



Assessment of heavy metal pollution in water using multivariate statistical techniques in an industrial area: A case study from Patancheru, Medak District, Andhra Pradesh, India

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ABSTRACT

Application of different multivariate statistical approaches for the interpretation of data obtained during a monitoring programme of surface and groundwater in Patancheru industrial town near Hyderabad (India) is presented in this study. A number of chemical and pharmaceutical industries have been established since past three decades. Effluents from these industries are reportedly being directly discharged onto surrounding land, irrigation fields and surface water bodies forming point and non-point sources of contamination for groundwater in the study area. Thirteen parameters including trace elements (B, Cr, Mn, Fe, Co, Ni, Zn, As, Sr, Ba and Pb) have been monitored on 53 sampling points from a hydrogeochemical survey conducted in surface and groundwater. Data set thus obtained was treated using R-mode factor analysis (FA) and principal component analysis (PCA). FA identified four factors responsible for data structure explaining 75% of total variance in surface water and two factors in groundwater explaining 85%, and allowed to group selected parameters according to common features. Sr, Ba, Co, Ni and Cr were associated and controlled by mixed origin with similar contribution from anthropogenic and geogenic sources whereas Fe, Mn, As, Pb, Zn, B and Co were derived from anthropogenic activities. This study indicates the necessity and usefulness of multivariate statistical techniques for evaluation and interpretation of the data with a view to get better information about the water quality and design some remedial techniques to prevent the pollution caused by hazardous toxic elements in future.

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1. Introduction

Anthropogenic influences as well as natural processes degrade surface and groundwater, and impair their use for drinking, industrial, agricultural, recreation or other purposes [1,2]. Due to spatial and temporal variations in water chemistry a monitoring programme that will provide a representative and reliable estimation is necessary [3]. Solid and liquid wastes emanating from the industrial activities are the inevitable by-products of manufacturing process. These wastes contain toxic chemicals such as chromium salts, sulfides and other substances including heavy toxic trace metals [4]. A number of natural and anthropogenic sources produce heavy metals. People are becoming more aware of the complexity of the nature and the delicate balance that exist within the global ecosystem [5]. The discharge of effluents and associated toxic compounds into aquatic systems represents an ongoing environmental problem due to their possible impact on communities in the receiving aquatic water and a potential effect on human health [6]. Further

these materials enter the surface water and subsurface aquifers resulting in pollution of irrigation and drinking water. Urbanization increases in population density and the intensification of agricultural activities in certain area is among the main causes of water pollution.

The application of different multivariate approaches viz. factor analysis (FA) for interpretation of these data matrices offers a better understanding of water quality and ecological status of studied systems, allows identification of possible factors/sources that influence water systems, and provides a variable tool for reliable management of water resources as well as rapid solutions on pollution problems [7,8]. In the present paper, data obtained were subjected to different multivariate statistical approaches: (i) to define geogenic and anthropogenic origin, (ii) to identify possible non-point sources of contamination and (iii) to estimate the contributions of possible sources on concentration of determined parameters.

2. Materials and methods

2.1. Study area

Patancheru industrial development area, covering about 120 km² has been established during mid-1970s on Hyderabad-

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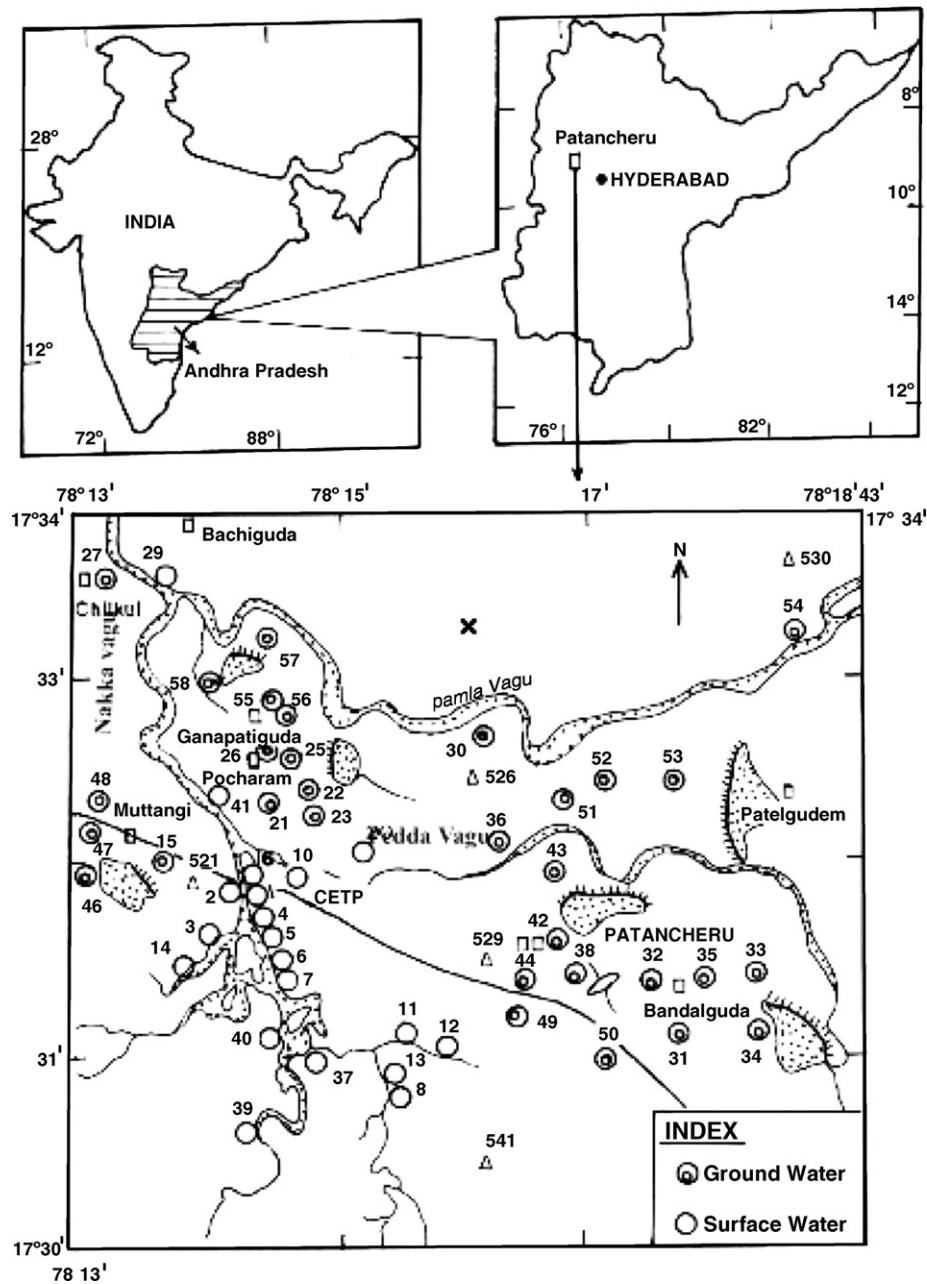


