ORIGINAL ARTICLE



Heavy metal concentration in groundwater from Besant Nagar to Sathankuppam, South Chennai, Tamil Nadu, India

S. G. D. Sridhar¹ · A. M. Sakthivel¹ · U. Sangunathan¹ · M. Balasubramanian¹ · S. Jenefer¹ · M. Mohamed Rafik¹ · G. Kanagarai²

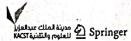
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Abstract The assessment of groundwater quality is an obligatory pre-requisite to developing countries like India with rural-based economy. Heavy metal concentration in groundwater from Besant Nagar to Sathankuppam, South Chennai was analyzed to assess the acquisition process. The study area has rapid urbanization since few decades, which deteriorated the condition of the aquifer of the area. Totally 30 groundwater samples were collected during premonsoon (June 2014) and post-monsoon (January 2015) from the same aquifer to assess the heavy metal concentration in groundwater. Groundwater samples were analyzed for heavy metals such as Fe, Pb, Zn, Cu, Ni, Cr, Co and Mn using atomic absorption spectrophotometry (AAS). Correlation matrix revealed that there is no significant correlation between heavy metals and other parameters during pre-monsoon except EC with Cr but Fe and Zn have good positive correlation during post-monsoon.

Keywords Groundwater · Heavy metals · BIS · Spatial distribution · Correlation matrix

Introduction

Recent trends show that our world is moving towards the greatest problem due to deficiency of quality and quantity of water. As a consequence, the research on quality and quantity of groundwater is in alarming stage. In Chennai, several researchers (Elango and Manickam 1987; Jayaprakash et al. 2010; Giridharan et al. 2008) and organizations like Central Ground Water Board, and Tamil Nadu Water Supply and Drainage Board are carrying out various research works using different techniques on groundwater and its aquifer by analyzing the groundwater samples and made suggestions to develop the groundwater condition of the area. When concerned about quality, even though major elements give quality index for drinking water, in particular, heavy metal concentrations are also noticed and reported because of its toxic nature. Some trace elements (Fe, Zn, Cu and Mn) are needed for biological consumption but they lead to several health issues when they are excess or deficient in water (Khan and Abbasi 2004). Some toxic elements are always having an adverse effect on humans at any dose level (lead and cadmium). Origin and source of the heavy metals in groundwater are from both point source and non-point source are reported by many authors (Sridhar et al. 2014; Kanagaraj et al. 2014). In the study area, groundwater samples are being collected during pre- and post-monsoon seasons (June 2014 and January 2015). They were analyzed for their heavy metals, such as Fe, Pb, Cd, Zn, Cu, Ni, Cr, Co and Mn. Their concentrations during pre- and post-monsoon seasons were compared. Using BIS (2012) the quality of groundwater at some locations is being warranted.



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Study area

The study area is located along the coastal tract of Bay of Bengal that covers 270 sq.km and lies between 12°51′ and 12°56′30″N latitude and from 80°3′30″ to 80°14′30″E longitude (Fig. 1). The area is having a tropical climate with mean annual temperature from 24.3 to 32.9 °C. Northeast monsoon highly contributes the rainfall to the study area and the average annual rainfall is 1200 mm (CGWB 2008). Buckingham canal runs parallel to the coast and connects Muttukadu Backwater that also gives an adverse effect to the aquifer (Jayaprakash et al. 2012).

Geologically, Archean crystalline rocks are in the basement of this region, which include charnockites, and these crystalline rocks are weathered on the top which is seen in the western part of the area. Sand and some of the silt are seen along the coastal area. The thickness of the weathered rocks varies from 4 to 15 m and the thickness of the sands varies from 3 to 5 m (Brindha et al. 2014). Hydrologically, the groundwater source occurs in the shallow aquifer consisting of charnockite, sand, quartz conglomerates and recent alluvium (Fig. 2). Seawater intrusion is being reported (Elango and Manickam 1987) at some places apart from industrial effluents. The Pallikaranai marshland is an important land feature in the

