

# Assessment of Groundwater Quality using Pollution Indices with respect to Heavy Metals



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## 1 Introduction

The environmental quality of an area depends on extent of industrial and development activities of an area, which causes adverse effect on human health and biota. The rate at which many natural and anthropogenic activities degrade the groundwater quality nowadays is alarming [1]. Industrialization and economic expansion in both developing and developed countries have also contributed heavy metals into groundwater which has become global issue. Groundwater is one of the significant and direct sources of water for many areas used by both rural and urban population for various purposes such as drinking, domestic use, irrigation. Groundwater occurs in widespread and local aquifer layers which can able to move one place to another place through the aquifers. The quality of groundwater is impaired by many factors like climate, soil composition, groundwater movement by rock types, region topography, infiltration of saline water into coastal regions and contaminants due to various man-made activities. Among the contaminants that can impact water quality, heavy metals are given more consideration because of their prevalence and high toxicity even though at low concentrations [2]. Contaminants of heavy metals such as Ni, Zn, Cu, Pb, Cr and Cd are usually more common than organic contaminants [3]. Heavy metals are high-density metalloids and non-biodegradable form that can persist through bioaccumulation in humans as well ecosystems and cause direct and indirect health effects [4]. Few heavy metals such as Zn, Cu, Ni, Fe and Mn are considered as micronutrients required for the growth of microbes, plants and animals. Besides, metals like Cr, Pb and Cd cause health risk beyond the prescribed

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limit and can easily pass into human body by ingestion (by mouth) and can able to cause cancer, kidney and neurological diseases [5].

Hence, study of groundwater quality assists in establishing methods to identify the source and mitigate groundwater contamination. This has contributed to a growing emphasis on groundwater quality work around the world. Understanding the current condition of groundwater quality in any region forms part of the essentials needed to make wise plans and policies on the safety and management of water quality [6].

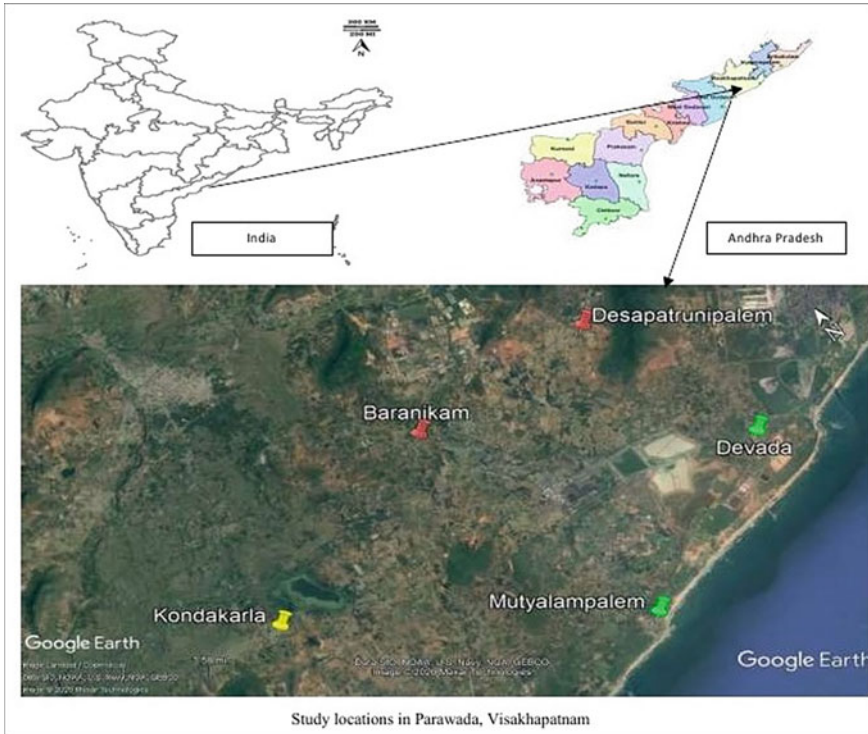
The present study was carried out at upcoming industrial area of Visakhapatnam. The objectives of the study are to find out the heavy metal concentration and its contamination level in groundwater along with identification of pollutant sources through principle component analysis (PCA).

