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IJIEMR Transactions, online available on 18th Feb 2022. Link :http://www.ijiemr.org/downloads.php?vol=Volume-12&issue=Issue 01

DOI: 10.48047/IJIEMR/V12/ISSUE 02/74

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Volume 12, ISSUE 01, Pages: 464-486

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An approach to assess Heavy metals contamination in groundwater of Pendurthi mandal, Visakhapatnam, Andhra Pradesh, India

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ABSTRACT

Groundwater is the major source of domestic, agricultural, industrial and other sectors. Reckless usage of ground water brings down the quality and quantity of water. Pendurthi is one of the major residential and commercial suburbs in Visakhapatnam. Rapid growth of population and urbanization affects the groundwater quality of the area. The present work evaluated the status of groundwater quality in and around Pendurthi Mandal, Visakhapatnam by analysing heavy metals. These parameters were compared with the BIS (10500:2012) drinking water standards. The objective of this study is to determine heavy metals contamination of groundwater samples using Heavy metal pollution Index (HPI), Heavy metal evaluation index (HEI), covariance, Pearson's coefficient correlation. 30 water samples were collected covering the entire mandal during pre-monsoon and post-monsoon seasons in the year 2020. The concentrations of heavy metals like lead, manganese, iron, zinc, copper and chromium were analysed using ICP-MS. All the HPI and HEI values show low heavy metal contamination. The covariance is high in pre-monsoon compared to the post-monsoon. Pearson correlation coefficient results shows that Chromium has good correlation with iron, Zinc, Manganese. Zinc has least correlation with iron and Manganese. The study concludes and recommends that the groundwater needs some treatment to reduce the heavy metals pollutants before consumption.

Keywords: Heavy metal pollution Index (HPI), Heavy metal evaluation index (HEI), covariance, Pearson's correlation coefficient (r), concentration of heavy metals, ground water samples, drinking water standards.

1. Introduction

Water is a precious natural resource and elixir of life. It is essential for all life forms on planet earth, without it there is no life on earth. It plays an important role in regulating climate and maintaining the ecosystem. Water is useful for domestic, agricultural and industrial purposes. Natural Water Policy (2002) aptly states that water is a basic human need, prime natural resource and a precious national asset. As water is the most important component of the eco-system, any imbalance created in terms of the number of impurities added to it can damage the whole eco-system (Kannan Krishnan, 1991, Hem *et al.*, 1961). Drinking water quality can change during its distribution as a result of both increased residence time and hydraulic changes (Prest *et al.*, 2021). Prolonged discharge of industrial effluents, domestic sewage and solid waste dump causes the groundwater to become polluted and create health problems (Raja *et al.,* 2002). Urbanization is the overall sustainable development and growth that encompasses economic development, social development, and environmental protection (Washington, 2015). Rapid population growth, industrialization and urbanization play a major role in groundwater pollution. The unplanned urbanization and industrialization have resulted in over use of environment in particular of water resource. (Singh *et al.*, 2002).

Due to seasonal variations and groundwater contamination water may contain microbes, silt, mud, chemicals, pesticides and heavy metals which pose serious health hazards. It is estimated that more than 60% of the communicable diseases are due to poor environmental health conditions arising from unsafe and inadequate water supply with poor hygienic and sanitation practices (Berhanu *et al*., 2015). According to WHO guidelines, 100 and 6.4% of groundwater samples were rated as unsuitable for drinking purpose due to high contents of Pb and As, respectively. Drinking hard water may result in human health problems such as kidney failure (WHO 2008). Heavy metals contamination of groundwater sources has been reported across the globe (Chakraborti *et al.*, 2016, Munyangane *et al.*, 2017).

Effluents from most of the industries without proper treatment are discharged into nearby open pits or otherwise passed through unlined channels that move towards the low-lying depressions on land and result in the contamination of groundwater (Purandara and Varadarajan 2003). Ground water may contain fluoride, and other toxic metals such as arsenic, lead and selenium in amounts that are harmful to health, as well as iron and manganese which cause other types of problems such as the staining of sanitary fixtures (Okoya *et al*., 2020).

Physico-chemical parameters and heavy metals need to be analysed to check the quality of water. Continuous monitoring is necessary for effective maintenance of groundwater quality. The quality of water is equally important to its available quantity. Every day the condition of groundwater is changing because of its abstraction, recharge, and interactions with underground parent materials.

2. Methodology

2.1 Study Area

Visakhapatnam District is one of the North Eastern Coastal districts of Andhra Pradesh and lies between the Eastern longitude from 18°- 54' to 83° - 30' and between the Northern latitude from 17°- 15' to 18°-32'. It is bounded by the Orissa State and the Vizianagaram District partly on the North, by the East Godavari District entirely on the South, by the Orissa State entirely on the West and by the Bay of Bengal entirely on the East. It is the third largest city on the East Coast of India, headquarters of the Eastern Naval Command and popularly known as Vizag, the 'The Jewel of the East Coast'.