Fig. 1. Location map of the study area showing sampling points.

Mumbai National highway (NH9) about 25 km from Hyderabad city in Medak district, Andhra Pradesh, India (Fig. 1). It is also identified as one of the most polluted area by Central Pollution Control Board, New Delhi, and referred to as an area of ecological disaster. The study area forms part of the catchment of Nakkavagu stream, a tributary of the Manjira River, which is one of the main sources of drinking water to Hyderabad city. The industrial effluents contain appreciable amounts of inorganic and organic chemicals and their by-products. Most of the industries are small to medium-scale sector and are not having any sewer lines. Many of them do not have proper wastewater treatment plants and they discharge industrial effluents in unlined channels/streams, thereby causing contamination of air, water and soil. As a result the highly coloured and toxic chemical effluents join Nakkavagu, polluting surface water and groundwater [9,10].

The central effluent treatment plant (CETP) was commissioned during 1994 for treating industrial wastewater. Industrial units located in the area are supposed to first treat the effluents before sending to CETP. The so-called treated end-product, which is not absolutely safe, is being let out into Peddavagu, which ultimately joins another stream Nakkavagu, thereby spreading pollutants over a larger area. The contaminants from Nakkavagu seep through streambed into the groundwater region, contaminating it and results in substantial degradation of groundwater quality [10].

2.2. Geology and drainage

The study area forms a part of Precambrian peninsular shield and is referred to as basement complex or peninsular gneissic complex. The area is a granitic terrain comprising both grey and pink granites. Granites are traversed by pegmatite and quartz veins in some

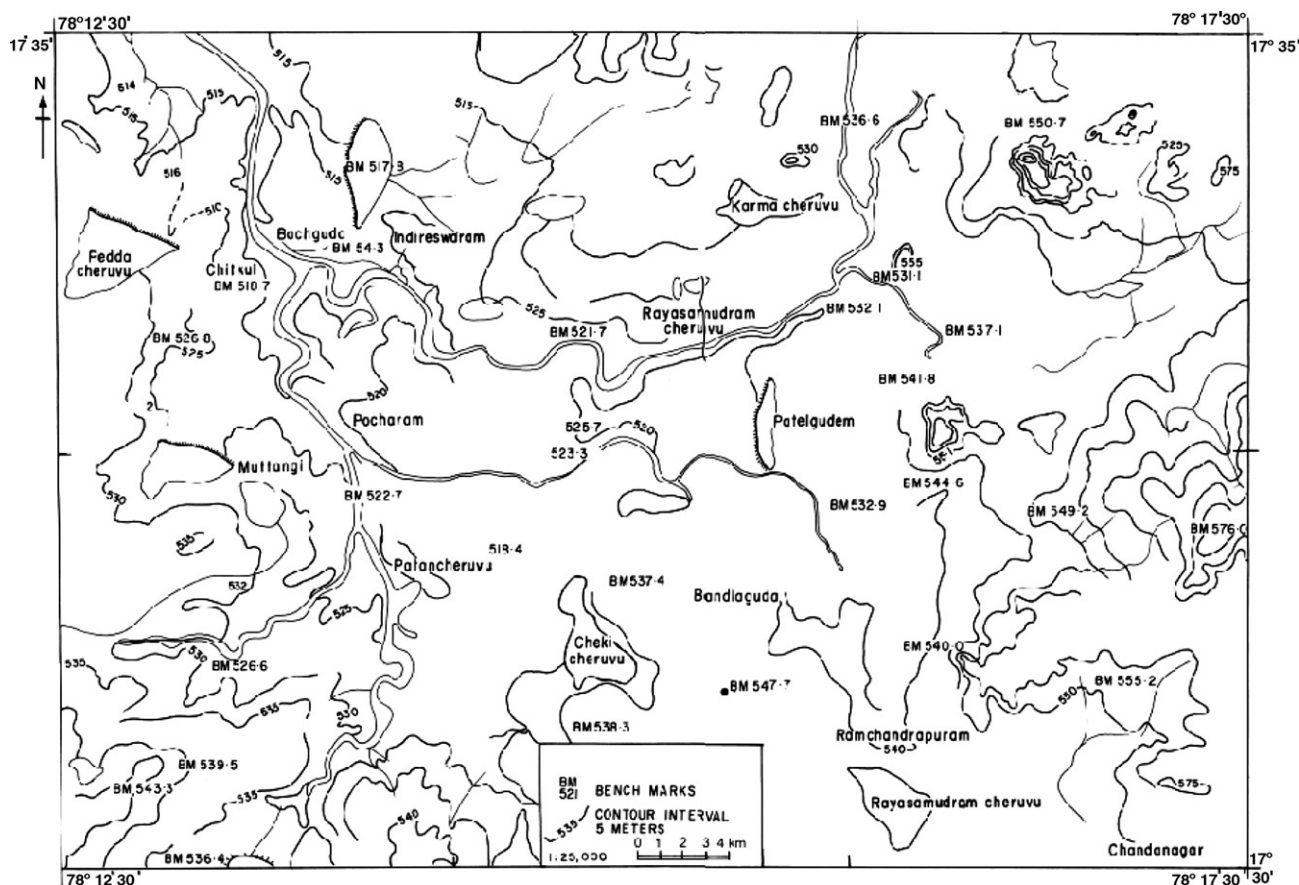


Fig. 2. Drainage and contour map of the study area.

