as an additional source of heavy metals in the groundwater, intra-annual geochemical data were normalized and quantified with the help of Normalised Difference Dispersal Index (NDDI) by using following expression (Suyash and Pawar 2008):

$$NDDI = \frac{Conc. (post - monsoon - pre - monsoon)}{Conc. (pre - monsoon + post monsoon)}$$

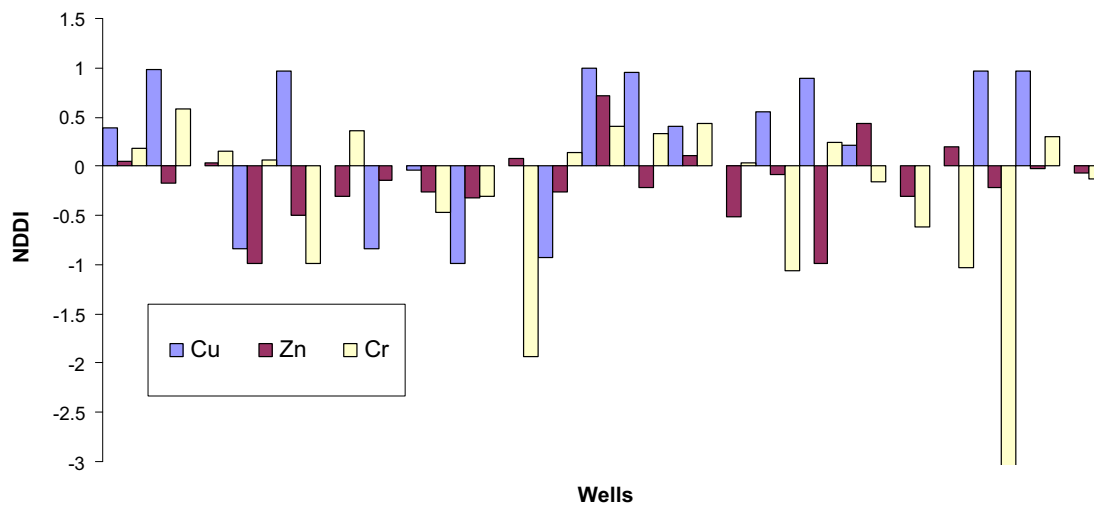
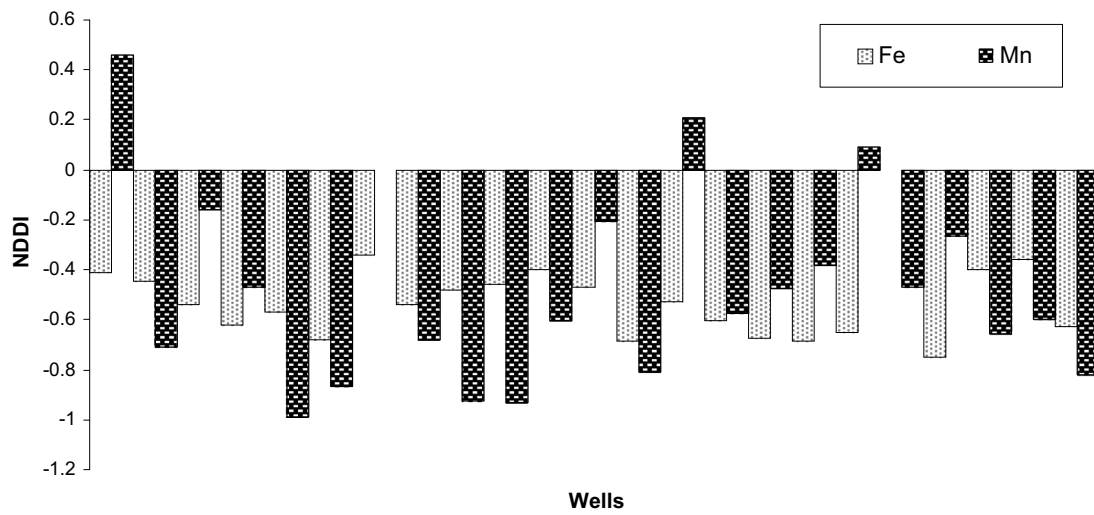
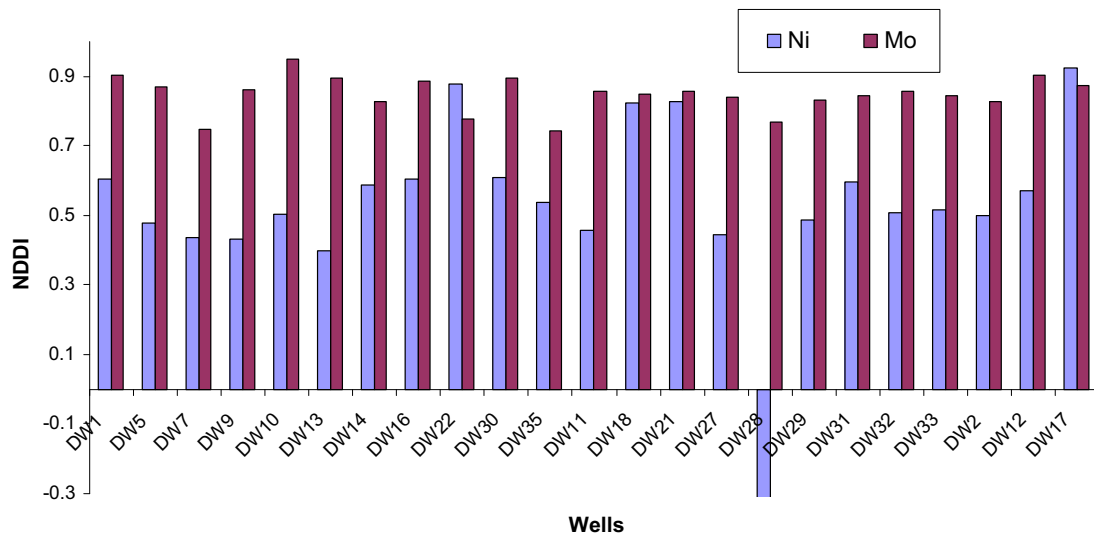
The values of NDDI range between  $-1$  and  $+1$  suggesting absolute dilution and absolute accretion respectively and make the intra-annual comparative evaluation possible. NDDI values for the wells portrayed three distinct patterns (1) Ni–MO displaying positive index values for all the wells (except DW-29), (2) Fe–Mn witnessing negative numbers (except DW-1, DW-29 and DW-31) and (3) the remaining elements (Cu, Zn and Cr) exhibiting mixed pattern (Fig. 8). The positive values of Ni and Mo, and partly Cu imply widespread and uniform, sampling-spot-specific enrichment of these elements related to embellishments from soil/vadose echelon to the phreatic zone during post-monsoon. Negative indices for Fe and Mn point to their consistent and absolute dilution possibly due to near absence or inactive sources in the upper soil/vadose horizon. Hence, groundwater is depleted with respect to them in post-monsoon. The mixed pattern implies depletion and enrichment in parts with respect to Cu, Zn and Cr, limited to explicit well locations possibly due to localized presence or absence of metal source. In nutshell, positive NDDI values replicate the dominance of soil/vadose zone as a chief transmitter of metals in the groundwater during post-monsoon, while negative values recommend host rock as a primary source of accretion of metals in pre-monsoon. Relatively higher values of Ni/Cr ratio for the wells in alluvial (post-monsoon av. = 5.99) and dyke (post-monsoon av. = 7) aquifers surrounded by fertile agriculture plain than the basaltic aquifer (post-monsoon av. 4.04) support this inference (Fig. 9a), suggesting profound input of the elements (Mo, Ni > Cu) from agriculture land use (animal waste related sources) in post-monsoon season. Increase in the values of the Ni/Cr in basaltic/dyke aquifers is spot-specific, thus indicating localized additions of these elements wherever patches of agriculture exist. On the other hand, there is substantial decrease in the Ni/Cr ratios in pre-monsoon (Fig. 9b) pointing to discontinued rain-water recharge dominated by heavy metals from soil/agricultural areas. Negative values of NDDI have been obtained for Fe and Mn and in part for Zn reflecting