## 2 Materials and Methods

Visakhapatnam is the fastest-growing city in Andhra Pradesh, India. The present identified five locations Baraniakam, Desapatrunipalem, Kondakarla, Mutyalampalem and Devada which are located near to the Parawada sub-urban area of Visakhapatnam (Fig. 1). These five locations are near to various major industrial areas like thermal power plants, steel plants, pharmaceutical and other minor industrials.

### 2.1 *Geography of Groundwater and Sampling*

The soils of the study area are red sandy loamy in nature, whereas fine sandy soils are confined only near coastal regions. The groundwater aquifers are having both hard and soft formations. In hard formation areas (granite gneisses, charnockites, khondalites, etc.), the groundwater is unconfined to semi-confined state, and in soft rock formations (sandstones and alluvium) areas, the groundwater is unconfined to confined state [7]. The samples were taken from the five boreholes (handle bore) on bi-month frequency for a period of two years. The total number of samples for each borewell is twelve. The water was extracted using handle-based grab sampling. Before sampling the handle, bore was operated for 5–7 min continuously to remove stagnate water. The sampling pretreated containers were cleaned with borewell water. Onsite pH was measured using portable battery-operated pH meter. After pH measurement, one liter of water taken is acidified with one ml  $\text{HNO}_3$ . The samples were immediately brought to laboratory and stored in refrigerator at 4 °C for further analysis. Before initiation of heavy metal analysis, the water samples were filtered with 0.45  $\mu\text{m}$  millipore size filter; further, it is sent to ICP-MS for heavy metal analysis.



**Fig. 1** Study area and sampling location

**Assessment of heavy metal**

The groundwater heavy metal is analyzed using ICP-MS model, ELAN DRC-II, Perkin-Elmer Sciex Instrument, USA. The instrument setup, data acquisition and calibration were carried out as [8] recommend (CRM-NIST 1640 used for calibration and CRM SLRS-4 used as unknown to make sure the accuracy and precision of the analysis). The recovery percentage of elements is within the allowable standard ( $\pm 4\%$ ).

To determine the water quality with respect to heavy metals, three indices HPI, HEI and Cd were used which provide overall heavy metal quality in the water.

Heavy metal pollution index (HPI): Heavy metal pollution index assesses the overall quality of water with reference to heavy metals calculated using following Formula [9].

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n Q_i}$$

where  $Q_i$  = sub-index of  $i$ th metal;  $n$  = total number of metals;  $W_i$  = unit weight of  $i$ th metal

**Table 1** Standard values for the indices

Metal	Si	Ii	Wi	Hmax or MAC
As	50	10	0.02	50
Cd	5	3	0.3	3
Cr	1	50	0.02	50
Cu	1000	2000	0.001	1000
Fe	300	200	0.005	200
Mn	100	500	0.02	50
Ni	20	20	0.05	100
Pb	100	10	0.7	1.5
Zn	5000	3000	0.0002	5000

$$Qi = \sum_{i=1}^n \frac{\{Mi(-)Ii\}}{(si - Ii)}$$

where  $Mi$  = measured value of  $i$ th heavy metals;  $Si$  = standard value (Table 1);  $Ii$  = ideal value of  $i$ th heavy metal; The  $(-)$  specifies the arithmetical variance of the two numbers, discounting the algebraic sign.

The classification of HPI value  $< 100$ , consider to be low heavy metal contamination; HPI value = 100, consider to be critical heavy metal contaminated; HPI value  $> 100$ , consider to be high heavy metal contamination (not recommended for drinking) [9, 10].

Heavy metal evaluation index (HEI): The HEI is also assessed by considering the total heavy metal content based the following Formula [11].

$$HEI = \sum_{i=1}^n \frac{Hc}{Hmac}$$

where  $Hc$  = measured metal concentration of corresponding metal;  $Hmac$  = maximum admirable concentration of corresponding metal (Table 1).

The classification of HEI value  $< 10$ , consider to be low heavy metal contamination; HEI value between 10 and 20, consider to be moderate contaminated by heavy metal; HEI value  $> 20$ , consider to be highly contaminated by heavy metal [12].