Pendurthi is one of the fastest growing sub-urban areas in Visakhapatnam. It is located at 17.8333°N 83.2000°E. It has a mean altitude of 22 meters (75 feet). Geographical area in Pendurthi Mandal is 12,019 hectares. It is located 15 KM towards North from District headquarters of Vishakhapatnam. The total population of Pendurthi Mandal is 106,513 sheltering under 24,543 Houses and 15 panchayats. Among them Male population constitute about 53,800 and that of the females constitute about 52,713. Out of them, a total of about 26,998 people hails from towns and that of about 79,515 are from villages. This Mandal has the least Rural area of about 63.79 Sq. Kms. Total area of villages in hectares is 6,379.00. Total number of voters in the Mandal are 23,3961. The location map can be seen in Figure 1.

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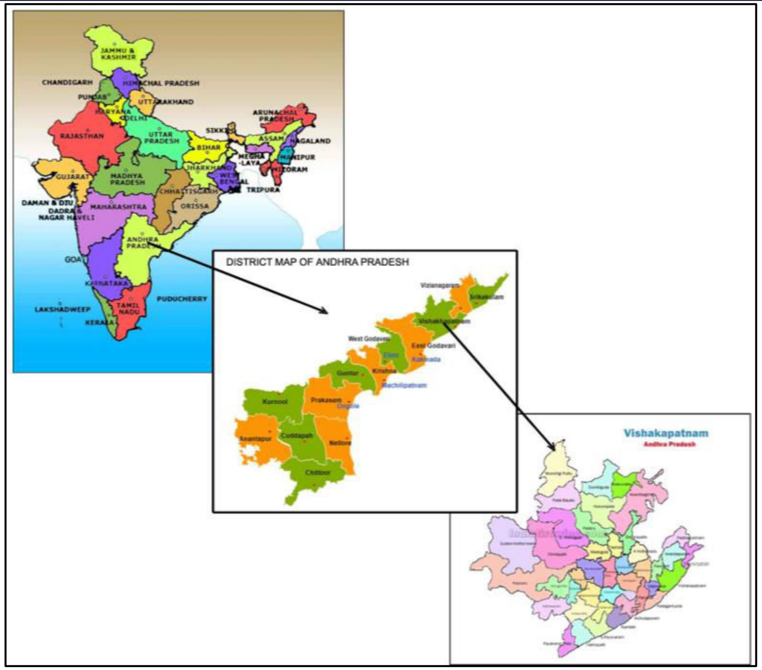

Figure 1: Location Map of Study Area

2.2 Ground water Sampling & Analysis

Water samples were collected in the pre-monsoon and post monsoon periods during the morning hours from 8am to 10pm between the month of March 2020 and September 2020. A total of 30 sampling stations have been considered for sampling. Sample locations can be seen in the map on Figure 2. Water was collected in sterilized 2 litre water cans labelled with the sample code and transported to the laboratory in an ice box and stored at 4°C. The acidified groundwater samples were analysed for heavy metals contents (Cu, Mn, Zn, Pb, Fe and Cr) using Inductively coupled plasma mass spectrometry ICP – MS (Agilent Technologies, Model 7700). Water samples were acidified by adding 5ml of supra pure nitric acid (HNO_3) and then heated at 70ºC until the solution becomes transparent (APHA 2005). The solution was allowed to cool and then filtered using 0.45 um micropore filter paper. The solutions were then kept to analyse for the determination of heavy metals in water during the three seasons and their concentration is assessed (mg/l).

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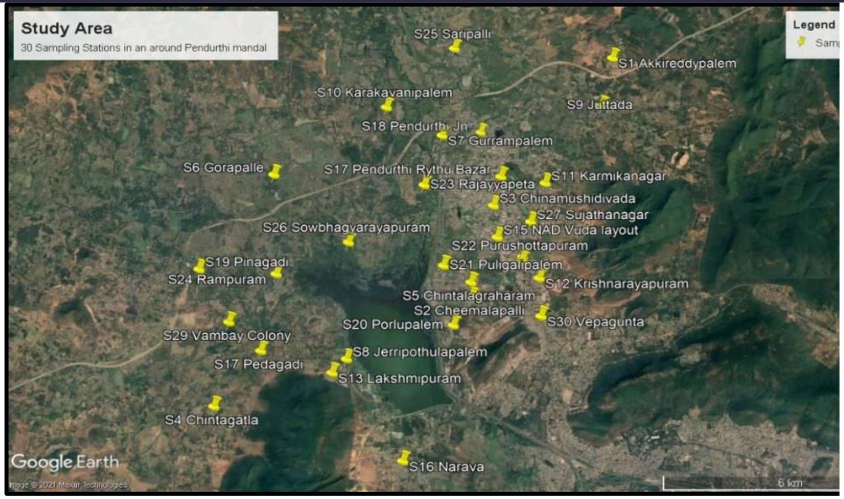

Figure 2: Locations and Sampling stations on Google Earth

2.3 Heavy Metal Pollution Index

Heavy metal pollution Index (HPI) is used to determine the overall quality of groundwater with respect to the heavy metals in the water. HPI is calculated with respect to metals contamination from the point of view of the suitability of ground water for human consumption. HPI calculates a rating that suggests a composite influence of specific heavy metal on the overall quality of water (Sheykhi and Moore 2012).