**Fig. 8** Normalized Difference Dispersal Index patterns for the wells from Panjhara basin, DVP India

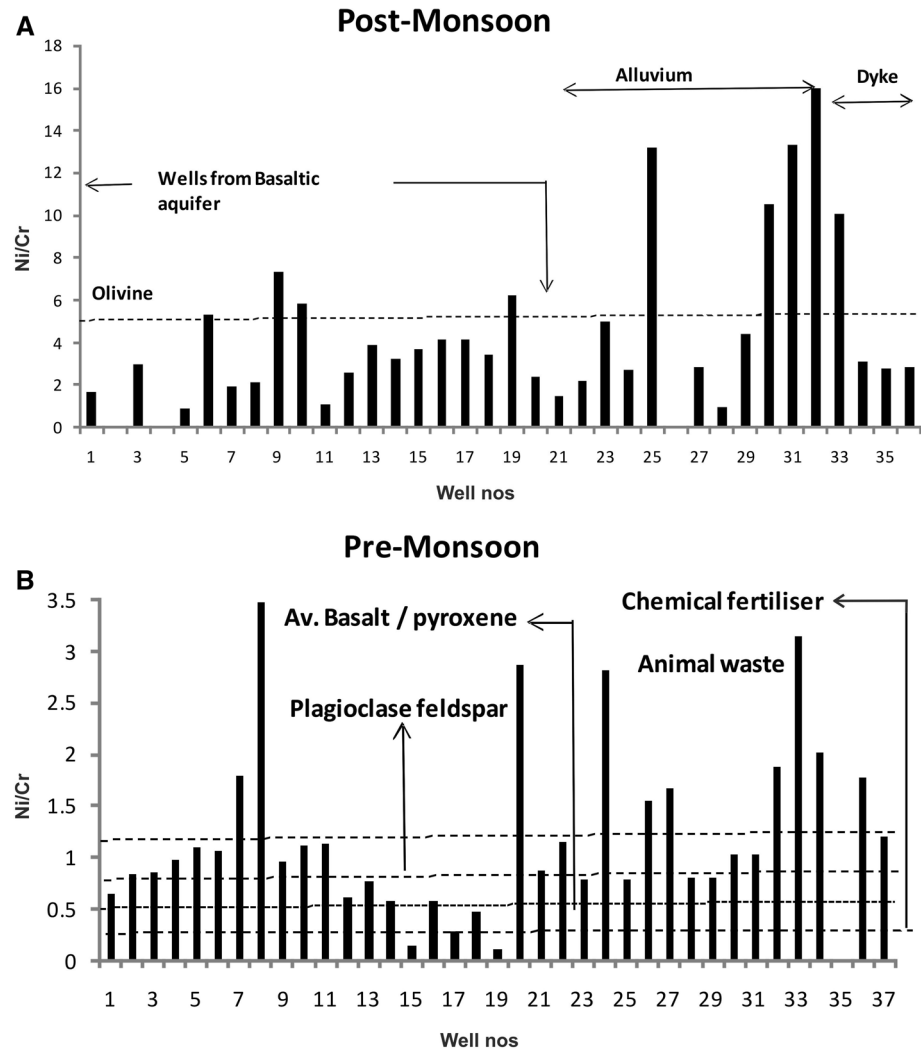
negligible role of recharge waters. This in turn puts forward the view that there is meager addition of these heavy metals from secondary sources in the soil zone. In view of this, it is plausible that elements that depict positive NDDI are supplied to the groundwater dominantly by soil and sediment as well as anthropogenic sources related to the agriculture. Negative NDDI values reflect involvement of primarily geogenic factors, when recharge through soil zone is absent. Thus, both NDDI and Ni/Cr ratios support the inferences made earlier.