Degree of contamination (Cd): Cd is the sum of the contamination factor (Cfi) of individual metals. The Cd is calculation using following Formula [13].

$$Cd = \sum_{i=1}^n \frac{CAi}{CNI} - 1 = \sum_{i=1}^n Cfi$$

where  $CA_i$  = measured metal conc. of  $i$ th metal;  $CNi$  = maximum permissible concentration of  $i$ th metal (Table 1);  $Cfi$  = contamination factor of  $i$ th metal.

The classification of Cd value < 1, consider to be low heavy metal contamination; Cd value between 1 and 3, consider to be medium heavy metal contamination; Cd value > 3, consider to be high heavy metal contamination.

The results were compiled and compared with Bureau of Indian Standards 10,500 and WHO [14, 15] for analyzing heavy metals. SPSS statistical package (Version 20) is used for correlation and principal component analysis (PCA).

### 3 Results and Discussion

The mean and standard deviations values of results obtained for groundwater samples of the study areas are presented in Figs. 2 and 3, with its BIS and WHO standard. The pH value ranges from 6.9 to 7.5 and within the permissible limits in all the five sites. The maximum mean pH was found in Baranikam (7.5) followed by Kondakarla (7.3) Mutyalampalem (7.3), Devada (6.9) and Desapatrunipalem (6.9).

Heavy metal distribution in the study area:

The concentration of nine metals was analyzed at five study areas, and the results were discussed metal-wise below:

**Arsenic:** Arsenic is present in the environment in organic and inorganic forms.  $As_4O_6$  is emitted from combusted fossil fuels and condensed and finally transferred to water reservoirs. The non-biodegradable waste can produce inorganic arsenic which is highly toxic and causes cancer to the humans even though at less concentration [16].

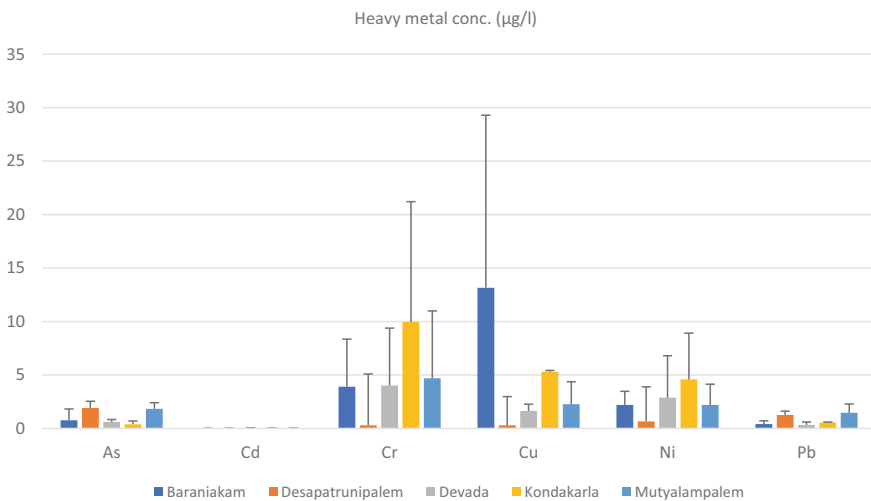


Fig. 2 Heavy metal concentration (As, Cd, Cr, Cu, Ni and Pb) in groundwater of study areas

