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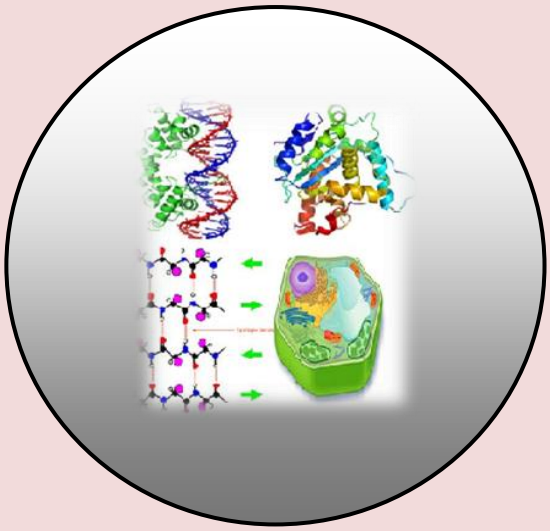

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J. Ranjitha
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Heavy Metal Accumulation in Groundwater Samples Collected Around Perungudi Dump Yard, Chennai, Tamil Nadu, India

Gopi Krishnan, *J. Ranjitha, **D. Magesh, ***M.C. John Milton

Environmental Monitoring Laboratory, PG and Research Department of Advanced Zoology and Biotechnology, Loyola College, Chennai 600034, Tamilnadu, India
*Research Scholar, Department of Advanced Zoology and Biotechnology, Guru Nanak College, Guru Nanak Salai, Velachery, Chennai-600042, Tamil Nadu, India
**Research Scholar, Environmental Monitoring Laboratory, PG and Research Department of Advanced, Zoology and Biotechnology, Loyola College, Chennai 600034, Tamilnadu, India
***Assistant Professor, PG and Research Department of Advanced Zoology and Biotechnology, Loyola College, Chennai, Tamilnadu, India

ABSTRACT
The Perungudi dumping yard which is being used for more than 28 years as municipal waste dumping site, beyond the lifetime of 20 years for any landfill, remains the major contributor for heavy metal pollution of groundwater in and around Pallikaranai, due to the leaching activity. The current study aims at assessing the ecological condition of the wetland. The objective is achieved by assessing the heavy metal concentration (Cd, Cr, Cu, Pb) in twelve ground water samples collected from four different sites. Of these four heavy metals Pb was found in all the water samples, whereas Cr was found in eight of the twelve ground water samples. Cd and Cu was found below detectable levels to be the highest and Cadmium (Cd) to be the least accumulated in the study area.
Keywords:
Pallikarnai Marshland, Heavy metals, Perungudi Dumpsite, Flame Atomic Absorption Spectrophotometer (AAS), Ground water.

INTRODUCTION
Groundwater is the water stored underground in rock fractures and pores that lay beneath the surface of the earth. Quantity of groundwater differs from place to place due to geographical and climate differences, land uses. On the other hand, the quality of groundwater may differ due to pollution from nutrient pollutant flows, disposal of storm water, sewage and other urban wastes (Mkude, 2015). The World is currently facing critical water supply and drinking water quality problems, whereby, in many parts of the world, water supplies are threatened by contamination and future water supplies are uncertain. High arsenic levels are often used to indicate improper well construction or the location or overuse of chemical fertilizers or herbicides (Borah *et al*., 2010).

As population grows and their need for water increases, the pressure on our groundwater resources also increases. In many areas of the world, groundwater is now being over extracted, in some places massively so, the results are falling water levels and declining well yield, land subsidence and ecological damage such as the drying out of wetlands (Jinwal *et al*., 2009).

GROUNDWATER AND HEAVY METAL POLLUTION

Rapid urbanization, improper waste disposal and landfill, excessive application of fertilizers and unsanitary conditions have threatened groundwater quality and consequently human health in many parts of the world by anthropogenic pollutants in addition to the naturally occurring pollutants (Keishiro, 2006). According to Fernández-Luqueño *et al.* (2013), pollution is defined as the introduction of elements, compounds or energy into the environment at concentrations that impair its biological functioning or that present an unacceptable risk to humans or other targets that use or are linked to the environment. Water pollutants are of many types, out of which heavy metals have become a question of considerable public and scientific concern in the light of evidence of their toxicity to human health and biological systems (Anazawa *et. al*., 2004).

According to Jinwal *et al*. (2009), many trace elements are essential nutrients, however certain trace elements such as As, Cd and Hg are known to be persistent environmental contaminants and toxic to most forms of life. Natural water systems contain trace elements in very small concentrations. Occurrence of trace metals in surface or ground water may be due to dissolution of trace element from minerals or due to anthropogenic activities such as mining, smelting of ores and from industrial wastes.

GROUNDWATER-SOIL CONNECTIVITY

Rock and organic matter have decomposed for many years and resulted in the formation of soil. Chemical elements occur in soil naturally as components of minerals though at certain concentrations some of those may be toxic. The chemical elements such as metals cannot break down, but their characteristics may change so that they can be easily taken up by plants or animals (Facchinelli, 2001). Certain anthropogenic activities such as past land use, current activities on the site and nearness to pollution sources tends to affect the properties of soil (Shayley*et al.,* 2009). Such activities result in contamination in various forms. Soils represents a major sink for heavy metal ions, which can then enter the food chain via water, plants or leaching into groundwater (Fernández-Luqueño *et al*., 2013). The transport mechanisms of heavy metals through soil has long presented great interest to both environmental and soil scientists because of the possibility of groundwater contamination through metal leaching

Heavy metals in groundwater are toxic even at low concentrations (Marcovecchio *et al.,* 2007)**.**There is also evidence of heavy metals in drinking water that are responsible for causing adverse effect on human health through food chain contamination (Fernández-Luqueño *et al*., 2013). Since the quality of water used for drinking and other domestic purposes is fundamental, analysis of contaminants with special reference to heavy metals in groundwater in and around the human settlements is being given the prime importance globally.