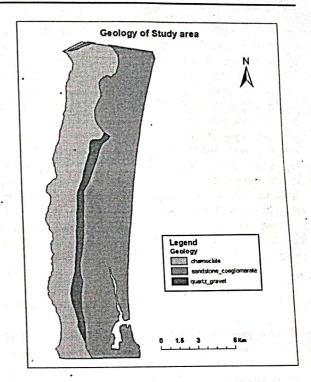


Fig. 2 Geology map of study area

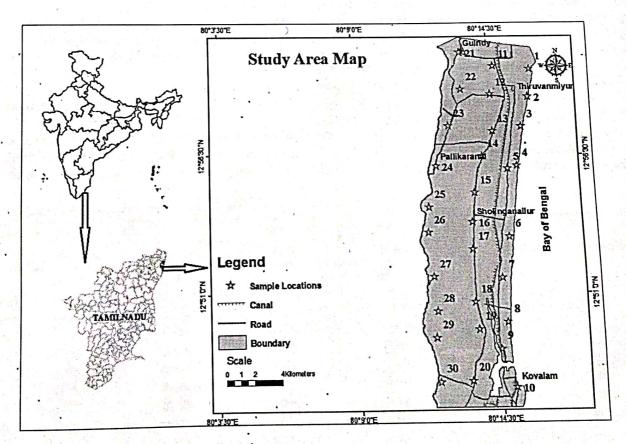
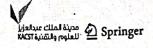


Fig. 1 Location map of the study area with sampling points



study area which is the home for many species such as fishes, frogs, reptiles and many birds. 60% of garbage in Chennai city is dumped in this marshland (Jayaprakash et al. 2010).

Method of sampling and analysis

Samples were collected in grid pattern, paralleling the coast 2 km internally during PRM (PRM) and POM (POM) seasons (June 2014 and January 2015). Totally, 30 samples were collected from both dug well and bore well, which are predominantly available in the area. As the groundwater occurs in shallow aquifer (< 20 m bgl), their analyses were compared together. Before sampling, high-density polyethylene sample bottles were cleaned by nitric acid. pH, electrical conductivity (μS/cm), total dissolved solid (ppm) and temperature (°C) were measured in the field itself using portable kit. Samples were immediately acidified with nitric acid to maintain the pH < 2. The concentrations of trace elements were quantitatively determined by atomic absorption spectroscopy (AAS). The results were processed in Statistical Package for the Social Sciences (SPSS) 16.0 package software for correlation analysis. The significance level (p < 0.05) based on Pearson's correlation method done for both seasons and spatial distribution of each trace element are expressed using Arc GIS 10.1 software and the values were compared with the Bureau of Indian Standards (BIS 2012). Bureau of Indian Standards (BIS 2012) for drinking water quality are used to compare with heavy metals to estimate the groundwater quality.

Results and discussion

The minimum and maximum values of results obtained for 30 samples that were collected during pre- and post-mon-soon seasons are presented in Table 1, with its BIS (2012)

limit. pH value ranges from 6.63 to 8.04 in PRM and 7.3-8.8 in the POM. During PRM all the samples are within permissible limit of Bureau of Indian Standards (BIS 2012) but five samples exceed the permissible limit in POM (Fig. 3), which indicate that rainwater helps to add salts from surface to groundwater during monsoon season. The result of TDS is shown in Fig. 4. Total dissolved solids during PRM ranges from 451 to 28,840 mg/l and they range from 333 to 7850 mg/l in POM. During PRM, 28840 mg/l of TDS was observed in Besant Nagar, but during POM the value decreases to 3230 mg/l, due to continuous pumping and less precipitation after the monsoon. EC values show the same trend with TDS values, its minimum value is 644 µS/cm and the maximum is 41,200 µS/cm during PRM. During POM, 514 and 12,070 μS/cm are the minimum and maximum values, respectively.

