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Assessment of heavy metal concentrations in groundwater sources adjacent to municipal solid waste disposal site at Thirunallar, Karaikal, India

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Abstract
This study was carried out to assess the extent of the heavy metal pollution level in the groundwater at Thirunallar temple town in the vicinity of MSW dump site at Thirunallar Municipality. Thirty groundwater samples were collected during March 2015 around the study area. Selected heavy metals and the key physico chemical parameters were analyzed by standard methods. The average concentrations of heavy metals -Cu, Zn, Mn, Pb, Cd, and Cr were 0.08, 0.37, 0.03, 0.17, 0.31, and 0.13 mg/l respectively. Correlation matrix indicates that the groundwater has assimilated various contaminants from the chemical industries, agricultural activities, and largely untreated municipal sewage systems. The concentrations of Cu, Mn, Pb, Cd, and Cr were beyond the prescribed CPCB standards (India), hence the groundwater near the vicinity of the solid waste disposal site can be used only for the irrigational and non drinking domestic purposes, while it is highly unsafe for drinking purpose.

Keywords: groundwater, heavy metals, solid waste, dump site, Thirunallar temple

1. Introduction

Solid waste causes environmental pollution if not disposed properly. Safe disposal of Municipal Solid Waste (MSW) is a worldwide concern, particularly in developing countries (Aderemi *et al*. 2011) [1]. Dumpsites have been recognized as one of the real dangers to groundwater assets. Water is one of the world's most significant assets, yet it is under constant danger because of the environmental change, anthropogenic activities (especially the climate change) frequent dry spells, hazardous development, and dumping of wastes from various sources. Population explosion and rapid urbanization has led to many natural resource issues including groundwater contamination (Mor *et al*. 2006, Longe and Balogun 2009, Patil *et al*. 2013 & Umarani and Ramu 2014) [22, 26, 31]. In India the groundwater contamination and water scarcity are serious problems (Jhansi and Mishra 2013) [17]. The nature of water has now turned into a critical point in all the nations, especially drinking water. Despite the fact that water assumes a vital part in human life, it has also a potential for transmitting a wide range of contagious diseases, almost 95% of the all diseases are water born (Selvam *et al*. 2015) [30]. According to Rai (2004) [27], around 80 % of the world's surface is secured by water yet subjectively 97 % of this is inconceivable normal asset, falls unfit for human utilization. The greater part of the fresh water bodies are turning out to be progressively dirtier, in this way diminishing the portability of water (Kumaravel *et al*. 2014) [19]. The purpose of the study was to assess the level of groundwater contamination through leachate pollution near municipal solid waste dumpsite at the Thirunallar temple town, where no previous study was done before.

2. Materials and Methods

Study area: Thirunallar temple town is a small town in Karaikal, India, in the Union Territory of Puducherry, and is situated at Latitude, 10.9256° N, and Longitude, 79.7917° E at a distance of 6Km from the sea. The enclave is found 140 km south of the city of Puducherry, 158 km East of Trichy and is known for its rich social legacy. Thirunallar is most noted for the sanctum of Lord Shani (Saturn).One the most important is a sacred bathing place or Nalatheertham is the only temple in India that is dedicated to Lord Shani. The Nalatheertham is a major water polluting and water scarcity zone due to the overexploitation of groundwater for mass bathing of devotees. Thirunallar municipality has 11 villages-Ambagarathur, Keezhavoor, Nallazhundur, Pettai, Sellur, Sorakudy, Sethur, Subrayapuram, Thennankudy, Thevamapuram, and Thirunallar. Thirunallar temple town generates larger quantities of municipal solid waste during festivals and these are dumped in the open agricultural lands. Geologically, the study area is mostly of clay, alluvium, sandstone, and sandy soils of quaternary age (Gopinath *et al*. 2015).