Weighted arithmetic index method has been used for calculation of HPI by the following equation:

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

where,

'W_i' is defined as the unit weightage of a heavy metal,

'Q_i' is a sub-index of heavy metal,

'n' is the number of heavy metals measured to determine HPI.

The subindex (Q_i) is calculated by the equation:

$$Q_i = \sum_{i=1}^{n} \frac{|M_i - I_i|}{(Si - Ii)} \times 100$$

where,

'M_i' is defined as the value of a heavy metal,

'S_i' is the highest permissible limit that is allowed by WHO (2012),

'I_i' is the maximum desirable value of the i^{th} heavy metal given by WHO (2012).

2.4 Heavy Metal Evaluation Index

Heavy metal evaluation index (HEI) is a method of evaluating the water quality with focal point on heavy metals in drinking water.

HEI is calculated by the following equation:

$$HEI = \sum_{i=1}^{n} \frac{H_c}{H_{mac}}$$

where,

'H_c' is the observed concentration value of the i^{th} Heavy metal for each station,

'H_{mac}' is the maximum admissible concentration of the i^{th} Heavy metal for each station, respectively.

2.5 Covariance

The covariance between a pair of variables (X1, X2) computes the estimator for the covariance. The covariance of the two variables was represented as:

$$COV_{(x1,\, x2)} = \frac{\sum_{i=1}^{n}(x1_i - \overline{x1})(x2_i - \overline{x2})}{(n-1)}$$

where,

'$COV_{(x1,\, x2)}$' is the covariance between two variables 'x1' and 'x2',

'$x1_i$' is a data value of 'x1',

'$x2_i$' is a data value of 'x2',

'$\overline{x1}$' is mean value of 'x1',

'$\overline{x2}$' is mean value of 'x2',

'n' is the number of values.

Since the mean of the entire population is 'unknown', the 'known' respective means of the samples of the two variables are considered in the formula and hence the denominator of the formula is '(n-1)' rather than 'n'.

2.6 Pearson's Correlation coefficient

The Pearson correlation coefficient (Pearson's 'r') is a value reflecting the linear correlation between two variables, giving a value between +1 and -1 inclusive, where a correlation value 1 is

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completely positive, value 0 is no existence of correlation, and -1 is total negative correlation (Sedgwick 2012).

It is calculated by using the formula:

$$r = \frac{\sum_{i=1}^{n}(x_i-\bar{x})\times(y_i-\bar{y})}{\sqrt{\sum_{i=1}^{n}(x_i-\bar{x})^2\times\sum_{i=1}^{n}(y_i-\bar{y})^2}}$$

where,

'r' is the correlation coefficient

'x_i' is the x-variable values of a sample

'$\bar{x}$' is mean of the x-variable values

'y_i' is the y-variable values of a sample

'$\bar{y}$' is mean of the y-variable values

3. Results and discussion

Sampling Location	Manganese (Mn)		Lead (Pb)		Copper (Cu)		Chromium (Cr)		Zinc (Zn)		Iron (Fe)		HPI		HEI	
	Pre-M	Post-M	Pre-M	Post-M	Pre-M	Post-M	Pre-M	Post-M	Pre-M	Post-M	Pre-M	Post-M	Pre-M	Post-M	Pre-M	Post-M
Station1	1.421	1.419	1.103	0.996	1.108	1.101	0.121	0.119	5.318	5.312	3.877	3.856	10.063	9.222	0.781	0.71
Station2	0.092	0.088	0.196	0.188	0.031	0.027	0.033	0.025	0.229	0.226	0.121	0.107	2.901	2.836	0.134	0.128
Station3	0.763	0.755	0.523	0.514	0.544	0.535	0.064	0.056	2.713	2.702	1.293	1.287	5.479	5.406	0.371	0.364
Station4	0.016	0.009	0.045	0.041	0.075	0.064	0.016	0.011	0.287	0.262	0.395	0.417	1.714	1.681	0.032	0.029
Station5	0.048	0.041	0.068	0.062	0.118	0.112	0.028	0.025	0.421	0.419	0.332	0.219	1.897	1.848	0.048	0.044
Station6	0.421	0.412	0.286	0.278	0.471	0.465	0.152	0.144	3.136	3.124	2.862	2.848	3.664	3.599	0.213	0.207
Station7	0.346	0.341	0.121	0.118	2.099	2.095	0.032	0.022	1.691	1.682	1.587	1.526	2.321	2.294	0.096	0.093