Heavy metal distribution

Iron is an essential nutrient for human consumption. Many metabolic processes and anemia can happen due to iron deficiency in human body and it is an essential component of hemoglobin and myoglobin. Besides, it is necessary for the activity of cytochromes, peroxides, catalase, and certain other hemoprotein and flavoprotein enzymes (Khan and Abbasi 2004). In the study area, it ranges from 0.001 to 0.838 mg/l in PRM season and 0.006-1.739 mg/l in POM. Average value of Fe is 0.227 and 0.320 mg/l for both PRM and POM, respectively. During PRM, in most of the samples, it is below the acceptable limit except the sample taken from Injambakkam which shows values above the acceptable limit. Its spatial distribution is shown in Fig. 5. The trend continues during POM except for the six samples that fall within the acceptable limit. The result of increasing value of iron during POM is due to rock-water

Table 1 Minimum and maximum concentration of each parameter with its BIS limit

Parameter	Pre-monsoon (PRM	I) June 2014	Post-monsoon (POM) January 2015			BIS limit (2012)	
. 4	Minimum	Maximum	Minimum	12.4	Maximum	 Acceptable	Permissible
pH	6.63	8.04	7.3	Marie -	8.8	 6.5-8.5	No relaxation
TDS mg/l	451	28,840	333		7850	500	2000
EC μS/cm	644	41,200	514	0.7	12,070		#4 g 19 je je je
Fe mg/L	0.001	0.838	0.006		1.739	0.3	No relaxation
Pb mg/L	0.112	0.594	0.031		0.781	0.01	No relaxation
Cr mg/L	0.229	0.971	0.363		1.484	0.05	No relaxation
Zn mg/L	0.003	0.149	0.001	CHANGE THE	0.65	5	15
Cu mg/L	0.004	0.112	0.001	A COLUMN	0.128	0.05	1.5
Ni mg/L	0.093	0.549	0.001		0.695	0.02	No relaxation
Co mg/L	0.085	0.565	0.273	Market 1	0.83	Y = - 다 '스크리 및	
Mn mg/L	0.01	1.518	0.02	AL HAR	1.276	0.1	0.3

Fig. 3 pH level in both monsoons (June 2014 and January 2015) with its acceptable and permissible limits of BIS.

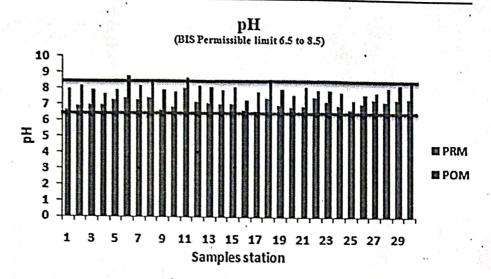
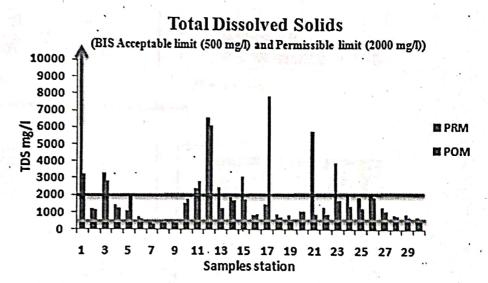


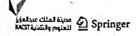
Fig. 4 TDS level in both monsoons (June 2014 and January 2015) with its acceptable and permissible limits of BIS

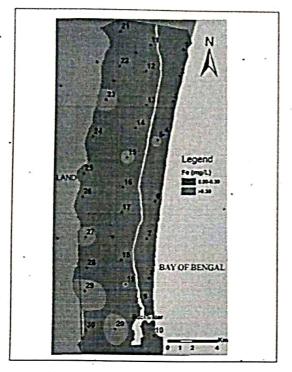


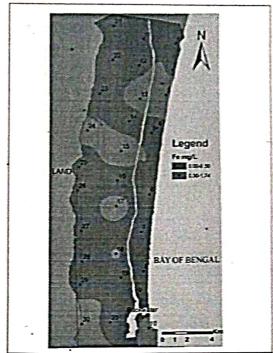
interaction (Ngah and Nwankwoala 2013). At some places, concentration of iron in groundwater is due to corrosion of household and leaching from pipes, fitting, smelting, and welding work places (WHO 2003a, b; Papachristodoulou et al. 2015).