2.1 Sample collection of groundwater

Water supplies in this region are from bore wells and hand pumps, which rely exclusively on groundwater resource. Groundwater samples were collected from 30 different sources consisting of 13 bore wells (temple 1, government guest house 1, Oil and Natural Gas Corporation quarters 1 (ONGC), 2 private hotels and 8 households) and 17 hand pumps (10 single household and 7 joint household) Out of 30 samples, 13 samples were collected from within the 2km from the dump site and 9 samples were collected from more than 2.1 to 5km away from the dumping site and other 8 samples were collected from above the 5.1km away the dumping site. The study was conducted during March 2015, over the period of 21 days. Polyethylene bottles (500ml) were used for sample collection (with replicates) and also to mark the latitude and longitude for the study area. Water samples were collected and mixed with a few drops of HNO3 (concentrations of 0.15%, pH is below 2) to preserve them for a week's period before heavy metals analysis. Key physical and chemical parameters (pH, Ec, salinity and TDS) were analyzed using international standard methods (APHA 1994).The heavy metals such as Cr, Cu, Cd, Mn, Pb, and Zn were analyzed by Atomic absorption spectroscopy (AAS). Table 1, 2 and 3 represents sampling location and water sources and Figure 1 indicates groundwater samples collected at location in and around Thirunallar municipality.