### Elemental alliances

In order to authenticate above inferences by means of exploring possible associations amongst the metals, Pearson correlation coefficients were determined (Table 4). Two distinct groups of the chemical components were formed on the basis of their seasonal relationships (1) static coalition and (2) dynamic assemblage. The static group does not illustrate changing inter-ionic links seasonally, whereas the dynamic group demonstrates distinct alteration in relationships seasonally (Pawar et al. 2008a). For instance, pH portrays positive affiliation with Zn, EC with Mo, Cu with Cr > Ni, Mn with Zn > Fe, Ni, and Cd with Mo, followed by pH vs. Ni and Fe vs. Mo negative alliance in pre-monsoon that remains identical even in post-monsoon. Further, heavy metal association indicates that majority of heavy metals are positively correlated with each other in post-monsoon season implying dominant role of soil sources and sediment disturbance by runoff (Zhou et al. 2007) and negatively correlated with each other in summer signifying geochemical diversity in the lithology (Ghosh 1983) and differing response of mineral constituents to weathering of rock affecting heavy metal release (Pawar et al. 2008a). Negative correlation between Fe and Mo in both the seasons shows their mobility as well as stability under contrasting redox conditions (Hem 1991). This is also evidenced by distinct NDDI patterns depicted by these elements. Interestingly, the affirmative link between EC and Mo ( $r = 0.23$ ) in pre-monsoon becomes stronger in post-monsoon ( $r = 0.64$ ) reflecting control of soil water recharge on Mo. Moderately strong relationship between Pb and Cu > Zn indicates their common source of origin from sulphide minerals (Sen 1986). Positive correlation of Cu further with Mo > Cr > Ni in pre-monsoon suggests their contribution from quartz normative tholeiitic basaltic flows as a common source (Ghosh 1983). Mn correlates positively with Zn > Fe (similar NDDI pattern) in pre-monsoon indicating Fe–Ti oxides as their possible



**Fig. 9 a, b** Comparison of Ni/Cr ratios for the ground waters from Panjhara basin with various lithogenic and anthropogenic sources



source and strengthens the relationship with almost all elements such as  $Cr > Cd > Ni > Zn > Mo > Fe$  in post-monsoon reflecting their derivation from diffuse soil sources and sediment disturbance by runoff (Zhou et al. 2007). From the positive correlation coefficients it is inferred that heavy metals have been introduced in the water column from a common source (soil/sediment) and lack of significant positive correlation between them suggests that these elements are associated with different aluminosilicate minerals in the basalts (Adomako et al. 2008). In nutshell, the elemental alliances point to their multi-source derivation and seasonal fluctuation in the water table conditions leading to the intra-annual variability in the heavy metal content of groundwater from the study area.

### THQ and implications on human health

In the study area metals have been introduced in the aquatic environment primarily from rock weathering, soil

and sediment sources followed by localized additions from anthropogenic factors (animal waste) related to agriculture. Since the area is tribal belt and least affected by industrial and urban sources, accumulation of metals in the groundwater is likely to have direct consequences on human health and ecosystem. It is to be noted that the local population is dependant on groundwater as their primary source of drinking water. Knowing the fact that certain heavy metals like Cu and Zn are essential for metabolic activity in the organisms, it is implicit that their lies narrow window between essentiality and toxicity (Adomako et al. 2008). Some of the constituents like cobalt, chromium, cadmium, lead etc. should be virtually absent from the drinking water supply however, in some instances values of metals (Mn, Cr, Cd and Pb) are though higher in the study area are comparable with the studies on Narmada and Tapi river basins (Sharma and Subramanium 2010). Further, pre-monsoon water quality with respect to heavy metals is poor (particularly in basaltic aquifer) as the number of wells exceeding standard limits for drinking water is higher