Acceptable limit for lead is 0.01 mg/l (BIS 2012). For the study area, lead concentration varies from 0.112 to 0.594 mg/l, and the average is 0.247 mg/l during PRM; and during POM, it varies from 0.031 to 0.781 mg/l, and the average is 0.381 mg/l. Its spatial distribution is shown in Fig. 6. Concentration of Pb in groundwater of the study area increases during POM due to the influence of rain during monsoon that takes the Pb along with petrol fuel from roadside (WHO 2011a, b). It is also due to the release of lead-containing plumbing material including unplasticized polyvinyl chloride (uPVC) pipes that react with slight alkaline nature of water (Zhang and Lin 2014). Drinking

such contaminated water is associated with hip fracture for both genders (Dahl et al. 2014), damage to the kidneys and creates hypertension for humans (WHO 2011a, b). Some of the natural organic components, such as garlic oil and vitamin E, act as detoxifying agents for lead in human body (Sajitha et al. 2010). The concentration of Cr is higher than the acceptable limit in all locations during both seasons. Its minimum and maximum concentrations were 0.229 and 0.971 mg/l during June 2014, and 0.363 and 1.484 mg/l during January 2015 (Fig. 7), respectively. Chromium is also an essential element to human, but it gives adverse effects when it exceeds its limit (WHO 2003a, b; Sutherland et al. 2000). Higher concentration of chromium in groundwater of this region is probably derived from dumping sites of municipal wastage, sewage and chrome plating industries by the influence of rainwater being precipitated during POM (Bartlett and Vesilind 1998). Due to



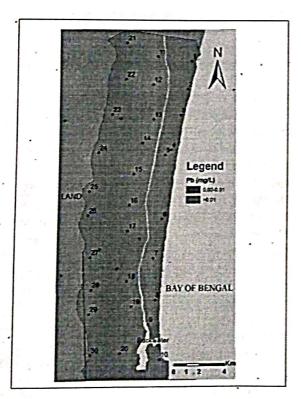


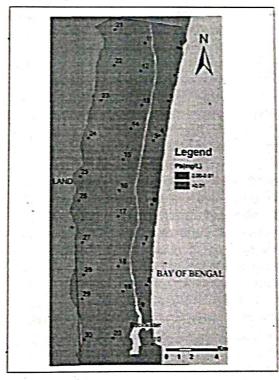


Premonsoon

Postmonsoon

Fig. 5 Spatial distribution of iron in pre- and post-monsoon with BIS (2012)

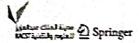


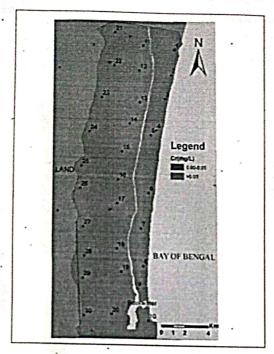


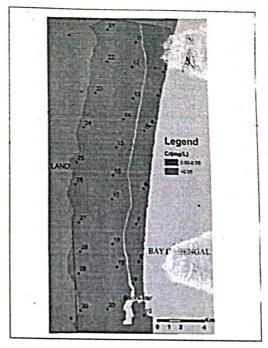
Premonsoon

Postmonsoon

Fig. 6 Spatial distribution of lead in pre- and post-monsoon with BIS (2012)







Premonsoon

Postmonsoon

Fig. 7 Spatial distribution of chromium in pre- and post-monsoon with BIS (2012)

rapid urbanization, the dumping of municipal wastes is increasing day by day in the study area. Zn is also an essential nutrient to human that is found in most of the natural foods (Umar et al. 2013) but its required and permissible limit are 5 and 15 mg/l, respectively (BIS 2012). Average value of Zn in PRM and POM is 0.054 and 0.088 mg/l, respectively. It ranges from 0.003 to 0.149 mg/ 1 in PRM and 0.001 to 0.650 mg/l in post-monsoon (Fig. 8). Zinc concentration in all samples, in both seasons, was below the required limit of BIS (2012). Humans need a required level of Zn, otherwise it affects the metabolism and immune system and as a result human beings are susceptible to infections, delayed sexual maturation in men, and anemia and birth defects in pregnancy women (ATSDR 2005). Concentration of the zinc in groundwater is due to corrosion of household and leaching from piping, fitting, smelting, and welding workplaces (WHO 2003a, b; Papachristodoulou et al. 2015). Concentration of copper in groundwater during PRM is ranging from 0.004 to 0.112 mg/l with an average of 0.054 mg/l and during POM it is ranging from 0.001 to 0.128 mg/l with an average of 0.037 mg/l (Fig. 9). Concentration of Cu was within permissible limit in both monsoons and at the same time, most of the samples were not having the required limit for drinking purpose during both monsoons. Even though the values are within permissible limit, the higher concentrations at some places are due to agriculture activity in the