pockets. Alluvium of recent formation is deposited by the stream action along flood plain of Nakkavagu. Alluvium comprises sand and gravel with small amount of silt and clay. Thickness of alluvium varies from 5 to 10 m and is covered with 1–2 m of soil. Precipitation is the main source of groundwater recharge and takes place during southwest monsoon, mostly between June and September. The groundwater recharge varies from 100 to 110 mm/year for an annual rainfall of 800 mm. Pamalavagu, Peddavagu and Nakkavagu streams while carrying effluents contribute as diffuse source of contamination all along their courses up to the confluence with Manjira River. Because of the presence of alluvium on the banks of Nakkavagu, there is more infiltration of contaminants into groundwater table through the stream–aquifer interaction and through advective dispersion. They also enter into subsurface water through fractures and joints. The rate of movement and consequent spread of pollutants depends upon the hydraulic gradient and groundwater velocity [9,11].

Red soils are prevalent in uplands of the watershed and black soils in Nakkavagu alluvium. Red soil is loose and sandy with little clay and silt and its thickness varies from 0.6 to 3 m. Black soil covers the major part and is transitive. The Nakkavagu drainage is detritic and is controlled by structural features such as lineaments (Fig. 2). Main crops grown are jowar, maize, groundnut and vegetables. Paddy and sugarcane are grown in the alluvium.

2.3. Sampling and preparation

Fifty-three water samples (surface and groundwater) were collected, covering entire Patancheru, Nakkavagu, Peddavagu, Pamalavagu basin. They include: (i) effluent discharges from indus-

tries, (ii) water samples along the course of Nakkavagu, (iii) water samples from open streams and (iv) groundwater samples from bore wells, handpumps and dugwells. All the samples were collected at considerable distances from the outlets of the industries after effluents had mixed with contaminated or less contaminated surface water. In order to understand the migration of pollutants and toxic heavy elements into groundwater system, subsurface water samples were collected from bore wells covering entire basin. The depth of these bore wells vary between 50 and 75 m in the study area. pH and TDS were measured onsite and samples were collected in 11 double cap, polythene bottles. Borehole water samples were collected after discharging first 50 l of the water sample. The samples were filtered in the lab and were acidified to pH 2 for the chemical analysis to be carried out by ICP-MS.

2.4. Instrumentation

All the surface and groundwater samples were analyzed for trace elements (Fe, Mn, As, B, Ba, Co, Cr, Ni, Sr, Zn and Pb) by using Plasma Quad ICP-Mass Spectrometer. 10% (v/v) Rh solution of 1 mg/l concentration was added in all water samples as an internal standard [12]. Calibration curves were prepared using multielement standard solution after dilution to $\mu\text{g/l}$ levels. Reference water samples 1640 from National Institute of Standards and Technology (NIST, USA) were used to check the reliability of calibration curve (Table 4). Lower limits of detection for all elements were better than 1 $\mu\text{g/l}$ [13]. The precision obtained in most cases was better than 5% RSD with comparable accuracy (for details see [14]).

Table 1a
Analytical data of surface water ($\mu\text{g/l}$) in Patancheru industrial area.

S. no.	Sample	pH	TDS (mg/l)	E	Cr	Mn	Fe	Co	Ni	Zn	As	Sr	Ba	Pb
1	P-1	7.72	1891	1015	13.0	132.1	76.5	1.8	10.3	49.0	18.3	838.2	78.1	0.7
2	P-2	7.67	1954	889.6	11.2	185.6	69.6	1.3	12.1	64.1	15.4	730.7	73.5	1.0
3	P-3	8.14	3060	1774	23.0	14.8	81.7	4.1	17.8	32.8	40.1	1109	68.9	1.0
4	P-4	7.39	1898	1024	21.1	180.2	93.5	2.1	13.8	56.8	30.3	652.3	67.4	1.3
5	P-5	7.38	2536	914.0	16.1	192.6	77.5	2.0	14.2	44.0	21.0	564.9	47.1	0.8
6	P-6	7.35	1970	858.0	20.1	135.3	79.0	1.7	14.9	57.6	20.0	553.2	59.4	1.3
7	P-7	8.21	2500	693.9	11.7	81.1	92.5	2.3	29.0	117.7	18.3	616.9	61.9	7.0
8	P-8	8.5	4250	426.9	13.1	32.2	81.2	11.5	35.3	130.2	17.5	425.0	45.4	1.3
9	P-10	8.39	7700	470.0	16.6	12.9	112.4	8.8	42.6	159.3	28.0	1544	102.0	1.1
10	P-11	10.08	6450	291.1	15.9	4.3	46.2	2.6	10.4	64.2	10.5	357.7	30.8	0.2
11	P-12	7.69	2700	525.8	42.8	89.0	91.8	2.5	14.1	99.2	13.6	575.8	63.4	0.8
12	P-13	7.63	1545	289.4	46.8	17.5	155.7	5.2	38.0	48.3	27.8	179.4	24.9	2.3
13	P-14	8.3	1500	89.6	4.6	4.8	52.4	0.3	4.9	78.3	5.5	241.3	47.0	2.7
14	P-15	8.09	1481	639.6	7.3	13.2	55.8	1.1	10.0	81.5	7.3	804.1	82.7	0.7
15	P-16	7.8	1728	846.2	11.2	48.9	62.6	1.4	51.2	364.8	18.4	856.9	52.4	0.6
16	P-15	7.83	752	634.2	4.2	2.9	42.0	0.6	7.4	64.1	8.5	1418	126.7	1.2
17	P-20	2.72	3660	1644	31.6	176.9	1886	2.2	34.2	337.1	108.9	433.0	86.1	13.8
18	P-29	7.63	511	103.5	7.3	4.9	69.9	1.4	38.7	51.8	19.2	745.5	160.2	1.3
19	P-37	8.1	1200	304.5	7.4	6.7	89.2	2.1	54.1	73.5	116.5	699.8	112.1	1.7
20	P-39	8.3	4300	371.1	12.8	34.1	64.1	3.2	40.8	37.7	55.7	2309	177.8	0.8
21	P-40	8.4	1800	437.3	16.4	227.2	84.3	2.0	45.8	45.6	17.6	506.1	69.6	0.9
22	P-41	8.6	2000	494.5	15.3	5.7	95.6	2.1	47.5	111.5	22.9	613.2	69.3	2.7