**Table 4** Pearson correlation coefficient matrix of heavy metals in groundwater form study area, DVP, India

	WT	pH	EC	Pb	Cu	Mn	Cr	Fe	Zn	Ni	Cd	Mo
Post-monsoon, 2004												
WT	1											
pH	-0.07	1										
EC	0.028	-0.59	1									
Pb	-0.24	0.114	-0.17	1								
Cu	-0.2	-0.21	0.298	-0.09	1							
Mn	0.234	-0.05	-0.05	0.089	-0.23	1						
Cr	-0.23	-0.24	0.12	0.196	0.376	-0.13	1					
Fe	-0.04	-0.36	0.214	<b>0.35</b>	-0.05	0.214	0.451	1				
Zn	0.01	0.271	-0.2	0.024	0.039	0.269	-0.01	-0.05	1			
Ni	-0.38	-0.11	0.023	-0.14	0.268	-0.28	-0.05	-0.19	-0.11	1		
Cd	-0	-0.12	0.179	-0.02	-0.06	-0.17	0.095	0.027	-0.25	0.042	1	
Mo	-0.13	-0.25	0.453	-0.17	0.764	-0.32	0.166	-0.1	-0.06	0.227	0.104	1
Pre-monsoon, 2005												
WT	1											
pH	-0.001	1										
Ec	0.4804	0.007	1									
Pb	-0.381	-0.344	-0.007	1								
Cu	-0.176	-0.421	-0.237	0.3962	1							
Mn	-0.055	-0.404	0.0133	0.3632	0.4356	1						
Cr	-0.221	-0.193	-0.339	0.3598	0.4328	0.522	1					
Fe	-0.271	-0.055	-0.325	0.2577	0.2791	0.1755	0.3794	1				
Zn	-0.139	0.1405	-0.29	0.3801	0.3161	0.4029	0.4429	0.1359	1			
Ni	-0.021	-0.382	-0.116	0.1674	0.4034	0.4632	0.3641	0.3544	0.0629	1		
Cd	0.0592	-0.208	-0.143	0.2117	0.3764	0.5138	0.5559	0.198	0.4906	0.3593	1	
Mo	0.286	-0.109	0.6372	0.0663	-0.05	0.2343	-0.091	-0.19	-0.188	0.1704	0.0734	1

in pre-monsoon than in post-monsoon season. Most of the wells in winter show heavy metal concentrations below desirable limit except in a few cases. Therefore, though it is suggested that metal speciation is more important in assessing the toxicity and mobility (Frieberg et al. 1986), importance of total concentrations of heavy metals in assessing metal pollution can not be downplayed, especially where baseline geochemical map data are non-existent (Adomako et al. 2008).

Several workers have proposed use of THQ for the assessment of the potential human health risks from exposure to chemical contaminants (Storelli 2008; Naughton and Petroczi 2008; Storelli et al. 2010; PuYang et al. 2015; Gupta et al. 2015). THQ is typically non-cancer risk assessment method based on a ratio between the estimated dose of contaminant and the reference dose below which there will not be any appreciable risk (Storelli 2008). Therefore, THQ was determined for all the metals using WHO and IS recommendations for consumption of drinking water. The values of THQ have been given in the Table 5a, b. It is observed that during pre-monsoon season

most of the metals (except Cr and Cd in a few cases) display THQ values less than one. The THQ of metals varies from Pb = 0.01–0.09, Cu = 0.00–0.05, Mn = 0.02–0.18; Cr = 0.01–0.6; Zn = 0.00–0.01; Ni = 0–0; Fe = 0.05–0.23 and Cd = 0.11–4.56. These results are comparable with those obtained by Gupta et al. (2015) for Gomati River in the northern part of India. The results further suggest insignificant non-cancer health hazard from majority of metals except a few wells with respect to values of THQ for Cd. In general, amongst all metals the values of Cd are on higher side and three wells (DW33, DW34 and DW37) exceed the THQ values above unity suggesting potential human health risk hazard if consumption of water is continued. It is possible that these wells are contaminated from chemical fertilizers and organic matter related to agriculture and animal waste (Han 2006). In the post-monsoon season all the wells display THQ values of metals far below unity except a few wells with respect to Cr and Cd. The THQ values for various metals in post-monsoon vary from Pb = 0.01–0.07; Cu = 0.00–0.04; Mn = 0.00–0.16; Cr = 0.06–1.23; Zn = 0.00–0.01;