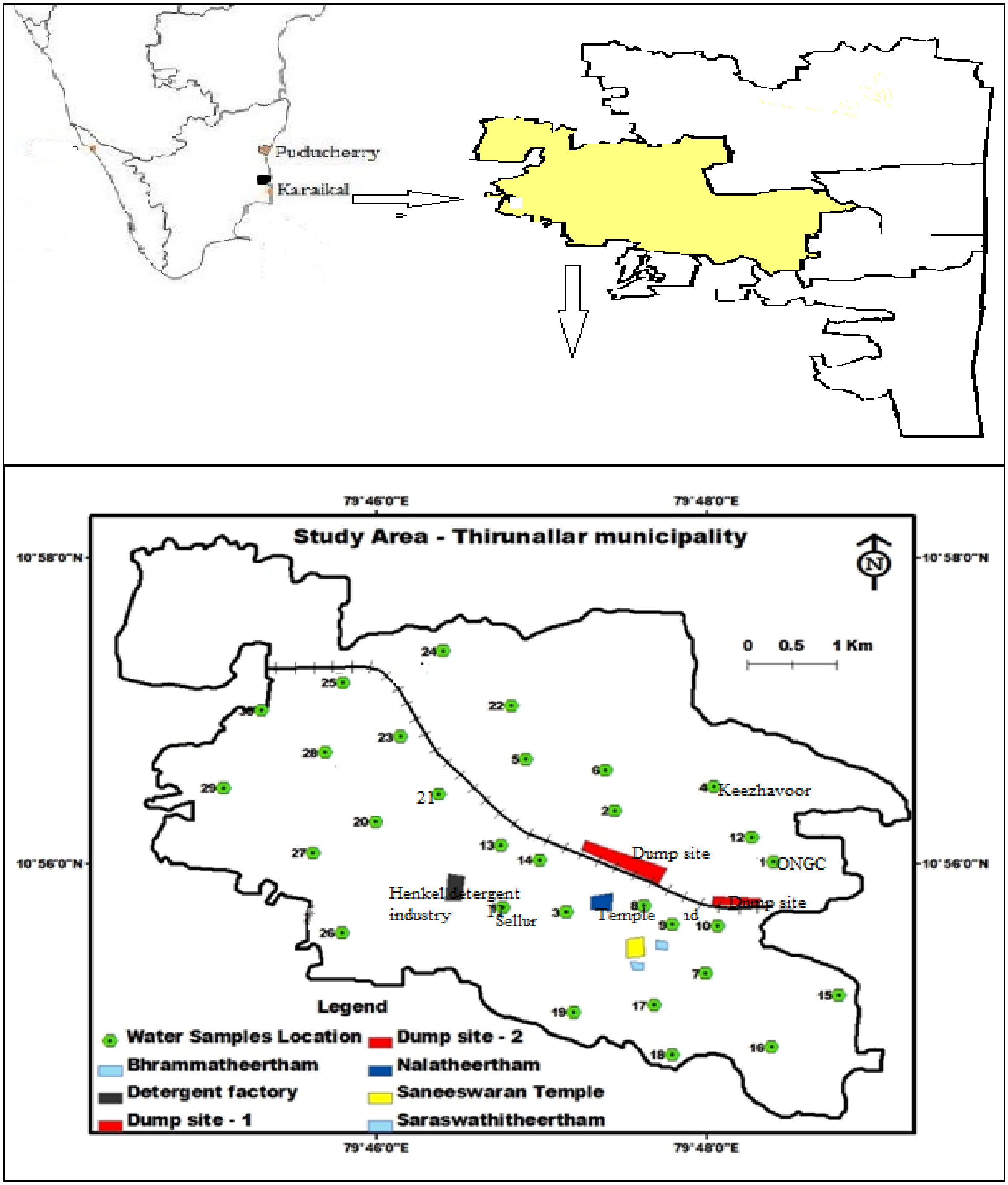

Fig 1: Map of the study area indicating the location of groundwater samples

Table 1: Sampling location and water sources within 2km from the dumping site

Sampling. No	Latitude	Longitude	Location name	Sources	Distance from the dump site(km)
1	10.9327	79.8052	ONGC	Bore well	0.25
10	10.9247	79.863	Thirunallar government guesthouse	Bore well	0.3
3	10.9265	79.7874	Thirunallar shaga nagar	Handpump	0.4
2	10.9519	79.7888	Ganesh nagar Thirunallar	Borewell	0.5
6	10.9257	79.8112	Keezha Subrayapuram	Borewell	0.5
14	10.9257	79.7569	Thirunallar Edison nager	Handpump	0.5

8	10.9278	79.7875	Nallankulam street	Bore well	0.6
5	10.9336	79.793	Mela Subrayapuram	Borewell	1
9	10.9352	79.7802	T. Pallivasal street Thirunallar	Handpump	1
7	10.9269	79.7988	Thirunallar melavithy	Bore well	1.3
12	10.9391	79.7991	Keezhavoor main road	Bore well	1.5
13	10.9262	79.7786	Sorakkudy main road	Borewell	1.5
4	10.9322	79.7988	Keezhavoor	Borewell	1.5

Table 2: Sampling location and water sources more than 2.1 to 5km away from the dumping site

Sampling. No	Latitude	Longitude	Location name	Sources	Distance from the dump site(km)
11	10.9328	79.8291	Sellur	Handpump	2.2
15	10.9266	79.8263	Thakloor	Bore well	2.5
16	10.9202	79.7986	Nivacherry	Bore well	3
17	10.9152	79.8132	Adhipadugai main road	Handpump	3
19	10.9223	79.8302	Pettai	Handpump	3.2
21	10.9363	79.7741	Karukkankudi	Handpump	3.5
22	10.9491	79.7777	PAJANCOA	Bore well	3.6
18	10.9077	79.7936	Adhipadugai	Handpump	4
20	10.9412	79.7428	Thennagudy	Handpump	4.8

Table 3: Sampling location and water sources above the 5.1km away from the dumping site

Sampling. No	Latitude	Longitude	Location name	Sources	Distance from the dump site (km)
27	10.9358	79.7438	Sethur	Handpump	5.5
23	10.9547	79.7661	Pathakudy	Handpump	6.5
24	10.9469	79.7558	Valathamangalam	Handpump	6
25	10.9483	79.7427	Nallambal	Handpump	6.5
28	10.9705	79.4421	Thamanakudy	Handpump	7
26	10.9222	79.7444	Kottapady	Handpump	7.5
29	10.9522	79.7269	Ambagarathur south	Handpump	8
30	10.9616	79.7291	Ambagarathur north	Handpump	8.2

3. Results and discussion

The heavy metal concentrations of groundwater from the bore-well and hand pump samples around the waste disposal site are presented in Table 4.

Table 4: Heavy metal concentration in groundwater in the sampling sites (mg/l)

Heavy metal concentration (mg/l)						
Samples ID	**Cu**	**Zn**	**Mn**	**Pb**	**Cd**	**Cr**
SP1	0.101	0.05	0.148	0.307	0.024	0.191
SP2	0.794	0.209	0.035	0.285	0.06	0.038
SP3	1.145	0.207	0.267	0.643	0.081	0.373
SP4	0.203	0.063	0.537	0.327	0.054	0.046
SP5	0.472	0.144	0.334	0.332	0.034	0.039
SP6	1.248	0.365	0.483	0.512	0.021	0.012
SP7	0.133	0.054	0.183	0.233	0.033	0.095
SP8	1.161	0.361	0.251	0.332	0.09	0.151
SP9	0.046	0.037	0.124	0.282	0.034	0.052
SP10	0.298	0.098	0.056	0.217	0.014	0.124
SP11	0.331	0.107	0.058	0.206	0.352	0.197
SP12	0.004	0.02	0.222	0.389	0.031	0.069
SP13	0.407	0.154	0.112	0.227	0.02	0.261
SP14	0.093	0.047	0.035	0.288	0.014	0.048
SP15	0.071	0.058	0.348	0.401	0.018	0.053
SP16	0.009	0.038	0.111	0.187	0.03	0.019
SP17	1.325	0.483	0.045	0.437	0.027	0.012
SP18	0.167	0.053	0.33	0.353	0.003	0.04
SP19	0.361	0.068	0.361	0.247	0.019	0.181
SP20	0.449	0.143	0.177	0.231	0.031	0.077
SP21	0.038	0.036	0.135	0.262	0.011	0.014
SP22	0.304	0.1	0.09	0.468	0.023	0.062
SP23	0.007	0.037	0.155	0.291	0.027	0.017
SP24	0.012	0.033	0.24	0.337	0.021	0.031
SP25	0.131	0.059	0.128	0.321	0.03	0.048
SP26	1.291	0.333	0.041	0.265	0.002	0.099