Station8	0.121	0.116	0.052	0.061	0.342	0.338	0.008	0.006	0.536	0.531	0.328	0.321	1.764	1.834	0.039	0.045
Station9	0.045	0.041	0.071	0.068	0.142	0.136	0.023	0.019	0.277	0.271	0.462	0.456	1.92	1.896	0.05	0.048
Station10	0.021	0.018	0.064	0.061	0.842	0.839	0.034	0.025	1.345	1.336	0.726	0.718	1.871	1.845	0.047	0.045
Station11	0.263	0.257	0.052	0.047	0.821	0.818	0.046	0.043	2.129	2.126	0.121	0.107	1.772	1.732	0.042	0.039
Station12	0.038	0.033	0.055	0.048	0.381	0.376	0.034	0.026	0.673	0.546	1.339	1.229	1.806	1.748	0.043	0.038
Station13	0.019	0.013	0.028	0.023	0.332	0.296	0.015	0.009	0.448	0.441	0.128	0.121	1.578	1.537	0.02	0.017
Station14	0.546	0.538	0.264	0.283	1.482	1.476	0.25	0.248	3.73	3.727	4.655	4.642	3.536	3.685	0.21	0.222
Station15	0.219	0.215	0.217	0.206	0.093	0.086	0.013	0.009	0.251	0.248	0.388	0.359	3.06	2.972	0.151	0.143
Station16	0.018	0.012	0.02	0.018	0.031	0.028	0.011	0.008	0.081	0.075	0.151	0.147	1.514	1.497	0.014	0.013
Station17	0.031	0.028	0.041	0.038	0.053	0.046	0.062	0.066	1.108	1.094	0.977	0.971	1.702	1.679	0.033	0.031
Station18	2.425	2.448	0.918	0.907	1.128	1.117	0.121	0.119	4.977	4.989	6.27	6.16	8.619	8.53	0.686	0.679
Station19	0.113	0.096	0.198	0.182	0.261	0.255	0.039	0.033	4.241	4.237	0.848	0.827	2.925	2.797	0.139	0.128
Station20	0.016	0.019	0.032	0.036	0.241	0.234	0.018	0.015	0.572	0.563	0.365	0.352	1.612	1.642	0.024	0.026
Station21	0.057	0.045	0.216	0.203	0.327	0.308	0.028	0.022	0.526	0.518	0.816	0.783	3.063	2.959	0.149	0.14
Station22	0.264	0.251	0.197	0.191	0.548	0.538	0.069	0.056	0.714	0.707	1.646	1.638	2.931	2.88	0.144	0.14
Station23	0.02	0.019	0.061	0.056	0.141	0.132	0.012	0.009	0.327	0.321	0.484	0.476	1.839	1.799	0.043	0.04
Station24	0.028	0.024	0.048	0.044	0.162	0.157	0.041	0.034	0.352	0.337	1.423	1.33	1.754	1.72	0.038	0.035
Station25	0.906	0.872	0.523	0.514	0.215	0.203	0.137	0.131	3.119	3.108	1.271	1.437	5.5	5.429	0.375	0.368
Station26	0.017	0.013	0.047	0.041	0.061	0.054	0.009	0.005	0.175	0.202	0.184	0.176	1.726	1.677	0.033	0.028
Station27	0.027	0.022	0.052	0.045	0.193	0.182	0.014	0.009	0.853	0.844	0.425	0.419	1.768	1.712	0.037	0.032
Station28	1.408	1.402	0.546	0.538	0.629	0.574	0.321	0.308	1.728	1.707	3.141	3.138	5.748	5.681	0.41	0.404
Station29	0.026	0.018	0.051	0.043	0.057	0.045	0.01	0.008	0.854	0.847	0.456	0.418	1.759	1.696	0.036	0.031
Station30	1.427	1.436	1.178	1.172	0.926	0.938	0.249	0.242	6.828	6.824	2.901	2.878	10.683	10.634	0.831	0.827

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Minimum	**0.016**	**0.009**	**0.02**	**0.018**	**0.031**	**0.027**	**0.008**	**0.005**	**0.081**	**0.075**	**0.121**	**0.107**	**1.514**	**1.497**	**0.014**	**0.013**
Maximum	**2.425**	**2.448**	**1.178**	**1.172**	**2.099**	**2.095**	**0.321**	**0.308**	**6.828**	**6.824**	**6.27**	**6.16**	**10.683**	**10.634**	**0.831**	**0.827**
Mean	**0.372**	**0.367**	**0.242**	**0.234**	**0.462**	**0.453**	**0.067**	**0.062**	**1.655**	**1.644**	**1.332**	**1.312**	**3.283**	**3.216**	**0.176**	**0.17**
Standard Deviation	**0.587**	**0.591**	**0.319**	**0.308**	**0.49**	**0.491**	**0.081**	**0.08**	**1.8**	**1.804**	**1.509**	**1.499**	**2.522**	**2.441**	**0.229**	**0.222**
Standard (BIS and WHO)	**0.3**		**0.01**		**1.5**		**0.05**		**5**		**0.3**		***N/A***		***N/A***	

Table: 1

Manganese (Mn)

Manganese (Mn) is a very common metal found in soils and sediment. On the surface of soil and rock grains, it is commonly found with iron as mineral oxide coatings. These oxides are dissolved and may be transported to the well through the ground water, when ground water contacts these coatings. A nervous system disease with symptoms like the Parkinson's disease has resulted from exposure to high concentrations of manganese over the course of years.