**Table 5** Target Hazard Quotient values for the ground waters from the Upper Panjhara Basin, DVP, India

Sr. no.	THQ-Pb	THQ-Cu	THQ-Mn	THQ-Cr	THQ-Zn	THQ-Ni	THQ-Fe	THQ-Cd
(a) Post-monsoon, 2004								
DW1	0.05	0.04	0.16	0.95	0.01	0.01	0.09	0.22
DW2	0.03	0.03	0.01	ND	0.00	0.01	0.10	0.13
BW3	0.03	0.01	0.03	0.32	0.00	0.01	0.10	ND
SW4	0.02	0.02	0.01	ND	0.00	0.01	0.06	0.02
DW5	0.03	0.02	0.03	1.23	0.00	0.01	0.07	ND
BW6	0.02	ND	0.05	0.23	0.00	0.01	0.06	ND
DW7	0.01	ND	0.07	0.55	0.00	0.01	0.06	ND
BW8	0.01	0.04	ND	0.46	0.01	0.01	0.03	ND
DW9	0.01	ND	0.04	0.15	ND	0.01	0.05	ND
DW10	0.01	0.00	0.00	0.19	0.00	0.01	0.05	ND
DW11	0.05	0.01	0.09	0.98	0.00	0.01	0.08	0.51
DW12	0.01	0.00	0.02	0.45	0.00	0.01	0.08	ND
DW13	0.02	ND	0.01	0.29	0.00	0.01	0.04	0.25
DW14	0.04	ND	ND	0.33	0.00	0.01	0.09	0.14
SW15	0.07	ND	0.03	0.30	0.00	0.01	0.06	ND
DW16	0.02	0.00	0.03	0.25	0.00	0.01	0.06	ND
DW17	0.04	ND	0.02	0.28	0.00	0.01	0.05	ND
DW18	ND	0.00	0.02	0.35	0.00	0.01	0.03	ND
BW19	ND	ND	0.02	0.17	0.00	0.01	0.07	ND
SW20	0.03	0.02	0.02	0.48	0.00	0.01	0.10	0.26
DW21	ND	0.02	0.10	0.98	0.00	0.01	0.06	0.80
DW22	0.04	ND	0.01	0.39	0.00	0.01	0.07	ND
SW23	0.05	ND	0.02	0.23	0.00	0.01	0.05	ND
BW24	0.07	ND	0.00	0.45	0.00	0.01	0.06	ND
BW25	0.06	ND	0.01	0.06	0.00	0.00	0.03	ND
SW26	0.02	ND	0.02	ND	0.00	0.00	0.07	ND
DW27	ND	ND	0.02	0.41	0.00	0.01	0.05	ND
DW28	ND	0.00	0.01	0.11	0.00	0.00	0.03	ND
DW29	0.06	0.00	0.04	0.25	ND	0.01	0.04	ND
DW30	ND	ND	0.00	0.11	0.00	0.01	0.07	ND
DW31	0.01	0.02	0.10	0.10	0.00	0.01	0.04	ND
DW32	0.04	ND	0.02	0.06	0.00	0.01	ND	ND
DW33	0.01	ND	0.03	0.10	0.00	0.01	0.03	ND
SW34	ND	ND	0.03	0.31	0.00	0.01	0.03	ND
DW35	ND	ND	0.02	0.41	0.00	0.01	0.08	ND
Min	0.01	0.00	0.00	0.06	0.00	0.00	0.03	0.02
Max	0.07	0.04	0.16	1.23	0.01	0.01	0.10	0.80
Avg	0.03	0.02	0.03	0.37	0.00	0.01	0.06	0.29
St. dev	0.020	0.013	0.035	0.289	0.001	0.002	0.022	0.248
(b) Pre-monsoon, 2005								
DW1	0.06	0.02	0.06	0.60	0.01	0.00	0.22	0.27
DW2	0.06	0.00	0.04	0.55	0.00	0.00	0.22	0.59
BW3	0.06	0.05	0.04	0.53	0.00	0.00	0.20	0.79
DW5	0.06	0.00	0.17	0.41	0.00	0.00	0.19	0.74
BW6	0.04	ND	0.15	0.24	0.00	0.00	0.22	0.47
DW7	0.07	ND	0.10	0.40	0.00	0.00	0.21	0.53
BW8	0.05	ND	0.10	0.20	0.00	0.00	0.18	0.64
DW9	0.09	0.00	0.12	0.13	0.00	0.00	0.23	0.33
DW10	0.06	ND	0.07	0.37	0.00	0.00	0.19	0.76