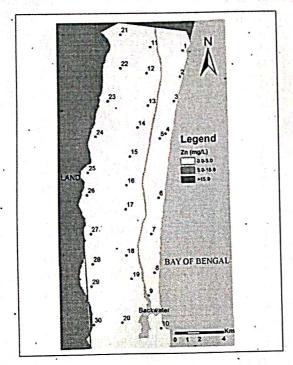
area where copper leached from copper-based fertilizer and fungicide is being added to groundwater by rainwater and irrigation water (Al-Subu et al. 2003; Mirlean et al. 2009), and some concentrations are dyr to leaching from open dumping sites of solid wastes Quantuani and Gandhimathi 2013), and corrosion of household materials (WHO 2004). Generally, nickel is present in Ni2+ form in natural water at a pH level of 5-9 (WHO 2005), concentration of nickei ranges from 0.093 to 0.549 mg/l with an average of 0.294 mg/l, and during the POM it ranges from 0.001 to 0.695 mg/l with an average of 0.097 mg/l (Fig. 10). PRM has higher concentration of Ni than POM. Based on BIS (2012) limit for nickel, all locations during PRM were exceeding their permissible limit and during POM, the concentration of Ni was lower than PRM but most samples were exceeding the permissible limit except at nine local tions. The USEPA (1995) reported the nickel will cause body weight loss, damage of i art and liver, and der matitis, when consumed long time above the maximiling contamination level. Source of nicke. In the study area is probably from sewage water and concentration in nonrosion of nickel alloy materials (Purushotham et al. 2013). Concentration of cobalt values ranges from 0.085 to 0.565 mg/l during POM, and ranges from 0.273 to 0.830 mg/l during POM (Fig. 11). Spatial distribution shows that the concentration of cobalt is higher along the west portion of the study area during POM. The higher

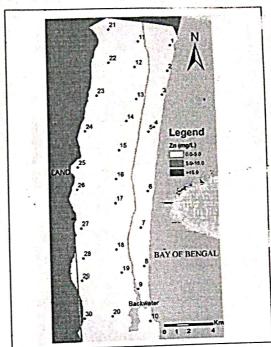
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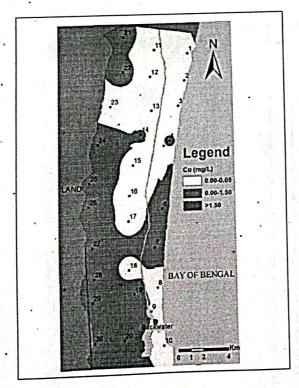




Premonsoon

Postmonsoon

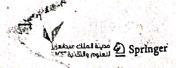
Fig. 8 Spatial distribution of zinc in pre- and post-monsoon with BIS (2012)

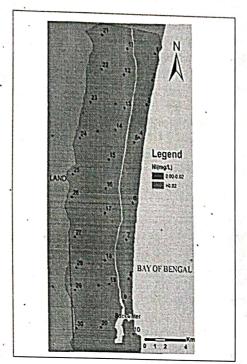


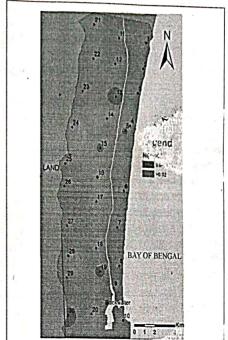
Premonsoon

Postmonsoon

Fig. 9 Spatial distribution of copper in pre- and post-monsoon with BIS (2012)