MATERIALS AND METHODS

STUDY AREA

Perungudi is a city in Kanchipuram district of Tamilnadu is a suburb of Chennai situated about 10 kilometers from Adyar. The neighboring areas include Kandhanchavadi to the north, Thoraipakkam to the south, Palavaakkam on the east and a combination of natural landscapes, including the Perungudilake, Pallikaranai marshes, barren excavated lands, and paddy fields on the western parts. The Perungudi dump site is located towards the northern limit of a large topographic depression termed as the Pallikaranai Depression which stretches approximately 10 km north to south and is up to 3 km wide from west to east. The area is low lying, close to sea and is connected to the sea via the Buckingham canal and the Kovalam estuary at the southern end of the depression. The dump site lies between 2 and 3 km west of the Buckingham Canal and is at 3.5 to 4.5 km west of the Bay of Bengal coastline. The satellite image of the study area is given in Figure 1.

Figure 1. Sampling sites around Perungudi dump yard.
Image courtesy: Google Earth.

Figure 2. Sampling points around Perungudi dump yard.
Image courtesy: Google Earth.

SAMPLING SITES

Four sites around the Perungudi dump yard with high residential density were selected. From each site, three groundwater samples were collected thus a total of twelve samples (G1 to G12) were collected. The four sampling sites are depicted in Figure 1. The GPS co-ordinates of the twelve sampling points were determined by 'GPS Essentials Application' (version 4.4.4) provided by 'Mictale.com'. The co-ordinates for twelve sampling points are shown in the Table 4 and Figure 2.

COLLECTION AND DIGESTION OF SAMPLES

Collection and digestion of samples were performed by following the procedure suggested by Nollet (2007). The groundwater samples were collected through taps connected to bore wells. From each sampling point, 1 litre of groundwater was collected in polyethylene bottles with tight caps. To avoid contamination, the polyethylene bottles were rinsed with 2% nitric acid prior collection of samples. In order to protect the water samples from addition of contaminants, loss of determinants (heavy metals) and any other unintended changes that affect the concentrations of determinants, the samples were subjected to digestion on the same day after collection. Digestion of water samples is performed to release the heavy metals bonded to different substrates (i.e., organic matter, complexes, etc.).

Table 1. GPS co-ordinates and types of samples.

SAMPLING SITE	SAMPLE	TYPE	CO-ORDINATES	
			LATITUDE	LONGITUDE
	G1	Bore well	12°57′16.98″N	80°14′28.62″E
1				
	G2	Bore well	12°57′14.52″N	80°14′20.76″E
	G3	Bore well	12°57′17.34″N	80°14′26.10″E
	G4	Bore well	12°56′48.25″N	80°12′27.21″E
2				
	G5	Bore well	12°56′47.73″N	80°12′39.08″E
	G6	Bore well	12°56′54.26″N	80°12′33.25″E
	G7	Bore well	12°57′48.47″N	80°14′43.04″E
3				
	G8	Bore well	12°57′50.45″N	80°14′34.58″E
	G9	Bore well	12°57′53.07″N	80°14′18.17″E
	G10	Bore well	12°58′56.01″N	80°13′14.82″E
4	G11	Bore well	12°58′55.84″N	80°13′23.46″E
	G12	Bore well	12°58′46.27″N	80°13′19.78″E

REAGENTS

All the reagents used in this study i.e., Nitric acid (69%, EMPARTA grade), Hydrochloric acid (37%, EMPARTA grade) and Hydrogen peroxide (30%, EMPLURA grade) were obtained from Merck Life Sciences Private Ltd., Mumbai.

PROTOCOL

40 mL of sample is taken in a round bottomed flask and 5 mL of concentrated Nitric acid (HNO3) was added followed by the addition of 2 mL of concentrated Hydrochloric acid (HCl). The sample is evaporated and refluxed using condenser for 15 minutes. The process is continued for another 10 minutes after adding 5 mL of concentrated HNO3 and 2 mL of Hydrogen peroxide (H2O2). Then the sample was allowed to cool and transferred to volumetric flask of 50 mL capacity. The sample is then made up to 50 mL by adding 2% HNO3. Then the sample is transferred to a plastic container with a tight cap and stored in darkness and refrigerated until the analysis in laboratory. The same procedure is followed for all the twelve groundwater samples.

ANALYSIS OF SAMPLES

The digested samples were analysed using Flame Atomic Absorption Spectrophotometer (Elico, SL 243 double beam) in the Environmental Monitoring Research Laboratory, Loyola college, Chennai. Prior to the analyses of samples, standard curves were obtained for all the four metals (Cd, Cr, Cu and Pb).

RESULTS

CONCENTRATION OF Cd, Cr, Cu AND Pb IN WATER SAMPLES

The results obtained after analysing the water samples using Atomic Absorption Spectrophotometer are recorded in Table 2. The concentration of Cadmium, Chromium, Copper and Lead in each water sample is recorded in the scale of mg/L.

Table 2. Concentration of heavy metals in groundwater samples.

SAMPLE		RECORDED VALUES (mg/L)		
	CADMIUM	CHROMIUM	COPPER	LEAD
G1	BDL*	8.07	BDL*	0.46
G2	BDL*	BDL*	BDL*	2.4
G3	BDL*	BDL*	BDL*	3.2
G4	BDL*	BDL*	BDL*	1.99
G5	BDL*	5.02	BDL*	2.1
G6	BDL*	21.54	BDL*	3.08
G7	BDL*	4.28	BDL*	5.19
G8	BDL*	8.7	BDL*	0.07
G9	BDL*	5.96	BDL*	1.56
G10	BDL*	6.91	BDL*	2.52
G11	BDL*	7.23	BDL*	1.67
G12	BDL*	BDL*	BDL*	2.31