The concentration of Manganese ranged from 0.01 mg/l to 2.43 mg/l with a mean value of 0.36 mg/l. Most of the samples exceeded the permissible limit of 0.3 mg/L (BIS, 2012) with the maximum value recorded at S18 (2.43 mg/L). Current results show 30% samples are with high Manganese concentrations, 33% of samples show within the acceptable limits and 36.67% of samples show below the limits of BIS, 2012 (0.3 mg/L). Similar results were observed in the study of Amadi *et al.*, (2020) who found manganese concentration range from 0.01 mg/l to 0.78 mg/l with an average value of 0.29 mg/l which is above the acceptable limit of 0.2 mg/l (NSDWQ. 2017). High concentrations of Manganese are due to domestic and industrial wastes. Mn is an essential element for plants and animals, and it is used in products such as batteries, glass and fireworks (Aboud *et al.*, 2009)

Lead (Pb)

If water corrodes due to Lead being dissolvable into it, a lead-containing material such as lead pipes, lead solder, or brass fittings emerges out of it. Even at low exposure levels, Lead can be harmful to human health being a toxic metal. Lead can also bio-accumulate in the body over time with it being persistent.

The concentration of Lead ranged from 0.01 mg/l to 1.17 mg/l with a mean value of 0.23 mg/l and the maximum value at S30 (1.17 mg/L). In the present study, all the samples are beyond the permissible limits of BIS. These results co-relate with the work of Amadi *et al.*, (2020), whose reports reveal that the concentrations of lead in the groundwater ranged from 0.02 mg/l to 1.05 mg/l with an average value of 0.04 mg/l. High Lead concentration may be due to contents of leaded gasoline, paint, pesticides. Leaded gasoline releases lead organo-metallic compounds that reach the surface water and pollute it (Mohan Meethu and Jaya 2021). High concentrations of Lead are seriously a concern to health. Presence of Lead in the food chain can result in bio-accumulation, thus becoming harmful to human health (Owamah 2013, Dahunsi *et al.,* 2012, WHO, 2019).

Ingestion of Pb usually happens through water or food, it usually accumulates in the skeleton where it causes health disorders including neurological, sub-encephalopathic, and behavioural defects (WHO, 1993, 2006). Lead poses health risks also to kids. Kids become very vulnerable on exposure to lead (Pb); it is permeable from blood brain barricade and has neurotoxin effects even at less level of exposure to Pb (Athar and Vohora 1995).

Copper (Cu)

Existence of Copper in the environment is due to the natural and anthropogenic sources such as phosphate fertilizers, paints, ceramics and mining activities. Copper can get into drinking water either directly through contaminated well water or from corrosion of copper pipes if the water is acidic. Copper concentrations in drinking water may fluctuate due to variations in water characteristics like pH, hardness, and its availability by the way it is distributed for various purposes (WHO, 2004).

The concentration of copper ranged from 0.02 mg/l to 2.09 mg/l with a mean value of 0.45 mg/l and maximum value was recorded at S25 (2.09 mg/L). According to the results in the present study, most of the samples exceeded the acceptable limits of BIS, 2012 for drinking water (0.05 mg/L). Similar observation was observed by Mahapatra *et al.*, (2020) who observed the Copper values are in the range from 0.028 to 0.395 mg/L during pre-monsoon and for the post-monsoon 0.01 to 0.419 mg/L.

Industrial wastes, agricultural wastes, and weathering of copper-bearing rocks are viewed as some of the main sources for copper in rural water bodies (Adeyemi and Ojekunle 2021). Drinking Water contaminated with excess copper causes a lot of health problems like base of nose, eyes, and mouth bothering, which can prompt cerebral pain, stomach ache, discombobulation, retching, and diarrhoea (Nwachukwu *et al*., 2014)

Chromium (Cr)

Chromium-6 naturally occurs in the environment as a result of the erosion of natural chromium deposits. It can also be created through industrial processes. There have been documented cases of chromium being released into the environment as a result of leakage, poor storage, or insufficient industrial waste disposal practices. Compounds containing hexavalent chromium are classified as a known human carcinogen. It has been linked to lung cancer in workers who have been exposed to high concentrations of it in the air.

The concentration of Chromium ranged from 0.007 mg/l to 0.31 mg/l with a mean value of 0.064 mg/l and maximum value was recorded at S28 (0.31 mg/L). In the present study 33.33% of samples are above the acceptable limits and 66.67% samples are within the acceptable limits. Similar studies were observed by Ukah *et al*., (2020) reported Cr concentration in the range of 0.00–0.32 mg/l with an average of 0.032 mg/l.

The excessive concentration of Cr is due to the usage of pesticides in plantation or agricultural land (George *et al.*, 2017). Elevated concentrations of chromium are carcinogenic, toxic and teratogenic. Chromium (VI) can enter the body through air, food, or water. Chromium in high concentration results in membrane ulcers and liver necrosis (O'Brien *et al.*, 2003). Chromium is toxic at higher levels of concentration in water and can cause damage to human organs such as the intestines, kidney, liver, lungs and stomach (Juang *et al.*, 2009).