3. Data treatment and multivariate statistical methods

Multivariate analysis of surface and groundwater data was subjected through FA technique [8,15]. Summary statistics of these data sets were first calculated to evaluate the distributions (Tables 2a and 2b). FA was applied on standardized data through z-scale transformation in order to avoid misclassification due to wide differences in data dimensionality [16,17]. Standardization tends to increase the influence of variables whose variance is small and vice versa. All the mathematical and statis-

tical computations were made using Statistical Package for Social Sciences [18].

3.1. Factor analysis/principal component analysis (PCA)

Factor analytical technique extracts the eigen values and eigen vectors from co-variance matrix of original variables. The principal components (PC) are the uncorrelated (orthogonal) variables obtained by multiplying original correlated variables with eigen vector, which is a list of coefficients (loading or weightings). Thus

Table 1b
Analytical data of groundwater ($\mu\text{g/l}$) in Patancheru industrial area.

S. no.	Sample	pH	TDS	B	Cr	Mn	Fe	Co	Ni	Zn	As	Sr	Ba	Pb
1	P-21	7.92	997	991.1	2.5	5.7	42.8	0.3	5.0	70.3	8.9	577.8	66.8	0.8
2	P-22	7.87	716	504.2	2.7	5.1	38.8	0.4	4.9	66.0	5.2	861.1	101.8	0.8
3	P-23	8.06	491	1145.0	2.2	61.1	43.5	0.2	6.3	37.0	3.0	210.2	28.8	0.6
4	P-25	7.54	1650	813.8	4.0	4.6	45.7	0.8	19.0	62.9	29.0	1255.0	44.9	0.7
5	P-26	7.66	661	1950.0	3.6	3.7	40.7	0.3	4.7	48.5	2.9	801.5	70.8	1.2
6	P-27	8.55	373	1287.0	4.4	2.9	41.6	0.2	3.9	40.8	3.6	487.4	80.0	1.0
7	P-30	8.25	1460	208.6	8.1	4.8	74.5	1.1	44.1	129.3	19.6	2170.0	232.3	0.8
8	P-31	8.6	1200	965.1	9.7	8.1	204.2	1.1	84.7	125.7	90.7	2254.0	106.2	3.4
9	P-32	7.1	4000	795.8	45.6	6,226.0	131.8	44.6	274.4	310.2	753.0	20,428.0	1236.0	7.2
10	P-33	6.9	5000	902.7	74.7	14,971.0	175.5	34.3	244.6	211.2	1257.0	27,754.0	2364.0	6.6
11	P-34	7.9	3600	651.9	44.0	1,640.0	134.1	13.3	164.9	174.4	743.6	9,800.0	615.5	4.6
12	P-35	9.4	600	609.1	22.1	12.4	92.9	1.3	89.7	138.7	197.6	1,033.0	132.1	4.1
13	P-36	8.3	600	866.2	17.5	10.8	99.5	1.3	100.9	126.3	161.7	979.0	123.8	6.6
14	P-38	8.9	400	146.3	6.3	5.5	88.6	1.3	49.5	49.3	8.2	1,12.7	18.0	0.8
15	P-42	8.3	400	175.8	7.6	5.7	90.0	1.3	42.7	58.6	9.3	484.7	372.0	1.2
16	P-43	8.1	1600	589.0	12.6	6.4	109.0	1.4	54.1	48.1	19.2	1,511.0	62.0	0.9
17	P-44	7.7	900	314.2	7.7	5.5	107.3	1.1	54.4	46.6	11.2	1,242.0	153.2	0.7
18	P-45	7.9	900	113.4	6.0	5.7	93.6	1.2	42.9	31.2	8.9	1,377.0	65.8	0.7
19	P-46	8.6	800	571.6	5.3	7.3	83.0	1.2	35.8	54.1	11.2	1,677.0	104.4	1.1
20	P-47	9.1	1200	3533.0	24.7	23.6	576.0	6.7	265.6	130.9	212.3	2,319.0	177.1	1.9
21	P-48	7.6	1700	159.3	4.5	5.9	110.0	1.4	45.9	31.1	7.6	608.8	131.8	0.8
22	P-49	7.9	600	125.0	6.5	7.0	105.8	1.5	36.9	47.6	9.8	693.3	117.7	0.8
23	P-50	8.5	300	105.5	6.5	5.2	107.9	1.0	44.4	25.2	8.8	733.9	107.2	0.4
24	P-51	7.9	500	839.7	9.6	13.5	228.4	1.4	99.7	145.4	132.9	3,579.0	18.8	2.6
25	P-52	7.9	400	679.2	19.7	10.2	114.5	1.1	87.4	97.3	160.9	702.8	200.9	6.1
26	P-53	8.2	500	833.4	18.5	11.9	116.4	1.1	96.0	102.3	197.0	788.3	181.6	4.1
27	P-54	8.3	600	484.0	20.4	11.8	131.0	0.9	99.5	76.4	217.5	1,184.0	91.2	5.0
28	P-55	9	600	649.6	20.7	11.3	139.9	1.2	95.6	190.7	213.3	846.7	101.1	3.3
29	P-56	8.9	500	122.6	6.5	6.2	89.5	0.9	39.7	41.0	14.3	1,614.0	188.7	0.4
30	P-57	8.2	1000	145.9	10.1	4.9	80.8	0.9	34.8	31.4	13.2	1,297.0	169.2	0.4
31	P-58	8.8	900	88.8	6.3	5.2	90.8	1.0	36.3	32.1	10.1	1,014.0	177.2	0.5