*BDL= Below Detectable Limit

GROUNDWATER SAMPLE G1

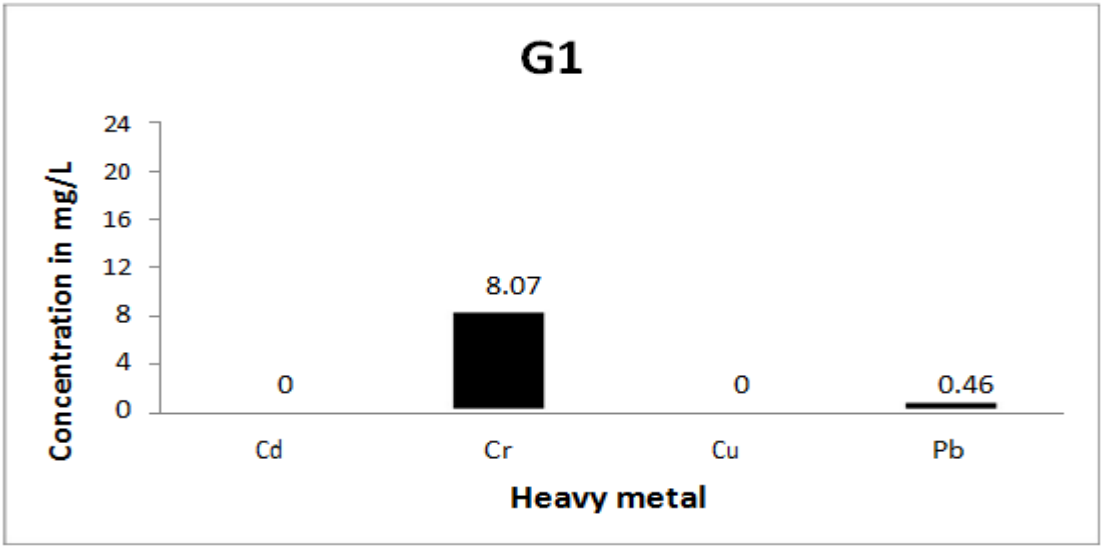

Figure 3.Concentration of Cd, Cr, Cu and Pb in sample G1.

Cr and Pb were detected in sample G1 while Cd and Cu were below the detectable limit. The concentrations of Cr and Pb were 8.07 mg/L and 0.46 mg/L respectively (Figure 3) and were above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS(2012) for drinking purpose.

GROUND WATER SAMPLE G

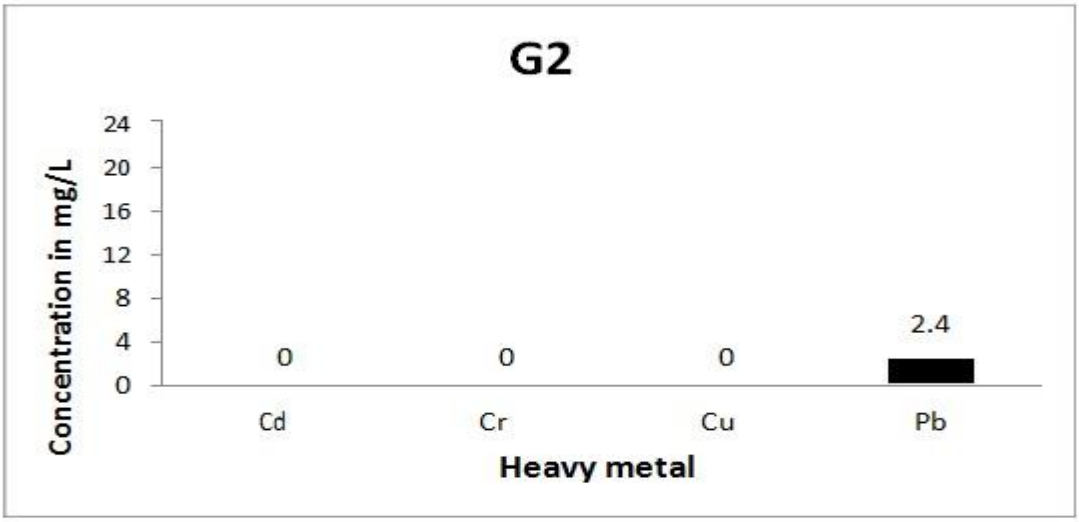

Figure 4. Concentration of Cd, Cr, Cu and Pb in sample G2.

Only Pb was detected in sample G2 while Cd, Cr and Cu were below the detectable limit. The concentration of Pb was 2.4 mg/L and was well above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinking purpose.

GROUNDWATER SAMPLE G3

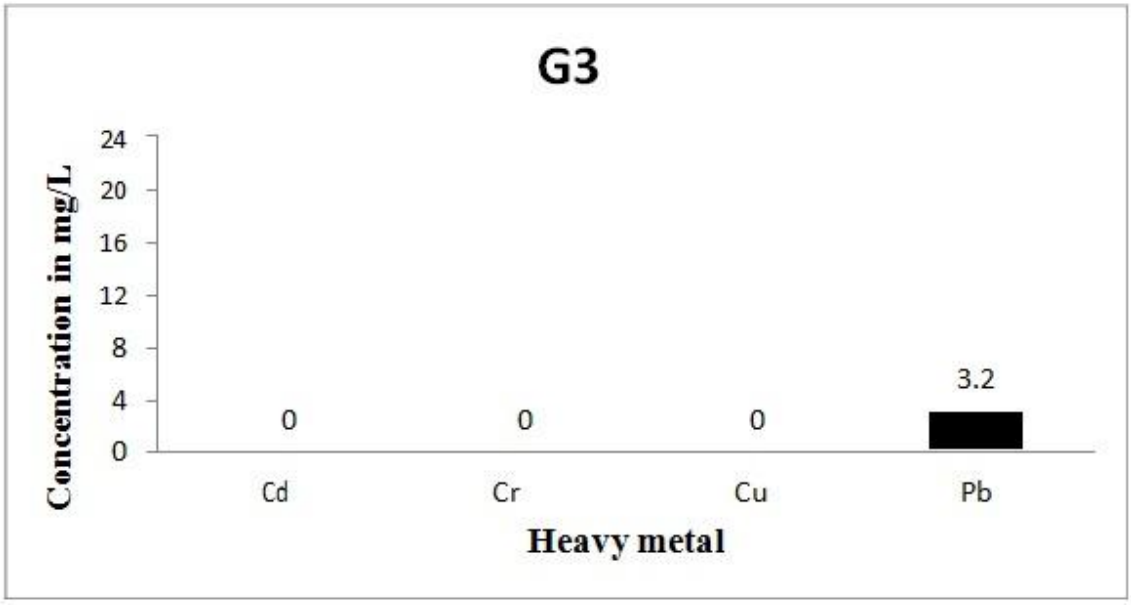

Figure 5. Concentration of Cd, Cr, Cu and Pb in sample G3.

Only Pb was detected in sample G3 while Cd, Cr and Cu were below the detectable limit. The concentration of Pb was 3.2 mg/L and was above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinking purpose.