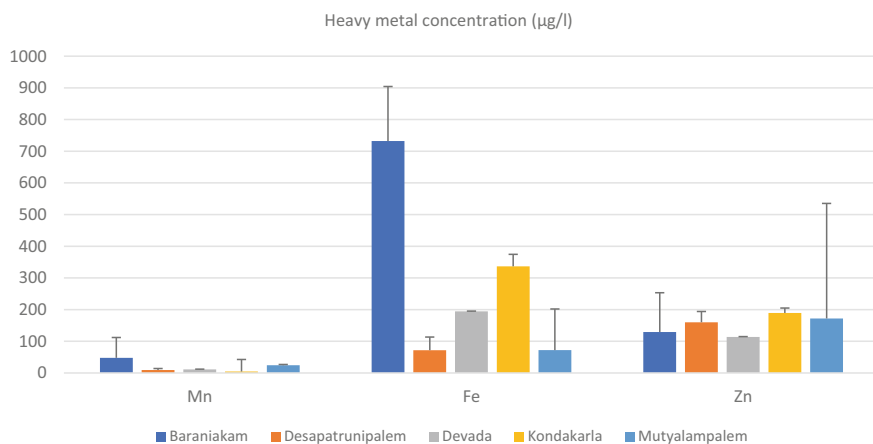


Figure 3: Heavy metal concentration. in ground water of study area

**Fig. 3** Heavy metal concentration (Mn, Fe and Zn) in groundwater of study area

The maximum mean concentration of arsenic (As) is reported in Desapatrunipalem (1.919  $\mu\text{g/l}$ ) followed by Mutyalampalem (1.838  $\mu\text{g/l}$ ), Baranikam (0.761  $\mu\text{g/l}$ ), Devada (0.616  $\mu\text{g/l}$ ) and Kondakarla (0.389  $\mu\text{g/l}$ ); however, these results are within the prescribed limits of WHO (10  $\mu\text{g/l}$ ) and BIS standards (50  $\mu\text{g/l}$ ) (Fig. 2). The natural origin from weathering of rocks and man-made sources of arsenic in groundwater is runoff from agricultural fields and contains remains of pesticides and fertilizers and sewage run off from urban areas.

**Cadmium:** In nature, cadmium is distributed uniformly throughout the soil crust. It exists as inorganic materials such as hydroxides, carbonates, sulfates or chlorides at relatively low levels in the aquatic ecosystem [17]. Upon absorption, cadmium is effectively stored and deposited in the human body over the entire life, where it is primarily toxic to the nerve system, kidneys and demineralizes the bones [18, 19]. The maximum Cd mean concentration is reported in Devada (0.031  $\mu\text{g/l}$ ), followed by Kondakarla (0.025  $\mu\text{g/l}$ ), Mutyalampalem (0.020  $\mu\text{g/l}$ ), Branikam (0.017  $\mu\text{g/l}$ ) and Desapatrunipalem (0.016  $\mu\text{g/l}$ ). These results are within the prescribed limits of WHO (3  $\mu\text{g/l}$ ) and BIS standards (3  $\mu\text{g/l}$ ) (Fig. 2). The major contributors of cadmium into the environment are emissions or effluents from industrial operations such as Ni–Cd batteries, rust-resistant coatings on metals, dyes on ceramics, plastics, enamels, glasses, as an additive in welding, electrical connections and compounds which are used in photovoltaic cells and electrical detectors [20].

**Chromium:** Chromium may be either helpful or harmful to biotic component based on their chemical nature and bio-available form.  $\text{Cr}^{3+}$  is an essential component of a healthy diet at less amount as it tends to avoid opposing effects on the metabolism of lipids and glucose (Piyush & Asha, 2016). Cr can inhibit the enzyme system and interference with numerous metabolisms at higher concentration due

to bonding nature with some organic compounds. Specific industries, like electroforming, processing of paints and pigments, fabric, pesticide and leather tanning, Cr discharged in two varieties, such as  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  in waste.  $\text{Cr}^{6+}$  is potentially lethal, carcinogenic and epigenetic modification due to its solubility and mobility [21]. The maximum Cr mean concentration is reported in Kondakarla (9.958  $\mu\text{g/l}$ ) followed by Mutyalampalem (4.697  $\mu\text{g/l}$ ), Devada (4.014  $\mu\text{g/l}$ ), Branikam (3.903  $\mu\text{g/l}$ ) and Desapatrunipalem (0.300  $\mu\text{g/l}$ ). These results are within the prescribed limits of WHO (50  $\mu\text{g/l}$ ) and BIS standards (50  $\mu\text{g/l}$ ) (Fig. 2).

**Copper:** Copper is abundance element in earth surface and widely used in daily activity in the human for electrical, electronic appliances. Apart from this, it plays an important role in metabolic activities, protein synthesis and catalyst in living being [22]. However, at higher concentration, it will interfere in biological pathways; therefore, it is considered as hazard element in ecosystem [23]. The maximum Cu mean concentration is reported in Branikam (13.160  $\mu\text{g/l}$ ), followed by Kondakarla (5.305  $\mu\text{g/l}$ ), Mutyalampalem (2.268  $\mu\text{g/l}$ ), Devada (1.639  $\mu\text{g/l}$ ) and Desapatrunipalem (0.294  $\mu\text{g/l}$ ), and these results are within the prescribed limits of WHO (2000  $\mu\text{g/l}$ ) and BIS standards (50  $\mu\text{g/l}$ ) (Fig. 2). The major sources of copper into the environment are electrical appliances, copper smelting operations, as well as copper-based pesticides.