Table 2a
Descriptive statistical data of surface water analysis.

	pH	TDS	B	Cr	Mn	Fe	Co	Ni	Zn	As	Sr	Ba	Pb
Mean	7.8	2608.5	669.8	16.8	72.9	161.8	2.8	26.7	98.6	29.2	762.5	77.6	2.1
Median	8.0	1962.0	580.0	14.2	33.1	80.1	2.1	23.4	64.1	18.8	634.6	69.1	1.2
Standard deviation	1.3	1755.1	434.4	11.1	77.5	385.9	2.6	16.3	87.9	29.2	478.6	38.3	3.0
Range	7.4	7189.0	1684.7	42.6	224.3	1844.1	11.3	49.2	332.0	111.0	2129.6	152.9	13.6
Minimum	2.7	511.0	89.6	4.2	2.9	42.0	0.3	4.9	32.8		179.4	24.9	0.2
Maximum	10.1	7700.0	1774.3	46.8	227.2	1886.0	11.5	54.1	364.8	116.5	2309.0	177.8	13.8

Table 2b
Descriptive statistical data of groundwater analysis.

	pH	TDS	B	Cr	Mn	Fe	Co	Ni	Zn	As	Sr	Ba	Pb
Mean	8.2	1133.8	689.3	14.2	745.4	117.0	4.1	74.5	89.7	146.5	2,916.0	246.5	2.3
Median	8.2	716.0	609.1	7.7	6.4	99.5	1.1	45.9	62.9	14.3	1,033.0	117.7	1.0
Standard deviation	0.6	1107.7	679.3	15.6	2,877.3	96.3	99	72.5	659	278.8	59,787.7	453.9	2.2
Range	2.5	4700.0	3444.2	72.5	14,968.1	537.2	44.4	270.6	285.0	1254.1	27,641.3	2346.0	6.8
Minimum	6.9	300.0	88.8	2.2	2.9	38.8	0.2	3.9	25.2	2.9	112.7	18.0	0.4
Maximum	9.4	5000.0	3533.0	74.7	14,971.0	576.0	44.6	274.4	310.2	1257.0	27,754.0	2364.0	7.2

principal components are weighted linear combinations of original variables. PC provide information on the most meaningful parameters, which describe whole data set affording data reduction with minimum loss of original information [19–21]. It is a powerful technique for pattern recognition that attempts to explain the variance of a large set of inter-correlated variables and transforming into a smaller set of independent (uncorrelated) variables (principal components). Factor analysis further reduce the contribution of less significant variables obtained from PCA and the new group of variables known as varifactors, are extracted through rotating the axis defined by PCA. A varifactor can include unobservable, hypothetical, latent variables, while a PC is a linear combination of observable water quality variables [22,23,19]. PCA of the normalized variables (surface and groundwater data set) was performed to extract significant PC's and to further reduce the contribution of variables with minor significance. These PC's were subjected to varimax rotation (raw) generating varifactors.

4. Results and discussion

The analytical results of trace metal concentration in surface and groundwater are given in Tables 1a and 1b, respectively. Main descriptive statistics for both surface and groundwater are shown in Tables 2a and 2b. Statistical treatment of these data indicates their association and grouping with four factors in surface water (Table 3a) and two factors in groundwater (Table 3b). pH of surface water varies from 7.7 to 10.1 with an average of 7.8, while in groundwater it varies from 6.9 to 9.4 (average = 8.2). Except sample P-20 (pH 2.72), all the water samples show neutral to basic and alkaline values. pH does not show significant positive correlation with any trace element in surface and groundwater, while it shows negative correlation with As, B, Fe, Pb and Zn in surface water, and Ba, Co, Mn and Sr in groundwater. This indicates that influence of pH on trace element is different in surface and groundwater of the study area, and is a major controlling factor especially in surface

Table 3a
Factor analysis of surface water data.

Element	Communality	Eigen	Total variance	Cummulative total variance	Factor 1	Factor 2	Factor 3	Factor 4
As	0.686	3.38	27.47	27.47	0.73	0.35	0.08	0.13
B	0.755	2.29	18.36	45.831	0.30	0.09	0.81	0.08
Ba	0.888	1.59	17.217	63.048	0.10	0.90	-0.16	-0.22
Co	0.789	1.03	12.307	75.355	-0.01	0.02	-0.23	0.86
Cr	0.674	0.80			0.16	-0.32	0.38	0.63
Fe	0.9	0.68			0.87	-0.04	0.38	0.03
Mn	0.555	0.48			0.10	-0.17	0.71	-0.09
Ni	0.721	0.43			0.50	0.23	-0.53	0.36
Pb	0.825	0.17			0.86	-0.13	0.25	-0.07
Sr	0.879	0.11			-0.14	0.93	-0.02	0.07
Zn	0.617	0.04			0.77	-0.15	-0.08	0.05

Table 3b
Factor analysis of groundwater data.

Element	Communality	Eigen	Total variance	Cummulative total variance	Factor 1	Factor 2
As	0.954	7.54	64.593	64.593	0.96	0.16
B	0.737	1.82	20.43	85.023	0.01	0.86
Ba	0.918	0.73			0.96	-0.03
Co	0.873	0.39			0.93	0.11
Cr	0.937	0.29			0.94	0.24
Fe	0.847	0.11			0.12	0.91
Mn	0.871	0.08			0.93	-0.04
Ni	0.939	0.02			0.75	0.61
Pb	0.589	0.01			0.72	0.27
Sr	0.95	0.00			0.97	0.04
Zn	0.737	0.00			0.78	0.37

Table 4

Analytical data of NIST 1640 analyzed by ICP-MS.