GROUNDWATER SAMPLE G4

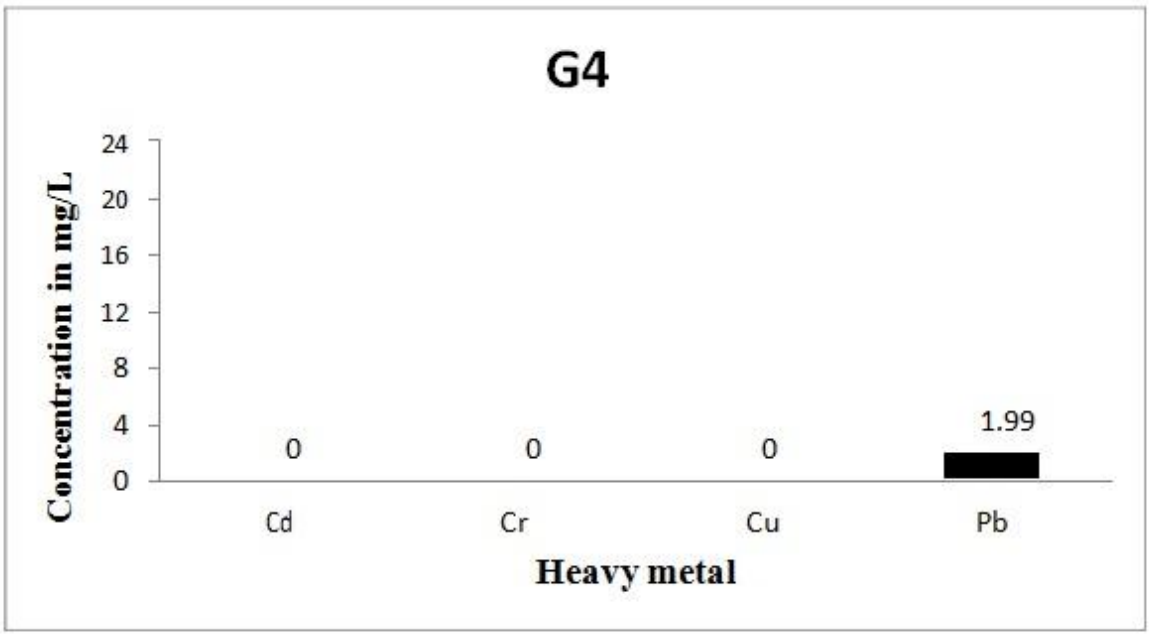

Figure 6. Concentration of Cd, Cr, Cu and Pb in sample G4.

Only Pb was detected in sample G4 while Cd, Cr and Cu were below the detectable limit. The concentration of Pb was 1.99 mg/L and was above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinking purpose.

GROUNDWATER SAMPLE G5

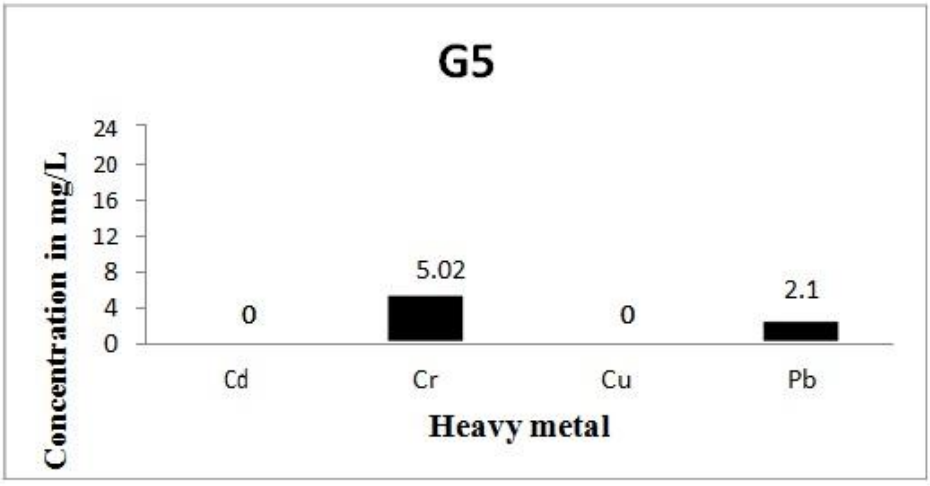

Figure 7. Concentration of Cd, Cr, Cu and Pb in sample G5.

Cr and Pb were detected in sample G5 while Cd and Cu were below the detectable limit. The concentrations of Cr and Pb were very high (5.02 mg/L and 2.1 mg/L respectively) and were above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinking purpose.

GROUNDWATER SAMPLE G6

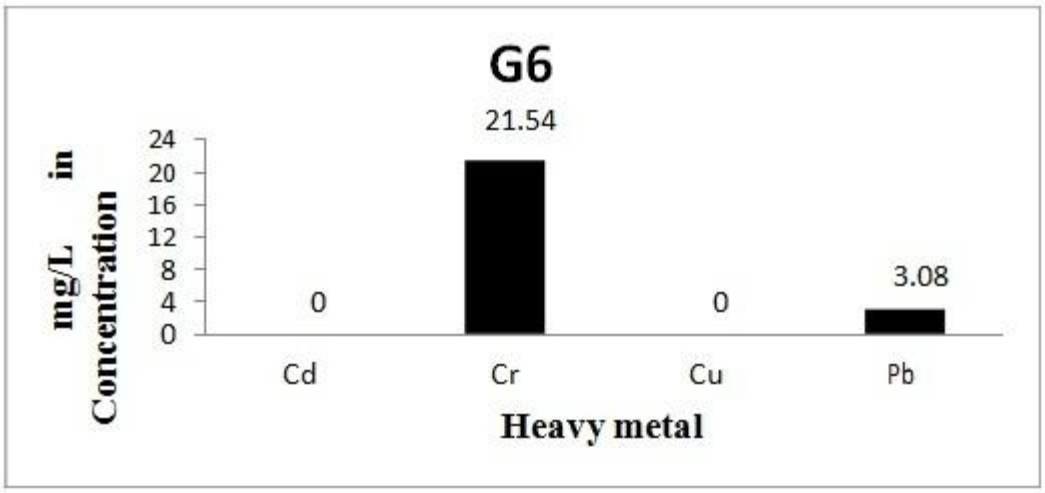

Figure 8. Concentration of Cd, Cr, Cu and Pb in sample G6.

Cr and Pb were detected in sample G6 while Cd and Cu were below the detectable limit. The concentrations of Cr (21.54 mg/L) and Pb (3.08 mg/L) were extremely high and were above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinking purpose. The concentration of Cr in this sample is the highest among other water samples.