SP27	0.063	0.037	0.048	0.306	0.017	0.051
SP28	0.485	0.116	0.047	0.217	0.03	0.007
SP29	0.061	0.052	0.072	0.175	0.019	0.04
SP30	0.115	0.53	0.043	0.238	0.011	0.012
SD	0.43	0.14	0.13	0.1	0.06	0.08
Average	0.37	0.13	0.17	0.31	0.03	0.08
Maximum	1.32	0.53	0.53	0.64	0.35	0.37
Minimum	0.004	0.02	0.035	0.175	0.002	0.007

Heavy metal concentration (maximum, minimum, mean and standard deviation) of the analysed groundwater samples from the Thirunallar municipality are presented in Table 4. Maximum Lead concentration in the groundwater was 0.64 mg/l and average - 0.31mg/l. Keezhavur site was located adjacent (within 1.5 km) to the solid waste dumping area. It was highly contaminated with lead in the range of 0.64mg/l. The lead contamination in groundwater may be due to the solid waste dump site, industrial effluents, household sewages, and agricultural runoff containing phosphatise manures human and animal excretion (Jameel *et al*. 2012). Lead enters the water through contact with the pipes. Lead can filter into water from channels, weld, apparatuses and spigots (metal), and fittings (Kavitha and Sugirtha 2013) [18]. It is well established that higher concentration of heavy metals in the groundwater causes serious health issues. It affects the central nervous system, stomach, kidney, eyes, causes loss of memory, and sometimes even death (WHO 2011, Jarup 2003, Momodu and Anyakora, 2010) [33, 16, 24]. Table 5 provides WHO and Indian standards for drinking water quality.

Table 5: WHO and Indian standards for drinking water quality

Parameter	WHO standards (2011) [33]	Indian standards (2012) [8]	Present Study Mean/SD value
Ph	6.5-8.5	6.5-8.5	7.5±0.43
EC	1000	1000	2490±984
Salinity	-	-	3.76±1.5
TDS	1000	1000	1210±453
Cu	2	0.05	0.37± 0.43
Cr	0.5	0.05	0.08±0.08
Zn	3	5	0.13±14
Mn	-	0.1	0.17±0.13
Cd	0.005	0.01	0.03±0.06
Pd	0.01	0.1	0.31±0.10