Analyte	Certified value	ICP-MS value (n = 3)	R.S.D.
B	301.10	292.03	5.45
Cr	38.60	36.95	4.43
Mn	121.50	115.00	4.90
Fe	34.30	34.10	2.62
Ni	27.40	25.78	4.44
Co	20.28	19.22	5.31
Cu	85.20	81.45	1.93
Zn	53.20	52.55	1.31
As	26.67	25.10	3.92
Sr	124.20	116.75	5.24
Ba	148.00	137.84	7.41
Pb	27.89	26.48	3.19

water. It was observed that there are some high values of Fe, Mn, As, Pb, Zn, B and Co due to point and non-point sources, which may be attributed to the industrial and agricultural activities. Unlike in surface water samples the pH in groundwater varied from 6.9 to 9.4 with an average of 8.2 ± 0.6 (1σ) and displays consistency in pH values. However, in surface water, the pH varies from 2.7 to 10.1 with an average of 7.8 ± 1.3 . In sample P-11 (pH 10.08) and P-20 (pH 2.72), the concentration of almost all the trace elements, particularly Fe, Co, Zn, As and Pb varies distinctly. The fact that surface water are either more acidic or alkaline in certain places, and that the trace elements concentrations in those samples are also varying accordingly, indicates that pH is a controlling factor in surface water. This situation suggests a strong variability due to presence of anthropogenic sources from surface water affecting groundwater.

4.1. Factor analysis

By factor analysis complex linear correlation between metal concentration in surface and groundwater was determined, which enabled interpretation of correlation of elements in the study area. Elements belonging to a given factor were defined by factor matrix after varimax rotation, with those having strong correlations grouped into factors. Considering the influence they exerted from surface water into the groundwater table by determining the distribution of elements in the study area of Patancheru industrial area, the said multielement factor were divided into two groups: (i) factors with strong scattered anthropogenic influence and (ii) factors caused by predominantly natural processes or other anthropogenic influences. The identification of factors is based on dominant influence. The distribution manner of individual association of element in surface and groundwater was determined by principal component method (results are shown in Tables 3a and 3b). Based on eigen values and varimax rotation four factors explained most of the variability (total variance explained was about 75% for the surface water data and 85% variance for the groundwater data).

4.2. Surface water

4.2.1. Factor 1

Factor 1 exhibits 27% of the total variance of 75% with positive loading on As, Fe, Ni, Pb and Zn. This factor indicates strong association ($r=0.5-0.87$) of As, Fe, Ni, Pb and Zn in surface water. Although it is difficult to differentiate background concentration due to geogenic processes in water, the high variability in the analytical data obtained is indicative of an external source for these elements in surface water. Arsenic levels were found to be almost high in all samples with concentration ranging from 5 to $116.5 \mu\text{g/l}$ with an average of $29.3 \mu\text{g/l}$. The high As values up to $25,000-40,000 \mu\text{g/l}$ were also reported near the exit of CETP. Ped-

davagu and Nakkavagu also show high concentration of arsenic varying from 1000 to $5000 \mu\text{g/l}$ [24], which proves that source of arsenic is anthropogenic and not from any surrounding rocks. The permissible limit of arsenic is $10 \mu\text{g/l}$ as per WHO guidelines [25]. Sample nos. P-3, P-4, P-20, P-37 and P-39 show abnormal values greater than background mean distribution of $29.2 \mu\text{g/l}$. Organic effluents discharged by the industries can complex with arsenic to form non-degradable metal complexes and they in turn enter the groundwater and migrate along natural hydrological gradient. Downward migration and NW movement of arsenic affected the groundwater [26] spreading over an area of approximately 20 km^2 . Arsenic contamination in Patancheru comes mainly from paint, pharmaceutical, fertilizer and pesticides industries.

Anthropogenic addition of Fe in surface water varying from 42 to $1886 \mu\text{g/l}$ with an average of $161.8 \mu\text{g/l}$ is low in the area; apparently effluent waters are only causing its increase in surface water. Fe does not show high concentrations in groundwater suggesting that there is little percolation of Fe from surface to groundwater. Ni concentration varies from 4.9 to 54.1 (average of $26.7 \mu\text{g/l}$), Pb varies from 0.2 to $13.8 \mu\text{g/l}$ (average of $2.1 \mu\text{g/l}$) and Zn varies from 32.8 to 364.8 ppm (average of $98.6 \mu\text{g/l}$). Sample nos. P-13 and P-20 show high values of Fe, Ni, Pb and Zn, which are near the vicinity of industrial areas.

4.2.2. Factor 2

Factor 2 exhibits 18.4% of the total variance with positive loading on Ba and Sr. Ba concentration varies from 24.9 to $177.8 \mu\text{g/l}$ with an average of 77.6 ppm, and Sr varies from 179.4 to $2309 \mu\text{g/l}$ (average = $762.5 \mu\text{g/l}$). Samples P-1, P-10, P-15 and P-39 show comparatively higher concentration. High values of Sr up to $1000 \mu\text{g/l}$ can be derived from the surrounding acidic rocks having Sr of about 400–500 ppm. Hence this factor can be attributed to mixed origin of Sr and Ba in the area from anthropogenic and geogenic source.