GROUNDWATER SAMPLE G7

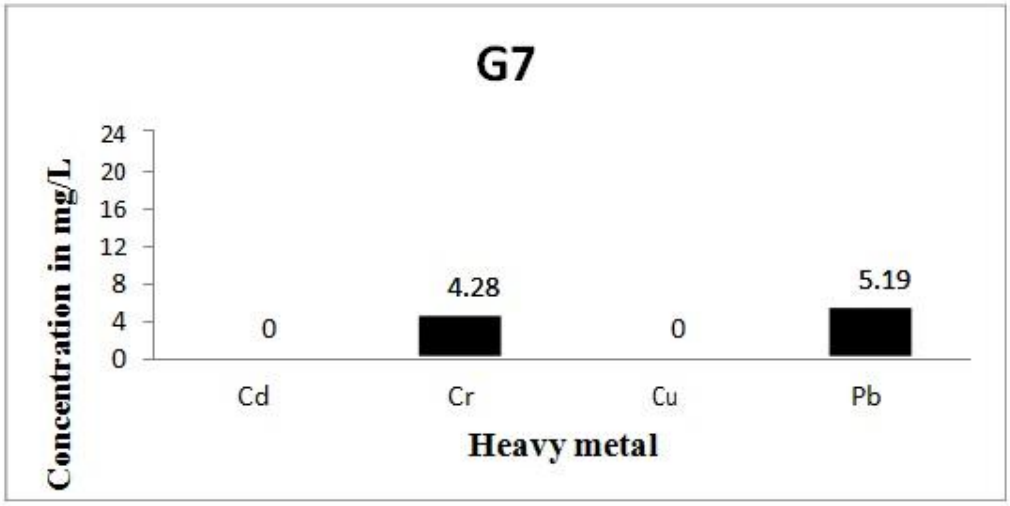

Figure 9. Concentration of Cd, Cr, Cu and Pb in sample G7.

Cr and Pb were detected in sample G7 while Cd and Cu were below the detectable limit. The concentrations of Cr and Pb were 4.28 mg/L and 5.19 mg/L respectively and were above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinking purpose. The concentration of Pb in this sample was the highest in this sample.

GROUNDWATER SAMPLE G8

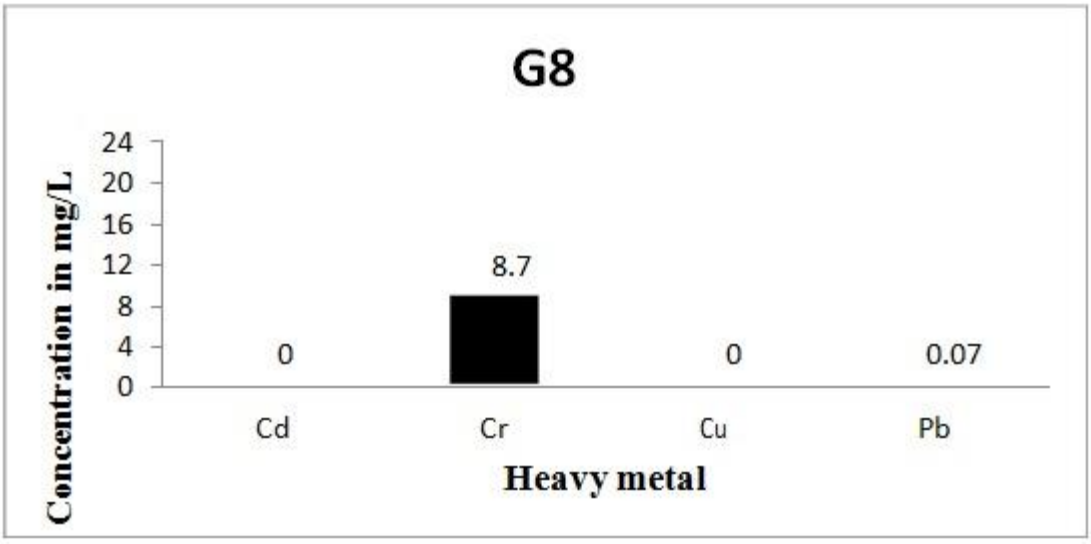

Figure 10. Concentration of Cd, Cr, Cu and Pb in sample G8.

Only Cr and Pb were detected in sample G8 while Cd and Cu were below the detectable limit. The concentrations of Cr and Pb were 8.7 mg/L and 0.07 mg/L respectively and were above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS(2012) for drinking purpose.

GROUNDWATER SAMPLE G9

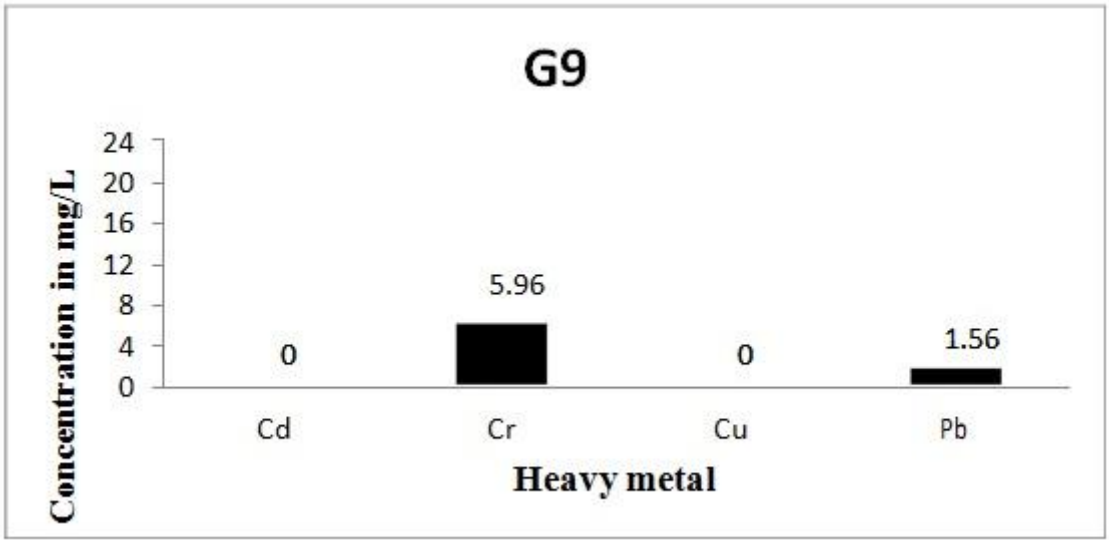

Figure 11. Concentration of Cd, Cr, Cu and Pb in sample G9.