The desirable limit of cadmium for drinking water standards is 0.01mg/l. The average value of cadmium present in groundwater was 0.03mg/l and maximum, minimum of 0.352mg/l to 0.002mg/l. Sample 11 had a higher amount of Cd. This may due to the sample location, located near an industry (Henkel Spic India Limited- Detergent Powder and Washing Soap). Mor *et al*. (2006) [22] in another study from a different area has arrived at this conclusion. By and large, higher amount of cadmium contamination in the groundwater could cause a number of ailments such as high blood pressure, kidney damage, destruction of testicular tissue and destruction of red blood cells as reported by Haileslassie and Gebremedhin (2015) [14]. Based on the Indian standard of drinking water, the permissible limits of Cu in drinking water is 0.05mg/l. The average value of Cu was 0.375mg/l and the maximum, minimum value of 1.325mg/l to 0.004mg/l. Water samples collected from Thirunallar, government guest house portrayed higher copper concentration which was slightly above the Indian standard 2012 [8]. The water samples collected had higher concentration of Cu 1.325mg/l and hence, all water samples were contaminated due copper, thus the corresponding water sources were not suitable for drinking. The present study conforms to the study carried out by Raman and Narayanan, (2008) [28] at Pallavaram solid waste landfill site in Chennai. Contamination of Mn to the surface water and groundwater could be ascribed due to the landfills leachate, industries, agricultural runoff, and domestic sewage (Nartey *et al*. 2012) [25]. The maximum and minimum range of Mn was 0.537mg/l and 0.35mg/l. Concentration of Mn was high in Khezhasubraya puram (0.5km) water sample - 0.537mg/l. Levels exceeding 0.1 mg/l, manganese in water supplies causes an undesirable taste and color (Ali 2013) [3]. The desirable limit of Zn is 5mg/l. The average concentration of Zn was 0.173mg/l and maximum, minimum values were 0.537mg/l to 0.035mg/l. Most of the groundwater pollution in our country are reportedly from industrial and domestic wastes (El-Fadel *et al*. 1997, Bhagure, and Mirgane 2011.) [9, 7]. Though Zinc is one of the fundamental components required for appropriate working of the body system, Zn becomes toxic from 20 to 50 μg g^{-1} (Babu *et al*. 2013, Gupta and Gupta 1998) [5, 13]. In our study area Zn concentration is well within its limits. Presence of Cr in the groundwater is generally due to the anthropogenic activities such as, leather, textile, electroplating industries and solid waste landfills (Agrawal 2006) [2]. The average value of chromium was 0.081mg/l and the max & min values were 0.373mg/l to 0.007mg/l respectively. As already found the concentration of Cr was very low. Analysis of Samples collected from the Khezhavoor village (1.5km) had given very different results- Cr was found to be in very high concentration due to the proximity to the dumping sites. Physico-chemical parameters in groundwater samples are represented in Table 6.

Table 6: Physico-chemical parameters in groundwater samples (mg/l)

Samples	Ph	Salinity mg/l	EC(µs/cm)	TDS mg/l
SP1	7.4	3.45	1830	910
SP2	7.86	3.34	1980	1010
SP3	8.47	2.36	1400	710
SP4	7.45	7.25	4360	2210
SP5	7.75	5.25	3100	1560
SP6	7.65	3.92	2340	1170
SP7	7.9	4.18	3510	1500
SP8	7.3	4.23	4300	1310
SP9	7.9	4.18	2510	1270
SP10	7.76	4.49	2700	1360
SP11	7.2	3	3100	1700
SP12	7.3	3.59	2160	1090
SP13	7.65	2	3900	1230
SP14	7.57	2.82	1680	840
SP15	7.22	6.81	3500	1760
SP16	8.23	3.77	2260	1130
SP17	7.6	6.47	3930	1930
SP18	7.98	4.76	2860	1430
SP19	7.31	3.2	2400	1050
SP20	7.43	2.27	1360	680
SP21	7.55	1.87	1080	540
SP22	7.24	3.13	1890	950
SP23	6.9	4.12	2710	1250
SP24	7.43	4.34	2620	1320
SP25	6.09	3.09	1960	1800
SP26	7.27	2.23	1330	660
SP27	7.08	2.47	1900	870
SP28	7.35	1.87	1120	560
SP29	7.42	6.48	3940	1980
SP30	7.9	1.86	1110	530
Average	7.5	3.76	2494.66	1210.33
Maximum	8.47	7.25	4360	2210
Minimum	6.09	1.86	1080	530
SD	0.43	1.5	984.38	453.81
Who standard (2006) [33]	6.– - 8.5	-	1000	1000
Indian standard (2012) [8]	6.– - 8.5	-	1000	2000