4.2.3. Factor 3

It exhibits 17.2% of the total variance with positive loading on B and Mn, and negative loading on Ni. This factor can be attributed to the influence of agricultural activity on these trace elements in the study area. Boron varies from 89.6 to $1774.3 \mu\text{g/l}$ (average = $669.8 \mu\text{g/l}$) and Mn varies from 3 to $227.2 \mu\text{g/l}$ (average = $72.9 \mu\text{g/l}$). High levels of B are mostly restricted to Patancheru industrial area where its concentration goes up to $1774.3 \mu\text{g/l}$. This element does not show appreciable migration, but percolates down and is concentrated in the groundwater without exhibiting much mobility. B is mainly of anthropogenic origin. Principal sources of B are due to agriculture. Sample nos. P-1, P-2, P-4, P-5, P-6 and P-7 show more than average concentration of B and Mn, and are located all along Nakkavagu, indicating dispersion of these elements from the untreated effluents released from CETP. The negative loading on Ni indicates that as the B and Mn concentration increases, Ni level decreases showing the existence of inverse relation with B and Mn in surface water. Nickel varies from 4.9 to $54.1 \mu\text{g/l}$ (average = $26.7 \mu\text{g/l}$) indicative of its background concentration. However, the inverse relation that it exhibits with B and Mn shows 'masking' of Ni due to external input of Mn and B.

4.2.4. Factor 4

Factor 4 exhibits 12.3% of the total variance and has positive loading on Co and Cr. Co varies from 0.3 to $11.5 \mu\text{g/l}$ with an average of $2.8 \mu\text{g/l}$, and Cr from 4.2 to $46.8 \mu\text{g/l}$ (average = $16.8 \mu\text{g/l}$). There is no contamination due to Cr and Co in surface water and the values represent natural concentration in granite terrain. This factor is attributed to the geogenic processes representing background concentration of Cr and Co in surface water.

4.3. Groundwater

Groundwater contamination can originate above or below the surface of the earth. Infiltration of polluted surface water causes contamination below the surface of the earth. When compared to water in streams and rivers, the movement of groundwater is very slow and hence once the contaminant reaches the groundwater; there is little scope for dilution and dispersion. The substances that can contaminate groundwater can be basically classified as natural and artificial.

4.3.1. Factor 1

Factor 1 shows 64.5% of total variance with high positive loading on As, B, Co, Cr, Mn, Ni, Pb and Zn ($r=0.7-1$). The minimum and maximum concentrations of these trace elements along with their average values are listed in Table 2b. This factor is attributed to anthropogenic influence of these trace metals in groundwater. The data reveal that these trace elements have migrated from surface water. Sample nos. P-32, P-33, P-34, P-35 and P-36 show abnormal values with respect to its average and are located near Bandalguda village in proximity to industries. Especially with reference to Sr and Ba values, very abnormal concentration of Sr (27,754 $\mu\text{g/l}$) can be attributed to anthropogenic source as there are pharmaceutical industries in the close vicinity and Sr is used to manufacture skin ointment and toothpaste. Ba was present up to 615 $\mu\text{g/l}$, except in two samples (P-32 and P-33), which also show high concentration of Sr and Ni indicating the source of the metals from industrial effluents. Sr and Ba are abnormally high in Bandalguda due to surrounding industries. However, Co, Cr, Ni, Pb and Zn concentrations are within the permissible limits prescribed by WHO (1996). Migration of trace elements in granitic terrain is through fractures and joints, and is much faster than that in sedimentary formation. Even though some trace element concentrations are within permissible limits, the values are indicative of an increase in their rate in due course of time.

4.3.2. Factor 2

Factor 2 shows 20.43% of the total variance with positive loading on B, Fe and Ni. Fe-oxyhydroxides are known to influence trace elements through their adsorbing characteristics. The geochemical nature of Fe has a bearing on the presence of Ni and B in groundwater. While Fe and Ni exhibit natural background concentration in groundwater, B shows migrative characteristics from surface water. However, it seems that geochemical behaviour of Fe-oxyhydroxides has influenced the B and Ni concentration. The Fe, Mn and Al are strongly hydrolyzed under basic/alkaline conditions [27] and they are flocculated along with organic matter and trace elements [28,29]. The Fe-oxyhydroxides should have selectively scavenged B and Ni, and hence has contributed to this factor.

5. Conclusion

The case study of groundwater/surface water pollution due to uncontrolled industrial effluent discharges and the results of factor analysis performed on 11 heavy metals, identified four factors for surface water and two factors for groundwater controlling their variability in waters of Patancheru. Pollution around the Patancheru industrial area increased during the past one and half decade due to discharge of industrial effluents in surface water bodies. Multivariate statistical approaches show that the polluted surface water is strongly influencing the quality of groundwater in the study area. Migration patterns of heavy metals released into the environment in the form of untreated effluents by CETP and industries of Patancheru indicate the point source of pollution. Central effluent treatment plant was found to be increasing the concentration of toxic metals in surface and groundwater which was confirmed

by high concentration of all the heavy/toxic metals in Peddavagu, adjacent to CETP.

Water streams Nakkavagu, Peddavagu should be lined in the bottom on both sides to prevent the spread of contaminants horizontally and vertically. Some remedial measures should be applied in agricultural fields by removing topsoil and applying bioremediation techniques. The present study suggests that regular monitoring of the quality of groundwater should be undertaken temporally and spatially to identify the source of toxic pollutants and other inhibitory chemicals which affect the water around industries in Patancheru.

6. Recommendations

The untreated effluents emerging from the industries must be monitored for maintaining the standards prescribed by the pollution control board for various industries in the region. The chemical analysis of the treated effluent from the CETP was found to contain some toxic metals like arsenic, selenium and manganese. As the CETP receives effluents from various industries in tankers and it is suggested to check for the trace metal and TDS concentrations before letting the untreated effluents into the CETP. The present study provides the baseline data for assessment of contamination in the Patancheru area. Periodical monitoring of the water quality has to be continued to check the rise in TDS concentrations of groundwater.