Zinc (Zn)

Zinc is an essential mineral that the human body uses in multiple ways. The fact is that Zinc is the second most abundant trace mineral and is present in every cell of the human body only after Iron. Zinc compounds are widely used in the industries to make castings, dyes, household utensils, ointments, paints, printing plates, rubbers and wood preservatives. Zinc is released into the environment through crude oil production, dumpsites, gas flaring, mining and steel production.

The concentration of Zinc ranged from 0.078 mg/l to 6.82 mg/l with a mean value of 1.64 mg/l and maximum value was observed in S30 (6.82 mg/L). The present study shows that very few samples are above the acceptable limits of BIS. Similar studies were observed by Karki *et al.*, (2020) and reported high concentration of Zn in soil samples of agricultural field at Kanpur village with concentration of 5.2-6.87 mg/kg in pre monsoon and 5.9-7.9 mg/kg post-monsoon season respectively. These values are 7-11 times and 10-13 times respectively above the permissible limit.

Zinc is considered as an essential trace metal to function as a catalyst in enzymatic activity of the human body (Tewodros *et al.*, 2017). However, its accumulation in the human body causes harmful effects such as: acceleration of anaemic conditions, decrease in good cholesterol, nausea, stomach cramps and vomiting (Reda, 2016). Excessive Zn causes health problems like nausea, dizziness, gastric ulcers, muscle pain, impairment of immune function, dehydration, poor muscle coordination, fatigue, increased blood pressure level of insulin-like growth and testosterone (Michael, Standford, 2003).

Iron (Fe)

Iron is a naturally occurring metal that can be found in the form of magnetite, hematite, and other minerals. It enters water during the extraction of metal from its ore. Aluminium waste products containing iron are also discharged into the water. It is an essential nutrient for most organisms, and it is a central atom in haemoglobin, which aids in the transport of oxygen to various organs via the blood. Excess amounts of iron in groundwater can be harmful to health. The Fe content in water samples also occurs from geologic attributes like the presence of weathered magmatic rocks (GSI, 2005).

The concentration of Iron ranged from 0.11 mg/l to 6.21 mg/l with a mean value of 1.32 mg/l and maximum value was recorded at S18 (6.21 mg/l). 83.33% of sample stations have shown values above the acceptable limits of BIS, 2012 (0.3 mg/L). The remaining 26.67% samples are below the permissible limits. Similar results were recorded by Lanjwani *et al.*, (2020) who noticed Fe results ranging between 15.4 and 279 mg/L. High concentration of iron in water could be either due to the wastewater's discharge domestically or it's leaching from the sewage farms and houses (Varghese J. & Jaya D.S, 2014).

The excess deposition of iron in the organs of humans may lead to shrinkage in the size of their liver and later also to fibrosis and cirrhosis (Mohan Meethu and Jaya 2021). Water containing excessive concentration of iron was reported to contribute for a human health hazard leading to hemochromatosis, whose signs

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include fatigue with also heart disease, liver complications and diabetes eventually (Nwachukwu *et al.*, 2014).

Heavy metal Pollution Index:

The HPI values in the study area during pre-monsoon and post-monsoon seasons can be seen in Table 1. The HPI values in both the seasons range from 1.497 to 10.683 respectively. The results indicated that Pre-monsoon values are higher than the post-monsoon season due to dilution effect. Sampling stations S1, S18, S30 have higher values due to urbanization effect and domestic effluents. All the HPI values show low heavy metal contamination.

The critical pollution index value for drinking water is 100. If the samples have heavy metal pollution index values greater than 100, water is not potable (Balakrishnan and Ramu 2016). As the HPI values are less than 100 the water is considered as potable water even though some heavy metals values have exceeded the desirable limits of BIS 2012 the water is not good for consumption.

Heavy metal Evaluation Index

The HEI was calculated for pre-monsoon and post-monsoon seasons using heavy metal concentration in sampling stations and maximum admissible concentration. The HEI values range from 0.013 to 0.831 which can be seen in Table 1.

According to Boateng *et al*., (2015) the values were divided into 3 classes using a multiple of the mean value. The three classes demarcated are HEI < 10 low, HEI 10- 20 medium and HEI > 20 high. All the stations were low in heavy metal concentrations.

HEI gives the overall water quality with respect to concentrations of heavy metals Edet and Offiong (2002).