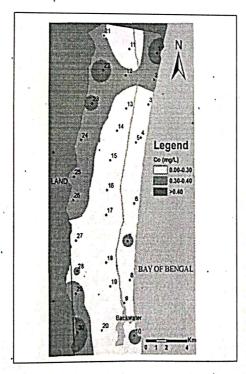




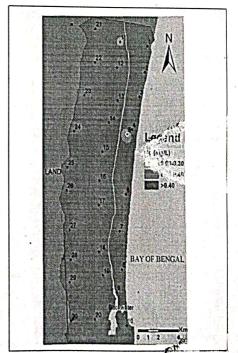
Premonsoon

Postmonsoon

Fig. 10 Spatial distribution of nickel in pre- and post-monsoon with BIS (2012)



Premonsoon



Postmonsoon

Fig. 11 Spatial distribution of cobalt in pre- and post-monsoon with BIS (2012)

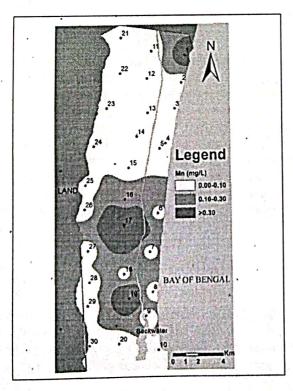


concentration of Co is due to leaching from solid waste sites in the study area (WHO 2006; Purushotham et al. 2013). Cobalt gives benefit or adverse effect to humans depending on its concentration level and types of isotope. Beneficially, it is a part of vitamin B12 and its continuous consumption above permissible limit adversely affects the heart (ASTDR 2004). There is no guideline value for cobalt in the Bureau of Indian Standards (BIS 2012). Mn concentration ranges from 0.010 to 0.518 mg/l with an average value of 0.167 mg/l in PRM, and during POM it ranges from 0.020 to 1.276 mg/l with an average value of 0.348 mg/l: Concentration of Mn is increased during POM, and during PRM most of the samples are within permissible limit, except at three locations (Fig. 12). The higher concentrations are due to rainwater being precipitated on dumping site of waste solids, which releases Mn from solid waste, from automobile emission (Loranger et al. 1994). Higher concentration of Mn will have neurological effect when continuously consumed (Zoni et al. 2007; WHO 2011a, b; Spangler and Reid 2010). As a result, the concentration of heavy metals such as Fe, Pb, Zn, Cr, Co and Mn increases in POM compared to PRM season. It indicates that the pathway of the heavy metals is that there is an accumulation of heavy metals in the soil initially when the industrial effluents and domestic dumping are spread on the ground and rainwater helps to add these metals to groundwater. Based on the Bureau of Indian Standards (BIS 2012) and average concentration of heavy metal, observed contamination level is in the order of Cr > Ni > Pb > Fe > Mn > Cu > Zn during pre-mon soon season and Cr > Pb > Ni > Ni > To > Cu > Zn during post-monsoon season.

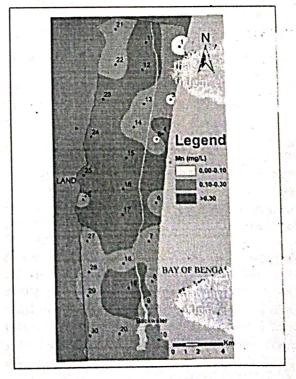
Correlation matrix

The principal component analysis was based on the eigen values in the correlation matrix. The close inspection of correlation matrix was useful because it can point out associations between variables that can show the overall coherence of the data set and indicate the participation of the individual chemical parameters, a fact which commonly occurred in hydrochemistry (Helena et al. 2000). A correlation of + 1 indicates a perfect positive correlation between two variables. A correlation of -1 indicates that one variable changes inversely with relation to the other. A correlation of zero indicates there is no correlation between the two variables (Marcal et al. 2009). In this study, correlation matrix was done to eight heavy metals and three field parameters. Only those with correlation, values higher than 0.5 were considered (Sappa et al. 2014) for both PRM and POM seasons, respectively.