**Table 5** continued

Sr. no.	THQ-Pb	THQ-Cu	THQ-Mn	THQ-Cr	THQ-Zn	THQ-Ni	THQ-Fe	THQ-Cd
DW11	0.06	ND	0.14	0.37	0.00	0.00	0.21	0.33
DW12	0.06	0.00	0.08	0.28	0.00	0.00	0.18	0.81
DW13	0.05	ND	0.17	0.01	0.00	0.00	0.18	0.43
DW14	0.04	0.00	0.07	0.35	0.00	0.00	0.18	0.43
DW16	0.08	0.00	0.14	0.45	0.00	0.00	0.20	0.22
DW17	0.04	ND	0.18	0.32	0.00	0.00	0.21	0.54
DW18	0.04	ND	0.17	0.20	0.00	0.00	0.16	0.44
BW19	0.05	ND	0.13	0.30	0.00	0.00	0.21	0.34
DW21	0.05	0.01	0.06	0.29	0.00	0.00	0.20	0.56
DW22	0.03	0.02	0.18	0.52	0.00	0.00	0.21	0.72
BW24	0.03	ND	0.15	0.16	0.00	0.00	0.14	0.21
BW25	0.05	ND	0.08	0.44	0.00	0.00	0.18	ND
DW27	0.02	ND	0.08	0.39	0.00	0.00	0.19	0.60
DW28	0.04	0.00	0.04	0.33	0.00	0.00	0.18	0.47
DW29	0.04	ND	0.08	0.04	0.00	0.00	0.21	0.11
DW30	0.03	ND	0.08	0.35	0.00	0.00	0.19	0.14
DW31	0.02	0.01	0.08	0.21	0.00	0.00	0.18	0.50
DW32	0.01	ND	0.07	0.19	0.00	0.00	0.19	0.36
DW33	0.04	ND	0.06	0.40	0.00	0.00	0.21	4.19
SW34	0.05	0.00	0.02	0.45	0.00	0.00	0.20	2.85
DW35	0.05	0.00	0.07	0.34	0.00	0.00	0.19	ND
DW36	0.03	ND	0.10	0.29	0.00	0.00	0.12	0.24
DW37	0.04	0.00	0.11	0.25	0.00	0.00	0.16	4.56
DW38	0.03	0.01	0.12	0.22	0.00	0.00	0.20	0.39
DW39	0.03	ND	0.11	0.31	0.00	0.00	0.21	0.55
BW40	0.03	0.02	ND	ND	0.00	0.00	0.05	0.55
DW41	0.04	0.01	0.09	0.39	0.00	0.00	0.20	0.60
DW42	0.03	0.04	0.10	0.58	0.00	0.00	0.19	0.38
Min	0.01	0.00	0.02	0.01	0.00	0.00	0.05	0.11
Max	0.09	0.05	0.18	0.60	0.01	0.00	0.23	4.56
Avg	0.05	0.01	0.10	0.33	0.00	0.00	0.19	0.76
St. dev	0.02	0.01	0.04	0.14	0.00	0.00	0.03	1.01