**Iron:** Iron is most abounded element in the earth crust as well groundwater in the form of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . It is the vital element for human and involves formation of blood, cytochrome, and metallo-enzymes. The excessive consumption of iron causes hemochromatosis which adversely effects on regular metabolism [24]. The maximum mean iron concentration is reported in Baranikamsite (732  $\mu\text{g/l}$ ) followed by Kondakarla (336  $\mu\text{g/l}$ ), Devada (194  $\mu\text{g/l}$ ), Desapatrunipalem (71  $\mu\text{g/l}$ ) and Mutyalampalem (72  $\mu\text{g/l}$ ) (Fig. 3). Baranikam and Kondakarla exceeded the BIS (300  $\mu\text{g/l}$ ) and WHO (300  $\mu\text{g/l}$ ) prescribed standards, and remaining three sites are well within the prescribed limit. The exceeded Fe in groundwater may influence by both natural and anthropogenic activities, including sewage wastewater disposal.

**Manganese:** Manganese is abundance in nature and essential element for biota. It acts as co-factor in many metabolic reactions, cholesterol, fatty acid synthesis and is bio-available form in the water in certain conditions [25]. At higher concentration, it accumulates into the body cells and causes postural dysfunction, mood disturbances and other shifts in psychiatry which are called manganese madness (characteristic neurotoxicity-linked disorder) [26]. The maximum Mn mean concentration is reported in Branikam (47.806  $\mu\text{g/l}$ ), followed by Mutyalampalem (24.480  $\mu\text{g/l}$ ), Devada (11.100  $\mu\text{g/l}$ ), Desapatrunipalem (9.383  $\mu\text{g/l}$ ) and Kondakarla (4.663  $\mu\text{g/l}$ ). However, these results are within the prescribed limits of WHO (50  $\mu\text{g/l}$ ) and BIS standards (100  $\mu\text{g/l}$ ) (Fig. 3). The key man-made sources of this element are sewage waste water and bio-solids.

**Nickel:** Nickel is present in less amount in both soil and water. The higher concentration exposure of human causes metabolic dysfunction, reducing body mass, allergy, cardiovascular, hepatic damage and carcinogenesis [27]. The maximum Ni mean concentration is reported in Kondakarla (4.590  $\mu\text{g/l}$ ), followed by Devada

(2.877  $\mu\text{g/l}$ ), Branikam (2.205  $\mu\text{g/l}$ ), Mutyalampalem (2.197  $\mu\text{g/l}$ ) and Desapatrunipalem (0.659  $\mu\text{g/l}$ ), and these results are within the prescribed limits of WHO (100  $\mu\text{g/l}$ ) and BIS standards (20  $\mu\text{g/l}$ ) (Fig. 2). The major sources of nickel to environment are various man-made activities such as metallic smelter, sewage treatment, pesticides and heavy metal-contaminated soils.

**Lead:** Lead is available in very minute quantity in the nature. The inorganic form of Pb could be highly toxic which causes lethal health effect on kidney, hemoglobin, digestive system, nerve system and carcinogenic [28]. Usually, it is non-biodegradable form emitted from fossil fuel, vehicular emission to the atmosphere, and later, it deposits into the soil which finally reached to groundwater [29]. The maximum Pb mean concentration is reported in Mutyalampalem (1.464  $\mu\text{g/l}$ ), followed by Desapatrunipalem (1.261  $\mu\text{g/l}$ ), Kondakarla (0.556  $\mu\text{g/l}$ ), Branikam (0.411  $\mu\text{g/l}$ ) and Devada (0.327  $\mu\text{g/l}$ ), and these results are within the prescribed limits of WHO (10  $\mu\text{g/l}$ ) and BIS standards (10  $\mu\text{g/l}$ ) (Fig. 2). The common man-made sources such as manufacture batteries, industrial reaction tanks, metal goods, plumbing paints, PVC pipes, waste land fill leachates, house hold items, alloys and electrical fuse cables as well process industrial like energy and automobile operations.