During the PRM season, there is no significant correlation between each parameter, but high negative correlation has been observed between EC and Cr with TDS



Premonsoon



Postmonsoon

Fig. 12 Spatial distribution of manganese in pre- and post-monsoon with BIS (2012)



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Table 2 Correlation matrix between heavy metals and other parameters during pre-monsoon (June 2014)

Et 1 1	pH	EC	TDS	Fe	Pb	Zn	Cu	Ni Cr	Co Mp
pН	1.000	12.1		1 4 4 4		4		WART TO THE MERCHANT AND	
EC	- 0.258	1.000						2	
TDS	- 0.258	1.000	1.000						
Fe	- 0.081	0.024	0.024	1.000					
Pb	- 0.163	0.140	0.140	- 0.017	1.000				ali e galat engala iko: Ranga angalat engala
Zn	- 0.099	-0.040	- 0.040	- 0.084	0.228	1.000			
Cu	0.114	- 0.388	- 0.388	0.120	- 0.208	- 0.202	1.000		
Ni	0.130	0.053	0.053	- 0.151	. 0.296	- 0.293	.0.249	1.000	
Cr	0.256	-0.872	- 0.872	0.068	0.022	0.035	0.392	- 0.059 1.000	
Co	-0.077	0.386	0.386	- 0.189	0.000	0.127	0.220	0.034 - 0.201	: 1.000
Mn	- 0.369	0.198	0.198	0.059	0.088	0.108	- 0.132	- 0.064 - 0.255	- 0.087 1.000
357 F. 1	S.					1 24 25			The World Con-

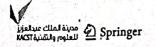
Table 3 Correlation matrix between heavy metals and other parameters during post-monsoon (January 2015)

	рН .	EC	TDS	Fe ,	Pb	Zn	Cu	Ni	Cr	Co Mn .
pН	1.000		44	54%	AND SE		170			17
EC	- 0.093	1.000					Maria . The			
TDS	- 0.094	0.998	1.000							
Fe	0.050	0.192	0.188	1.000						
Pb ·	0.168	0.139	0.135	0.189	1.000					
Zn	0.155	0.042	0.042	0.865	0.171	1.000		de plan		
Cu	- 0.102	-0.042	- 0.037	0.335	- 0.124	0.374	1.000	Y. (1) 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	4.4	4.
Ni ·	0.377	0.019	0.014	- 0.163	- 0.030	- 0.019	0.101	1.000		
Cr	- 0.019	- 0.013	- 0.019	- 0.052	0.172	-0.047	- 0.212	- 0.035		
Co	- 0.272	0.160	0.132	0.033	0.166	- 0.064	- 0.299	- 0.194	0.230	1.000
Mn	- 0.179	. 0.553 ·	0.542	- 0.044	- 0.033	- 0.243	- 0.171	0.039	0.257	0.299 1.000

(Table 2). Sources of heavy metals and other parameters are not common to any specific sources. During the POM season, highly positive correlation is observed between Fe and Zn as well as good correlation of EC with Mn. Correlation between iron and zinc indicates that they might have been derived from the same source such as corrosive activity of iron-zinc alloy of household material (WHO 2003a, 2003b; Papachristodoulou et al. 2015; Anonymous. 2016) and leachate of discharge in soil from automobile industry in POM season (Kanamar and Morita 1994) (Table 3).

Conclusion

The study identifies the seasonal variations and utility of heavy metals in groundwater. The higher pH values are noted in POM due to rainwater which adds salts from surface to groundwater during monsoon season. The samples are compared with the Bureau of Indian Standards (BIS 2012) and average concentration of heavy metal which shows contamination level in the order of Cr > Ni > Pb > Fe > Mn > Cu > Zn during POM seasonand Cr > Pb > Ni > Mn > Fe > Cu > Zn during POM season. The concentration of heavy metals such as Fe, Pb, Zn, Cr, Co and Mn increases in POM compared to-PRM season. It indicates that the pathway of the heavy metals is that there is an accumulation of heavy metals in the soil initially when the industrial efficients and domestic dumping are spread on the ground. Concletion matrix revealed that there is no significant correlation between heavy metals and other parameters during pre-monsoon except EC with Cr, but Fe and Zn have good positive correlation during post-monsoon. The groundwater being contaminated due to rapid urbanization that causes increase of industrial effluents and dumping of domestic wastage and at the same time agriculture activities enhances the pollution to contamination level. The state of the s



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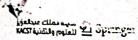
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