Covariance

Covariance (Pre-M)	HPI	HEI
HPI	6.36	
HEI	0.576	0.052

Table 2

Covariance (Post-M)	HPI	HEI
HPI	5.959	
HEI	0.541	0.049

Table 3

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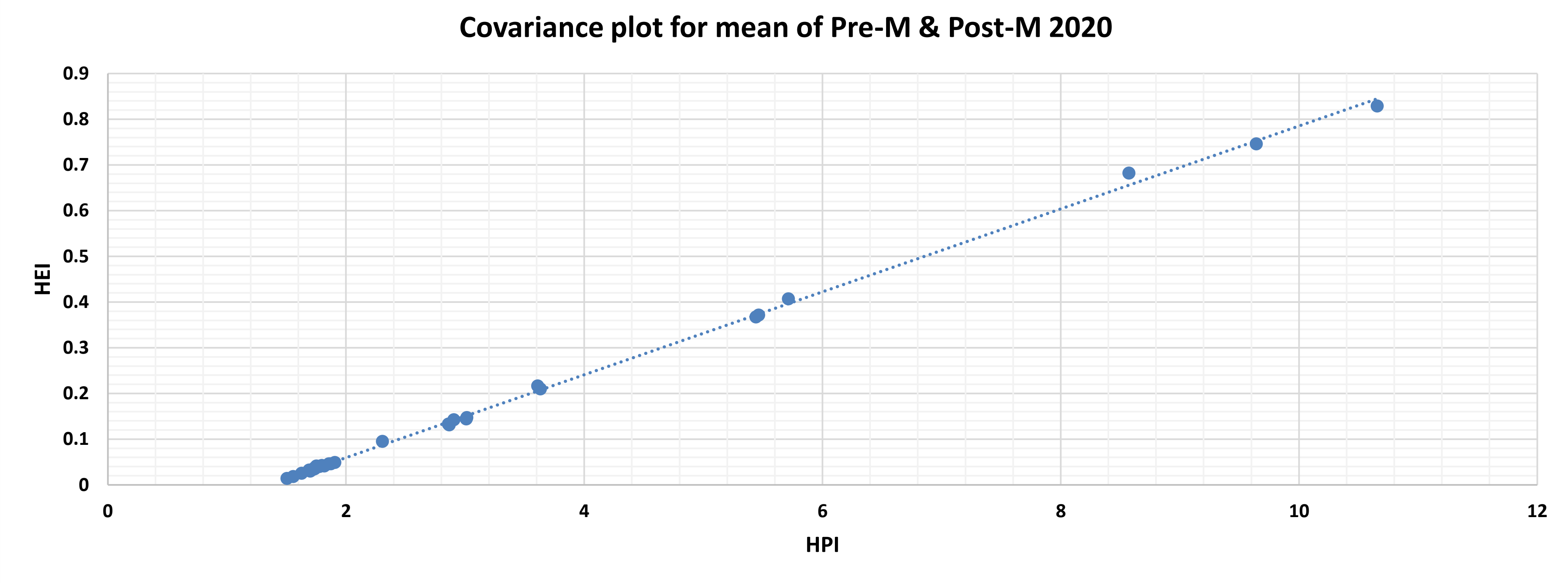

Graph 1

Covariance indicates the relationship of two variables whenever one of them changes. If an increase of value in one variable also results in an increase in value of the other variable, then both variables are said to have a positive covariance. If decrease in the value of one variable also causes a decrease of value in the other, then both variables are said to have a negative covariance. If a change (increase or decrease) in the value of one variable doesn't alter value of the other, then both variables are said to have zero covariance.

Unlike variance whose range is from 0 to +∞, as covariance could also assume a negative value with a range from -∞ to +∞, so while variance always only has magnitude, covariance always has both magnitude and direction.

The heavy metal evaluation index (HEI) shows strong covariance with heavy metal pollution index (HPI) and serves as a good tool for forecast of future heavy metal pollution trends.

For each (pre-M and post-M) of the two seasons, the individual variances of HPI and HEI for each station from their respective means is further calculated together as a single bi (HPI and HEI) -variate covariance value representing the entire set of the 30 sampling stations.

As the values per each (Pre-M and Post-M) season are to be analysed individually to arrive at inferences specific to the season they (values) are tabulated as covariance matrices. The covariance for the pre-monsoon season is 0.576 and for the post-monsoon is 0.541 which can be seen in Table 2 and Table 3. The variance of HPI is 6.36 and the variance of HEI is 0.052 during the pre-monsoon season. The variance of HPI is 5.959 and the variance of HEI is 0.049 during the post-monsoon season which can also be seen in Table 2 and Table 3.

As it is just sufficient to arrive at the prevailing covariance trend (of positive or negative or zero) to forecast the future pollution levels, so a scatter plot of the mean (rather than individual season) values for the two seasons is depicted as a Covariance-graph in Graph 1. Because the covariance between HPI and HEI is positive, so a change (increase or decrease) in value for one (HPI or HEI) of them will also cause the same change (increase or decrease respectively) in the value of other (HEI or HPI respectively).

The covariance is high in pre-monsoon compared to the post-monsoon; this is due to higher concentration of heavy metals in the dry season. During monsoons the concentration of heavy metals is low, thus decreases the heavy metal values in post-monsoon season.

Pearson’s correlation coefficient

Correlation between heavy metals is calculated to understand the relationship between various metals (Muhammad *et al*., 2010; Belkhiri and Narany 2015)

Degree of correlation: (Source: www.statisticssolutions.com)

1. Perfect: If the value is near ±1, then it is said to be a perfect correlation: as one variable increases, the other variable tends to also increase (if positive) or decrease (if negative).