**Zinc:** Zinc is a most abundance earth crust element and available in atmospheric emission which can be able to adsorb water-borne suspended particulates threatened to the water ecosystem [30]. Zinc serves as a co-factor for many biomolecules (enzymes and protein) required to reproduce and convert genetic material in many organisms [31]. The excessive Zn can induce system disorders like yellowing of the mucous membranes, kidney and liver damage and effect on growth and reproductive system [30]. The maximum Zn mean concentration is reported in Kondakarla (189.347  $\mu\text{g/l}$ ) followed by Mutyalampalem (172.076  $\mu\text{g/l}$ ), Desapatrunipalem (160.038  $\mu\text{g/l}$ ), Branikam (129.444  $\mu\text{g/l}$ ) and Devada (113.851  $\mu\text{g/l}$ ). These results are within the prescribed limits of WHO (5000  $\mu\text{g/l}$ ) and BIS standards (5000  $\mu\text{g/l}$ ) (Fig. 3). Untreated residential and industrial sewage waste, land fill leachates and agricultural runoff are the major man-made sources of Zn into the groundwater.

### Pollution Indices

**Heavy metal pollution index (HPI):** HPI score gives an idea on overall heavy metal contamination in the study areas. The sum of HPI results is present in Table 2 for the five sites. Among the five sites, Baranikam (55.976) has shown the maximum HPI followed by Kondakarla (51.490), Desapatrunipalem (51.345), Devada (51.161) and

**Table 2** HPI results of groundwater in the study area

Study area	$\Sigma Q_i \cdot W_i$	$\Sigma W_i$	HPI	Pollution status
Baranikam	62.481	1.116	55.976	Low
Desapatrunipalem	57.312	1.116	51.345	
Devada	57.106	1.116	51.161	
Kondakarla	57.473	1.116	51.490	
Mutyalampalem	56.842	1.116	50.924	



**Table 3** HEI results of groundwater in the study area

Study area	HEI	Pollution status
Baranikam	7.841	Low
Desapatrunipalem	1.476	
Devada	1.568	
Kondakarla	2.452	
Mutyalampalem	2.022	

Mutyalampalem (50.924) (Table 3). According to Prasad and Bose (2001), HPI value less than 100, consider to be low in heavy metal contamination, in all the five study sites is scored less than 100; hence, all the five sites are low heavy metal contamination. The HPI has given an indication on heavy metal quality in the groundwater of five sites that are well within the range. However, tremendously increasing heavy metal content in the water may cause adverse health effect on living organisms.

Heavy metal evaluation index (HEI): HEI is another index for the heavy metal quality assessment. It gives an overall heavy metal contamination approach based on maximum admissible value (MAC). Sum of HEI values is present in Table 3 for the five sites. Among the five sites, Baranikam (7.841) has shown the maximum HEI followed by Kondakarla (2.452), Mutyalampalem (2.022), Devada (1.568) and Desapatrunipalem (1.476). Due to the higher Fe concentration, Baranikam scored the highest HEI value. HEI value less than 10, consider to be low heavy metal contamination. In all the five study sites are scored less than 10, indicates low heavy metal contamination. The HEI has given an indication on heavy metal quality in the groundwater of five sites that are well within the range. Rapid increasing heavy metal concentration in the water may cause adverse health effect on biota.

Degree of contamination (Cd): Cd score is a cumulative heavy metal contamination in the study areas. The sum of Cd values is present in Table 3 for the five sites (Table 4). Among the five sites, Baranikam (−1.159) has shown the maximum Cd followed by Kondakarla (−6.548), Mutyalampalem (−6.978), Desapatrunipalem (−7.432) and Devada (−7.524). Cd value less than 1, consider to be low heavy metal contamination; in the study area, all the five sites are scored less than 1; hence, all the five sites are low heavy metal contamination. The Cd has given an indication on heavy metal quality in the groundwater of five sites that are well within the range.