One of the important factors for water quality assessment is pH. Normal acidity and alkalinity ranges are 6.5 to 8.5 for drinking water as per WHO standards. The result of mean values was 7.5, maximum and minimum 8.47 to 6.09. Hence, pH as such is not a problem. The mean, maximum and minimum concentration of salinity in the groundwater near Khezha subrayapuram(0.5km) were 3.76ppt, 7.25ppt and 1.86ppt respectively. There are many reasons for increased salt content in the groundwater such as- seawater intrusion, human activity, and dissolved salts rocks in this region (Gopinath *et al*. 2015, Selvam *et al*. 2015 and Mondal *et al*. 2010) [30, 23]. The main reasons for sea water intrusion may be due to the over exploitation of groundwater for filling the holy temple pond, agricultural and industrial uses. The higher levels of salinity in the groundwater are due to the higher concentration of sodium ions in groundwater. The higher concentration of salt water is harmful in the long run (Goyal, 2013) [12]. The average of EC was 2494.667(µs/cm) and the maximum, minimum values were 4360(µs/cm) and 1080(µs/cm) respectively. The highest EC was noticed in the Kheezha suprayapuram. The EC in study area were over the desirable limit prescribed by BIS and WHO. The higher concentration of EC in groundwater indicates salinity hazards (Begum *et al*. 2009) [6]. The average TDS was found to be 1210.333mg/l and the maximum, minimum were 2210mg/l and 530mg/l respectively. The highest TDS was present in the Kheezha suprayapuram (0.5km). The waste water from the temple Holy pond was released into the small canal that is linked to canal supplying irrigation water for the agricultural fields. Thus due to seepage, the groundwater quality has changed in this region. The desirable limit of TDS was 1000mg/l for drinking water according to WHO standard (2011) [33]. The high levels of TDS in water may be objectionable to consumers owing to the undesirable taste and to excessive scaling in water pipes, heaters, boilers, and household appliances.

Table 7: Correlation matrix of groundwater quality

Ph	Ph	Salinity	EC	TDS	Cu	Zu	Mn	Pb	Cd	Cr
Salinity	0.009	1								
Ec	-0.023	.766**	1							
TDS	-0.218	.850**	.850**	1						
Cu	0.189	-0.039	0.028	-0.117	1					
Zn	0.203	-0.081	0.025	-0.167	.740**	1				
Mn	0.068	.449*	.384*	.383*	0.086	-0.086	1			
Pb	0.118	0.129	0.004	0.067	.456*	0.244	.434*	1		
Cd	0.014	-0.002	-0.045	-0.086	0.105	0.012	-0.077	-0.071	1	
Cr	0.21	-0.274	,062	-0.116	0.269	0.003	0.055	0.227	.366*	1

*- 10%, **-5% and *** - 1% level of signification respectively

Correlation matrix (Table7) indicates that the groundwater is polluted with various contaminants from chemical industries, such as, ceramic tiles industry, carton boxes industry, sodium silicate industry, detergent powder, washing soap industry, and laminations for transformers factories. Thirunallar temple town is polluted with agricultural activities, municipal sewage systems and specifically due to the Thirunallar Saneeshwaran temple pond and soil pollution.EC has positive relationship with salinity. If there is any change in salinity it will reflect in EC. Zinc is strongly correlated with copper. Manganese has positive relationships with salinity, EC and TDS (Mor *et al*. 2006) [22]. Significant negative correlation has been found among Na^+, EC, TDS and distance from the landfill, showing that the concentration of pollutants in the groundwater usually decreases with an increase in distance from the source of pollution as reported by several earlier workers (Lee and Jones 1994, Fatta *et al.* 1999, Aderemi *et al*. 2011 and Mor *et al*. 2006) [20, 1, 22]. Pb has positive and significant correlation with Cu and Mn. Cr has strongly associated and has significant correlation with Cd. The results shows that vast majority of the parameters, such as Pb, Mn, Cu, Cd and Cr were found to bear statistically significant correlation with each other demonstrating close relationship of this parameter with each other. The waste discharged from the industries, landfill leachate, and municipal sewage were the major sources of heavy metal pollution in the groundwater (Singaraja *et al.* 2015) [30]

4. Conclusion

This study has shown that the groundwater in the Thirunallar Municipality of Karaikal (TMK) have heavy metals such as copper, manganese, lead, cadmium, and chromium that are found to be above the permissible limits (WHO 2011 and Indian standard 2012) [33, 8]. The higher concentration of these heavy metals in the groundwater of the study area could be derived from the solid waste dump site, Thirunallar Saneeshwaran temple pond, agricultural runoff and industrial activity. Hence, it can only be used for non drinking domestic purposes like washing and gardening. Thus, it requires periodical quality assessments and appropriate treatment before it can be used for domestics purposes. The present study suggests that the solid waste management rules (2016) and water pollution act (1974) have to be strictly adhered to. It is recommended that appropriate eco-technologies (Eg.value added composting of source segregated biodegradable solid wastes) have to be used for sustainable management of municipal solid wastes and waste water treatment strategies (Eg. bio- remediation). In addition, local farmers should be advised to use ecologically and economically sustainable natural farming techniques that will reduce the use of inorganic chemicals which are known to pollute the surface and ground water sources and reduce agro bio diversity.

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