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References

- [1] S.R. Carpenter, N.F. Caraco, D.L. Correll, R.W. Howarth, A.N. Sharpely, V.H. Smith, Nonpoint pollution of surface waters with phosphorus and nitrogen, *Ecological Applications* 8 (1998) 559–568.
- [2] J.E. Fergusson, The heavy element chemistry, in: J.E. Fergusson (Ed.), *Environmental Impact and Health Effects*, Pergamon, New York, 1990, p. 720.
- [3] U. Aswathanarayana, *Geoenvironment: An Introduction*, A.A. Balkema Publishers, Rotterdam, 1995, p. 270.
- [4] S.R. Tariq, M.H. Shah, N. Shaheen, A. Khalique, S. Manzoor, M. Jaffar, Multivariate analysis of trace metal levels in tannery effluents in relation to soil and water: a case study from Peshawar, Pakistan, *Journal of Environmental Management* 79 (2006) 20–29.
- [5] D. Ahmet, Y. Fevzi, A.L. Tuna, O. Nedim, Heavy metals in water, sediment and tissues of *Leuciscus cephalus* from a stream in southwestern Turkey, *Chemosphere* 63 (2006) 1451–1458.
- [6] F.M. Abbas Alkarkhi, N. Ismail, A. Mat Easa, Assessment of arsenic and heavy metal contents in cockles (*Anadara granosa*) using multivariate statistical techniques, *Journal of Hazardous Materials* 150 (2008) 783–789.
- [7] M.M. Morales, P. Marti, A. Llopi, L. Campos, S. Sagrado, An environmental study by factor analysis of surface seawaters in the gulf of Valencia (Western Mediterranean), *Analytica Chimica Acta* 394 (1999) 109–117.
- [8] D.A. Wunderlin, M.P. Diaz, M.V. Ame, S.F. Pesce, A.C. Hued, M.A. Bistoni, Pattern recognition techniques for the evaluation of spatial and temporal variations in water quality. A case study: Suquia river basin (Cordoba–Argentina), *Water Research* 35 (2001) 2881–2894.
- [9] V.V.S. Gurunadha Rao, R.L. Dhar, K. Subramanyam, Assessment of contaminant migration in groundwater from an industrial development area, Medak district, Andhra Pradesh, India, *Water, Air and Soil Pollution* 128 (2001) 369–389.
- [10] P.K. Govil, G.L.N. Reddy, A.K. Krishna, Contamination of soil due to heavy metals in the Patancheru industrial development area, Andhra Pradesh, India, *Environmental Geology* 41 (2001) 461–469.
- [11] NEERI, A report on Patancheru industrial area, National Environmental Engineering Research Institute, Nagpur, India, 1989, 85 pp.
- [12] V. Balaram, C. Manikyamba, S.L. Ramesh, K.V. Anjiah, Rare earth and trace element determination in iron formation reference samples by ICP-mass spectrometer, *Atomic Spectroscopy* 13 (1992) 19–25.
- [13] P.K. Govil, T. Ganeswara Rao, R. Rao, Environmental monitoring of toxic elements in industrial development area: a case study, in: 3rd International Conference on the Analysis of Geological and Environmental materials, Colorado, USA, June 1–5, 1997 (Abs. vol. 77).

- [14] V. Balam, Characterization of trace elements in environmental samples by ICP-MS, *Atomic Spectroscopy* 6 (1993) 174–179.
- [15] V. Simeonov, J.A. Stratis, C. Samara, G. Zachariadis, D. Voutsas, A. Anthemidis, M. Sofoniou, T.H. Kouimtzi, Assessment of the surface water quality in Northern Greece, *Water Research* 37 (2003) 4119–4124.
- [16] P. Kunwar Singh, M. Amrita, M. Dinesh, S. Sarita, Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti river (India): a case study. *Water Research*, available online from 8th September 2004.
- [17] G. Biksham, K. Shivkumar, T. Mohan Reddy, Scientific Evaluation of Pollution around Patancheru and Bolaram Industrial Areas, Medak District, Andhra Pradesh, Deccan Development Society, Hyderabad, 1993, p. 120.
- [18] SPSS® (Statistical Package for Social Studies) version 6.1, USA. Professional Statistics 6.1, 385, Marija J. Norusis/SPSS Inc., Chicago, 1995.
- [19] M. Vega, R. Pardo, E. Barraado, L. Deban, Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis, *Water Research* 32 (1998) 3581–3592.
- [20] B. Helena, R. Pardo, M. Vega, E. Barrado, J.M. Fernandez, L. Fernandez, Temporal evolution of ground water composition in an alluvial aquifer (Pisuerga river, Spain) by principal component analysis, *Water Research* 34 (2000) 807–816.
- [21] S. Shrestha, F. Kazama, Assessment of surface water quality using multivariate statistical techniques: a case study of the Fuji river basin, Japan, *Environmental Modelling and Software* 22 (4) (2007) 464–475.
- [22] U.C. Panda, S.K. Sundaray, P. Rath, B.B. Nayak, D. Bhatta, Application of factor and cluster analysis for characterization of river and estuarine water systems—a case study: Mahanadi River (India), *Journal of Hydrology* 331 (3–4) (2006) 434–445.
- [23] J.C. Davis, *Statistics and Data Analysis in Geology*, 2nd edn., Wiley, New York, 1986.
- [24] P.K. Govil, T. Gnanaswara Rao, A.K. Krishna, Arsenic contamination in Patancheru industrial area, Medak District, Andhra Pradesh, *Environmental Geochemistry* 1 (1998) 5–9.
- [25] WHO, Guidelines for drinking water health criteria and other supporting information, vol. 2, World Health Organization, Geneva, 1996, p. 973.
- [26] K. Shivkumar, A.K. Pande, G. Biksham, Toxic trace element pollution in groundwaters around Patancheru and Bolaram industrial areas, Andhra Pradesh, India: a graphical approach, *Environmental Monitoring and Assessment* 45 (1997) 57–80.
- [27] R.H. Byrne, L.R. Kump, K.J. Cantrell, The influence of temperature and pH on trace metal speciation in seawater, *Marine Chemistry* 25 (1988) 163–181.
- [28] E.R. Sholkovitz, Flocculation of dissolved organic and inorganic matter during the mixing of river water and seawater, *Geochimica et Cosmochimica Acta* 40 (1976) 831–845.
- [29] L.M. Mayer, Aggregation of colloidal iron during estuarine mixing: kinetics, mechanism and seasonality, *Geochimica et Cosmochimica Acta* 46 (1982) 2527–2535.