**Table 4** Cd results of groundwaters in the study area

Study area	Cd	Pollution status
Baranikam	−1.159	Low
Desapatrunipalem	−7.524	
Devada	−7.432	
Kondakarla	−6.548	
Mutyalampalem	−6.978	

**Table 5** Correlation analysis among the parameters

	pH	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
pH	1.00									
As	-0.26	1.00								
Cd	-0.33	-0.64	1.00							
Cr	0.48	-0.68	0.46	1.00						
Cu	0.83	-0.49	-0.27	0.25	1.00					
Fe	0.70	-0.45	-0.28	0.08	0.98	1.00				
Mn	0.70	0.01	-0.47	-0.21	0.80	0.82	1.00			
Ni	0.35	-0.81	0.65	0.97	0.22	0.08	-0.26	1.00		
Pb	-0.13	0.93	-0.57	-0.37	-0.52	-0.56	-0.13	-0.55	1.00	
Zn	0.24	0.24	-0.28	0.48	-0.21	-0.37	-0.40	0.28	0.54	1.00

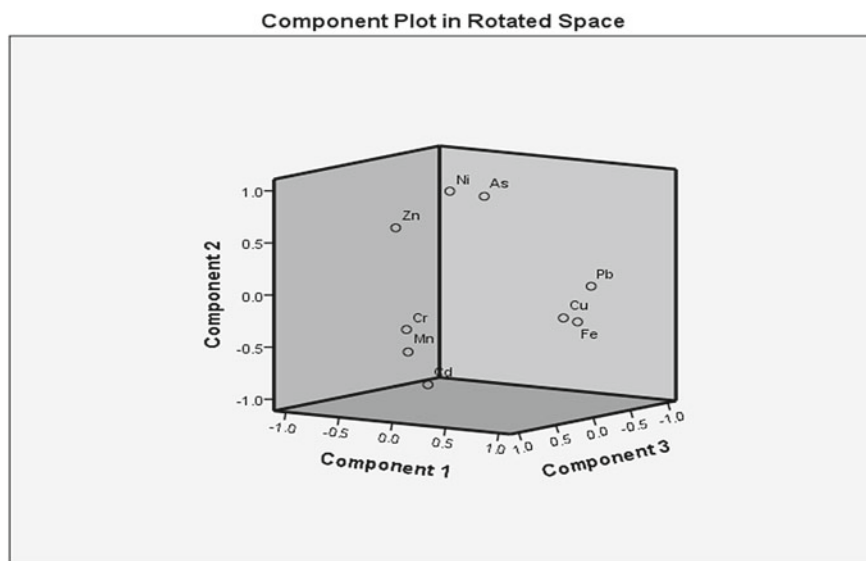
## 4 Statistical analysis

Correlation analysis: The correlation matrix was performed between the pH and metals. The strong correlation ( $r > 0.60$ ) among the pH has shown significant correlation with Cu–Fe–Mn. Similarly, relation between As–Pb, Cd–Ni, Cu–Mn–Fe metals is observed (Table 5).

Principle component analysis: PCA was plotted for the five location among the nine variants to recognize the heavy metal source. PC with eigen values greater than one considered to be significant and the loading value greater than forty were taken into consideration for the data interpretation [19]. The screen plot total variance about 96.8%. PC-1 with 4.15 eigen and 46.21% of total cumulative variants have shown the highest loading for Cu, Fe and Pb. PC-2 with 2.97 eigen and 33.03% of total cumulative variants have shown loading for As, Ni and Zn. PC-3 with 1.58 eigen and 17.61% of total cumulative variants have shown considerable loading for Cr and Mn (Fig. 4) indicating significant contribution of metals from mixed source of natural soil crust (red soil) and common man-made source.

## 5 Conclusion

The finding from the present study is heavy metals concentration in the groundwater in the five study areas that are well within the prescribed standards of WHO and BIS. Fe in Baranikam and Kondakarla areas was exceeded due to mixed sources of natural and man-made. The three pollution indices HPI, HEI and Cd have shown low heavy metal content. PCA has given three principal components with a total variance of 96.8%. PC-1 grouped with Cu–Fe–Pb; PC-2 grouped with As–Ni–Zn; and PC-3 grouped with Cr and Mn. Cd is not fit in the PCA due to its very low concentration. Even though the present values were well within the permissible limits,



**Fig. 4** Principle component analysis for heavy metals of groundwater

the PCA gives an idea to categorize the possible sources of metals based on their groupings. The results are useful for the future pollution source management to avoid groundwater contamination particularly in areas where residential and industrial activities commingled.

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