Cd = 0.02–0.8 and Fe = 0.03–0.1. The THQ values of Cr in four wells (DW1, DW5, DW11 and DW21) are close to one or above one reflecting possibility of health risk hazard linked to chromium. In Raipur area of central India, Tiwari et al. (2015) reported much higher values of Cr in contaminated waters and opined that, a frequent ingestion of Cr contaminated water can cause anemia and stomach cancer. Further, the THQ values for Cd (post-monsoon) vary from 0.02 to 0.8 (DW21) indicating reduced health risk hazard as compared to pre-monsoon possibly due to rainwater recharge causing dilution of groundwater. The THQ values reported for sea foods range from <1 (safe) to >10 (of concern) to greater than 100 for red wine (Naughton and Petroczi 2008; Petróczi and Naughton 2009). In addition, Hague et al. (2008) and Naughton and

Petroczi (2008) are of the opinion that the THQ is not a measure of risk but it indicates a level of concern. He also stresses that as it is additive function and not multiplicative, the level of concern for THQ of 20 is larger but not tenfold of those at THQ = 2. Nonetheless, in absence of any data on occurrence of heavy metals in groundwater from basaltic aquifers of the area, the results generated have highlighted the concern for human health from metal toxicity point of view. Since, heavy metals are extremely persistent in the environment; they are nonbiodegradable and nonthermodegradable and readily accumulate to toxic levels (Sharma et al. 2007); environmental baselines are needed in order to assess the present status of the surface environment (Galan et al. 2008). In view of the fact that geochemical baselines provide guidelines and quality

standards for environmental legislation and decision making, the present study calls for taking necessary steps to establish periodic monitoring network to assess intake of metals due to consumption of poor quality water and the level of health risk associated with it.

## Summary and conclusions

Studies were undertaken in the headwater unit of Panjhara basin in the northern part of Deccan Volcanic Province (DVP), India with the main aim of studying the (1) intra-annual distribution of geochemical baseline and background (geogenic) levels of harmful heavy metals in the groundwater on spatial scale and (2) identifying their lithogenic and anthropogenic sources. Geochemical baseline levels of heavy metals in the groundwater depicted variability on spatio-temporal scale. Classification of metals has been done into Group I (Fe > Mn > Zn > Pb) and Group II (Mo > Ni > Cr > Cu), which indicated contrasting enrichment and depletion patterns on the intra-annual scale related to the changing water table conditions attributable to climatic fluctuations. While, fortification in Mo–Ni in post-monsoon is on account of combined lithogenic + anthropogenic contribution, pre-monsoon augmentation in Fe–Mn is entirely lithogenic. Positive values of NDDI, replicate the dominance of soil/vadose zone as a chief supplier of metals in the groundwater during post-monsoon, while negative values recommend host rock as a primary source of accretion of metals in pre-monsoon. This inference is supported by higher Ni/Cr ratio for the wells in alluvial aquifer and dyke surrounded by fertile agriculture plain than the basaltic aquifers, suggesting input of the elements (Mo, Ni > Cu) from agriculture land use in post-monsoon season. Values of Ni/Cr ratio above unity for majority of the wells in post-monsoon and >50 % wells in pre-monsoon suggest privileged weathering of olivine, followed by pyroxene > plagioclase feldspar (Ni/Cr <1) as major contributor of heavy metal load to the groundwater. Pearson correlation coefficients authenticate above inferences by means of elemental associations. Elemental alliances also point to the multi-source derivation of metals and seasonal fluctuation in the water table conditions leading to intra-annual variations in heavy metal content in the groundwater from the study area. As heavy metals persist in the environment and they possess bio-accumulative nature and toxicity, they are the serious cause of concern from human health point of view. Therefore, though it is suggested that metal speciation is more important in assessing the toxicity and mobility, importance of total concentration of heavy metals in assessing metal pollution can not be downplayed, especially where baseline geochemical map

data are non-existent. The THQ values exceeding unity reflect possibility of health risk hazard that further emphasizes the need to establish periodic monitoring network for baseline geochemical mapping to avoid health risk hazards.

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