Only Cr and Pb were detected in sample G9 while Cd and Cu were below the detectable limit. The concentrations of Cr and Pb were 5.96 mg/L and 1.56 mg/L respectively and were above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinking purpose.

GROUNDWATER SAMPLE G10

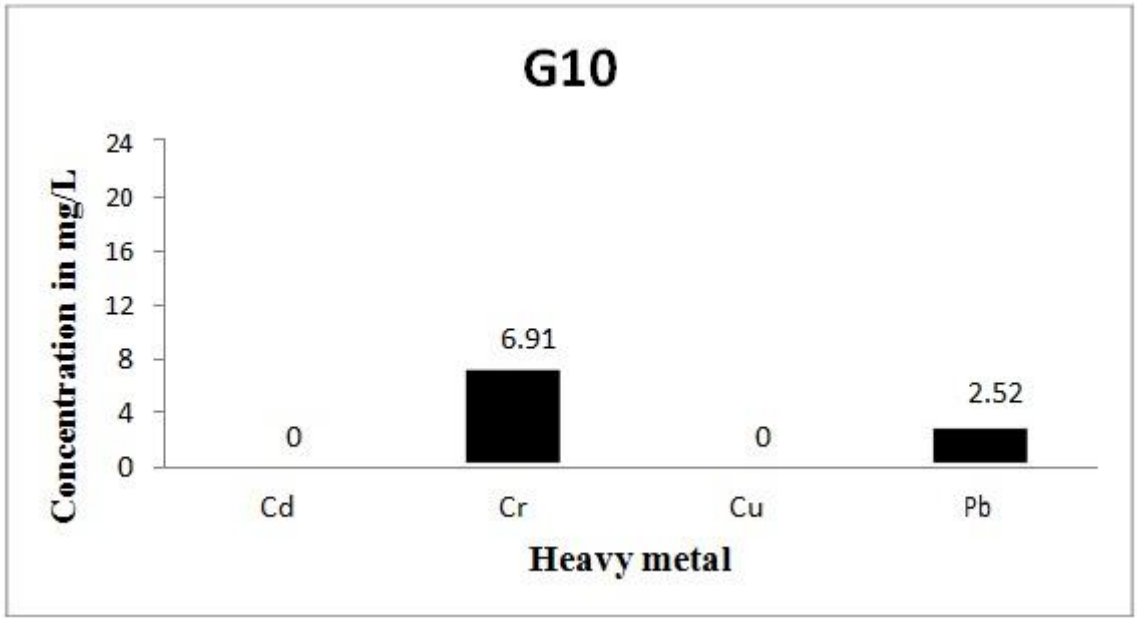

Figure 12. Concentration of Cd, Cr, Cu and Pb in sample G10.

Only Cr and Pb were detected in sample G10. The concentrations of Cr and Pb were 6.91 mg/L and 2.52 mg/L respectively and were above the permissible levels suggested byWHO (2006), USEPA (2009) and BIS (2012) for drinking purpose.

GROUNDWATER SAMPLE G11

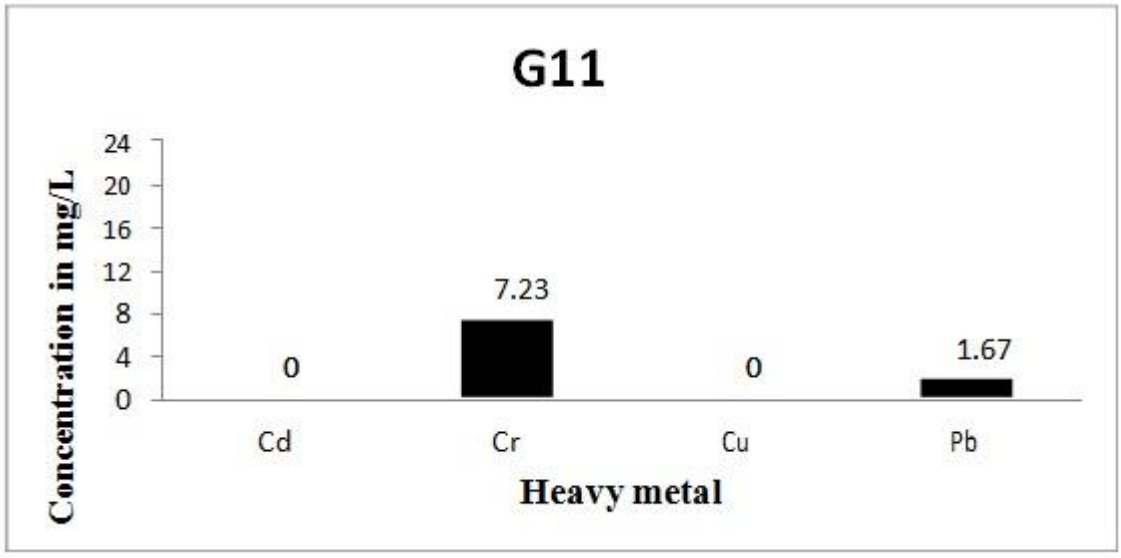

Figure 13. Concentration of Cd, Cr, Cu and Pb in sample G11.

Cr and Pb were detected in sample G11 while Cd and Cu could not be detected. The concentrations of Cr and Pb were 7.23 mg/L and 1.67 mg/L respectively and were above the permissible levels suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinkingpurpose.