2. High degree: If the coefficient value lies between ± 0.50 and ± 1, then it is said to be a strong correlation.

3. Moderate degree: If the coefficient value lies between ± 0.30 and ± 0.49, then it is said to be a medium correlation.

4. Low degree: when the value lies below ±0.29, the it is said to be a small correlation.

5. No correlation: when the value is 0.

The correlative relationships between heavy metals were analysed and presented in Table 4 to Table 7

Pre-M Correlation	Mn	Pb	Cu	Cr	Zn	Fe
Mn	1					
Pb	0.842	1				
Cu	0.841	0.436	1			
Cr	0.697	0.668	0.454	1		
Zn	0.126	0.319	0.144	0.888	1	
Fe	0.14	0.254	0.318	0.951*	0.049*	1

Table 4

Low Degree (r < ±0.29)	Moderate Degree (±0.30 < r < ±0.49)	High Degree (±0.50 < r < ±1.0)
Zn – Fe (0.049*), Mn – Zn (0.126), Mn – Fe (0.14), Cu – Zn (0.144), Pb – Fe (0.254)	Cu – Fe (0.318), Pb – Zn (0.319), Pb – Cu (0.436), Cu – Cr (0.454)	Pb – Cr (0.668), Mn – Cr (0.697), Mn – Cu (0.841), Mn – Pb (0.842), Cr – Zn (0.888), Cr – Fe (0.951*)

Table 5

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* Least co-relation value is marked in red, and highest co-relation value is marked in green.

In the pre-monsoon season Chromium has high degree correlation with iron (r = 0.951), then with Zinc (r = 0.888), then with Manganese (r = 0.697). Manganese shows good correlation with lead (r = 0.842), then with copper (r = 0.841). Zinc has least correlation with iron (r = 0.049), then with Manganese (r = 0.126). Manganese has weak correlation with Zinc (r = 0.126), then with Iron (r = 0.14); along with many other correlations which can be seen in correlation matrix (Table 4) and 'degree' of correlation can be seen in Table 5.

Post-M Correlation	Mn	Pb	Cu	Cr	Zn	Fe
Mn	1					
Pb	0.865	1				
Cu	0.816	0.442	1			
Cr	0.698	0.689	0.442	1		
Zn	0.123	0.318	0.144	0.917*	1	
Fe	0.141	0.264	0.322	0.754	0.05*	1

Table 6

Low Degree (r < ±0.29)	Moderate Degree (±0.30 < r < ±0.49)	High Degree (±0.50 < r < ±1.0)
Zn – Fe (0.05*), Mn – Zn (0.123), Mn – Fe (0.141), Cu – Zn (0.144), Pb – Fe (0.264)	Pb – Zn (0.318), Cu – Fe (0.322), Pb – Cu (0.442), Cu – Cr (0.442)	Pb – Cr (0.689), Mn – Cr (0.699), Cr – Fe (0.754), Mn – Cu (0.816), Mn – Pb (0.865), Cr – Zn (0.917*)

Table 7

* Least co-relation value is marked in red, and highest co-relation value is marked in green.

During the post-monsoon season Chromium has good correlation with Zinc (r = 0.917), then with Iron (r = 0.754), then with manganese (r = 0.699), then with lead (r = 0.689). Manganese shows good correlation with lead (r = 0.865), then with copper (r =

0.816). Zinc has least correlation with iron (r = 0.05), then with Manganese (r = 0.123); along with many other correlations which can be seen in correlation matrix (Table 6) and 'degree' of correlation can be seen in Table 7.

By seeing the correlation of heavy metals in both the seasons it can be concluded that there is positive correlation between metals and slight change in correlation of heavy metals between the seasons, the source of contamination is same which is due to domestic sewage, use of inorganic fertilizers, land leachates, septic tank effluents.

4. Conclusions

- In this study, the concentration of heavy metals in the groundwater samples of Pendurthi were analysed by calculating Heavy metal pollution index, Heavy metal evaluation index, covariance and Pearson's correlation coefficient.
- The concentrations of heavy metals like lead, manganese, iron, zinc, copper and chromium are above the acceptable limits of BIS standards. All the HPI values in the study area show low heavy metal contamination. As the HPI values are less than 100, so the water is considered as potable water. The HEI values indicate low heavy metal pollution.
- Pearson's correlation coefficient shows good correlation between Cr-Zn, Cr-Fe, Mn-Pb and with other metals. Mn has weak correlation with Zinc and iron. Heavy metals like manganese, lead, copper, chromium, zinc and iron have exceeded the acceptable limits of BIS 2012 in some of the sampling stations.
- The present conditions in the study area did not meet the standards which may lead to severe contamination in the near future. Groundwater gets contaminated with heavy metals from both natural & anthropogenic sources, such as run-off containing domestic sewage, use of inorganic fertilizers, land leachates, septic tank effluents. Degradation of water quality is due to rapid population growth, urbanization, indiscriminate use of resources, industrial and anthropogenic activities.
- It can be concluded that ground water situation in Pendurthi mandal is not good, due to the multiple sources of pollution based on this study. The study concludes and recommends that the groundwater needs treatment to reduce the pollutants and heavy metals before consumption.

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