GROUNDWATER SAMPLE G1

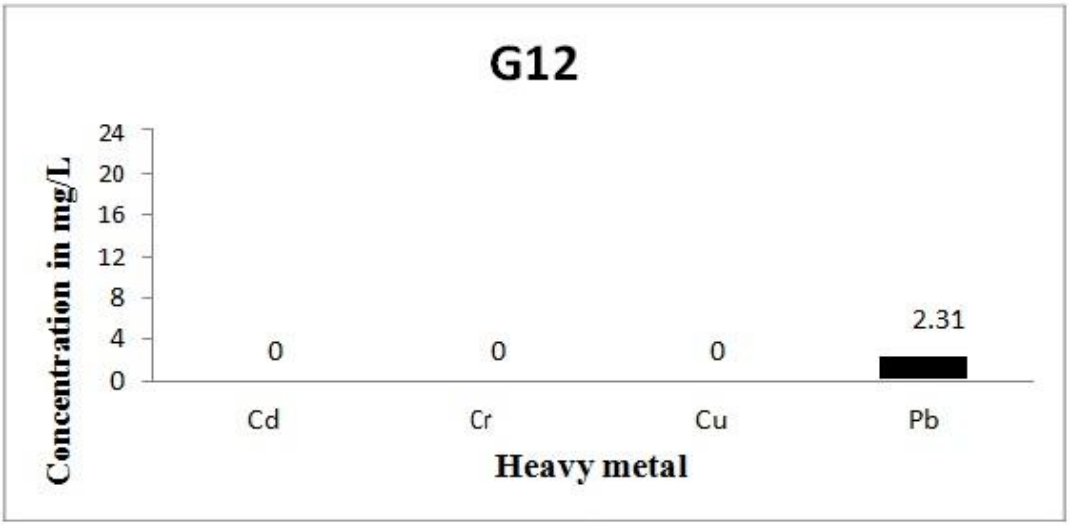

Figure 14. Concentration of Cd, Cr, Cu and Pb in sample G12.

Only Pb was detected in sample G12 while the other three metals could not be detected. The concentration of Pb was 2.31 mg/L and was well above the permissible level suggested by WHO (2006), USEPA (2009) and BIS (2012) for drinking purpose.

DISCUSSIONS

CADMIUM IN WATER SAMPLES

In the present work, Cd was not detected in any of the twelve samples analysed. This indicates that the groundwater around the Perungudi dump yard is not contaminated with Cd. Karpagavalli*et al*. (2012) analysed the surface waters of Pallikaranai wetland and found that the levels of Cd in the water samples ranged between BDL to 0.019 mg/L as it was present in the samples as the second least concentrated heavy metal next Cu and was well within limit prescribed by Irrigation standards. Similar results were obtained by Vasanthi*et al*. (2008) in Perungudi dumping yard, where Cd was detected in leachate samples but were not found above the permissible levels in groundwater samples. Since Cd is used extensively in solar cells, pigments, alloys for telegraph and telephone wires, photoelectrical and electron optical devices, they do not play a big role in day to day urban life. This might be the reason that Cd did not find its place among the common heavy metal pollutants of groundwater. However, Cd interferes with tubular resorption of proteins and results in toxic effects and renal failure (Bawaskar*et al*., 2010). Even a small amount of Cd in water may turn lethal to those who consume and hence the permissible level in drinking water for Cd is suggested as 0.003 mg/L by WHO and BIS, and as 0.005 mg/L by USEPA.

CHROMIUM IN WATER SAMPLES

In the present work, Cr was detected in 8 out of the 12 water samples analysed. In all the eight samples Cr was present in very high concentrations ranging from 4.28 mg/L to 21.54 mg/L. The permissible level of Cr in drinking water prescribed by WHO, USEPA and BIS are 0.05 mg/L, 0.1 mg/L and 0.05 mg/L respectively and it can be seen that the level of Cr in the eight water samples (G1, G5, G6, G7, G8, G9, G10 and G11) were extremely above than the standards prescribed by the above mentioned organizations and cannot be used for drinking and cooking purposes. The concentration of Cr in the water samples can be arranged as follows, starting from the highest to the lowest.

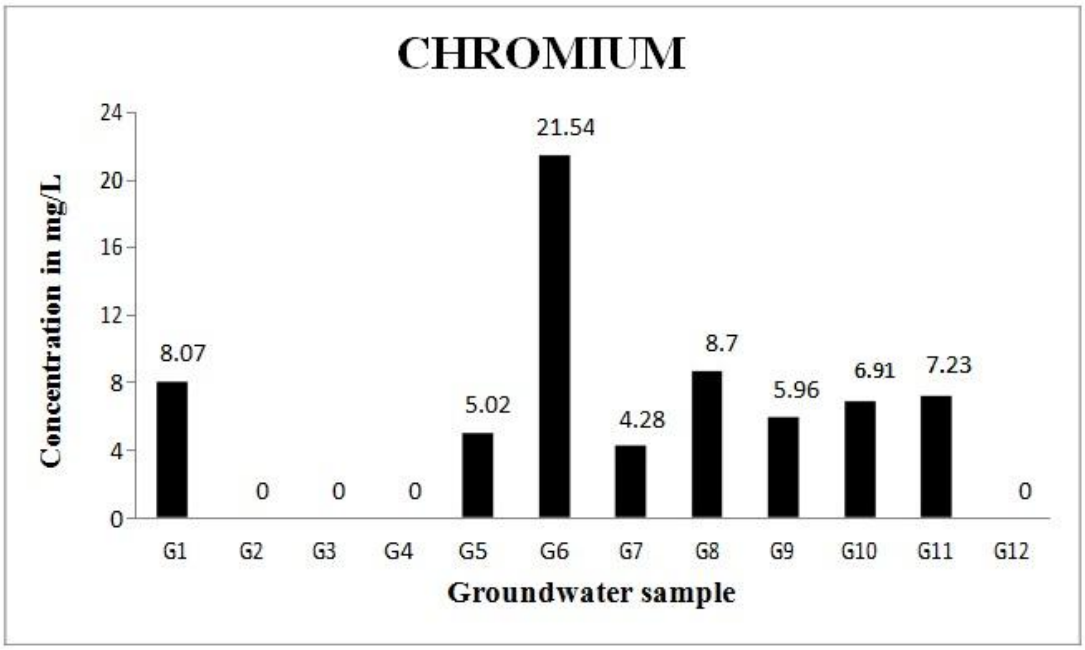

Figure 15. Concentration of Cr in samples G1 to G12.

A study by Karpagavalli et al. (2012) in Pallikaranai revealed that only Cr was exceeding the prescribed limit in maximum sampling locations. Chromium has wide applications in day to day life since they are used in matches, storage media for computers, chrome plating dyes, tanning of leathers, cassette tapes, pyrotechniques and photography. Hence it finds its way to the ecosystem easily, thanks to the anthropogenic activities and pollution. Since the Perungudi dumping yard is situated within the Pallikaranai wetland, the Cr in the municipal waste could have leached into the soil to contaminate groundwater. Chromium is an essential trace element, required for the metabolism of lipids and proteins and to maintain a normal glucose tolerance factor. However, higher levels of Cr causes allergic reaction and skin corrosion since immunologically active forms of Cr are absorbed easily by dermal membranes. Cr also causes cancer by damaging DNA through interference with DNA-polymerase (Athar and Vohora, 1995).

COPPER IN WATER SAMPLES

Similar to Cd, Cu was also below the detectable limit in all the water samples analyzed. Jayanthi and Padmavathi (2014) analysed the water samples in and around Pallikaranai marsh and found the average level of Cu to be 0.06 mg/L which was well below the permissible limits suggested by WHO, USEPA and BIS (2.0 mg/L, 1.3 mg/L and 1.5 mg/L respectively). Similarly, Karpagavalli *et al*. (2012) analysed the surface waters of Pallikaranai wetland and found that Cu was present in the water samples in the least concentration levels. Since Cu is used in electrical goods like wires and coils, kitchenware and alloys, Cu is not generally thrown in waste. Like Iron, Cu is one of the few heavy metals which is recycled. Since Cu is generally used as a whole metal in wires and vessels, it is less likely to be broken down and leached into the soil. Though Cu is less toxic when compared to other heavy metals such as Pb, Cr and Cd, it may bring about toxic effects at higher concentrations. Cu causes local irritation in gastric mucosa and damages liver and brain cells.

LEAD IN WATER SAMPLES

In the current work, Pb was detected in all the water samples. The concentration of Pb lead ranged from 0.07 mg/L to 5.19 mg/L. The permissible level of Pb in drinking water prescribed by WHO (2006), USEPA (2009) and BIS (2012) are 0.01 mg/L, 0.015 mg/L and 0.01 mg/L respectively and it can be seen that the level of Pb in all the water samples were above than the drinking water standards prescribed by the above mentioned organizations.

The highest concentration of Pb (5.19 mg/L) was observed in sample G7 and it is evident that none of the twelve water samples are fit for drinking or cooking purposes. The concentration of Pb in the water samples can be arranged as follows, starting from the highest to the lowest.

G7> G3> G6> G10> G2> G12> G5> G4> G11> G9> G1> G8

The level of Pb in the twelve water samples are cumulatively shown in Figure 16.

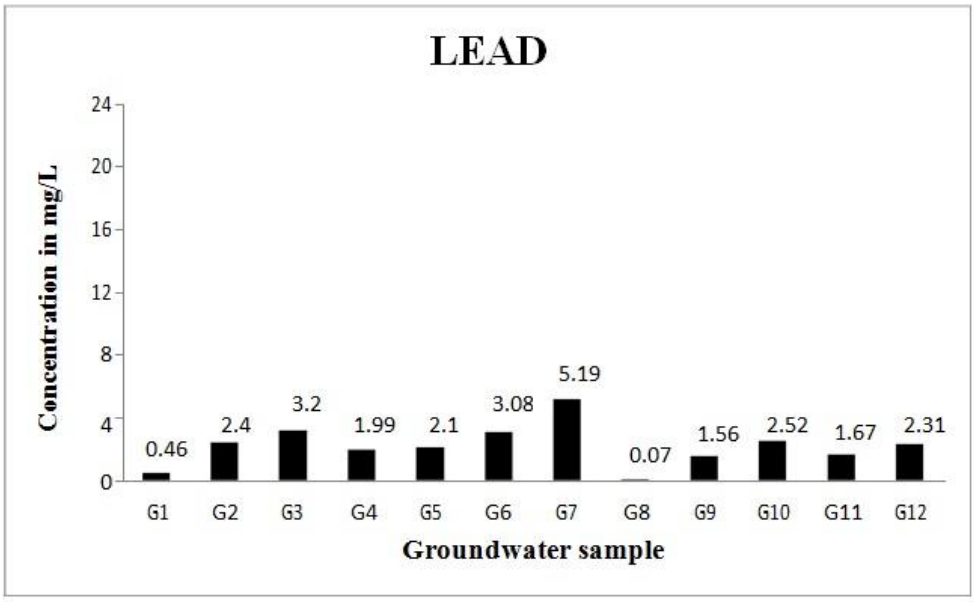

Figure 16. Concentration of Pb in samples G1 to G12.

Jayanthi and Padmavati (2014) found that the levels of Pb (average content of 0.06 mg/L) in the dug wells, tube wells and surface water of around Paliikaranai were above the desirable limit set by CPHEEO. Lead is extensively used in storage batteries, antiknock agents in petroleum and gasoline, paints, glassware, ceramics, printing press and many other. Being a metro city with huge population, Chennai generates huge amount of garbage every day. Since Lead is generally not recycled and being used as an additive in various industrial processes, they accumulate in the environment easily and enter into groundwater by percolation through soil. Lead is an highly toxic heavy metal and it damages erythrocytes, causes chronic renal failure and neurogenetic disorders (Jones and Miller, 2008).

Heavy metal contamination of groundwater either through natural or anthropogenic sources is a matter of prime concern to the global health. Remediation of contaminated groundwater is of highest priority since billions of people all over the world use it for drinking purpose (Hashimet al., 2011). Since the Perungudi dumping yard remains within the Pallikaranai wetland and has been used to dump wastes for several decades, it remains the major contributor to the groundwater pollution in and around Pallikaranai. With the purchase and utilization of electrical and electronic goods are increasing in the city day by day, the generation of e-waste also increases. Most components of electronic equipments are made up of heavy metals. The crude way of recycling them releases more of the heavy metals into both the soil and the water environment. The presence of the heavy metals above the natural levels in the study area can also be attributed to other sources such as atmospheric deposition, domestic waste water discharges, transport sectors, sewage wastewater, etc. Since the Pallikaranai wetland is the principal aquifer of the groundwater table in and around Pallikaranai, any contamination in the wetland directly affects the status of groundwater.

Even though the wetland has been declared 'Protected Area' by the forest department, due to the pollution through vehicular emission and the dense population of 22, 503 residents (2011 census), Pallikaranai is being contaminated through many ways. The government must implement new policies to relocate the dumping yard from Perungudi and to prevent further waste disposal around the Pallikaranai wetland.

CONCLUSION AND RECOMMENDATIONS

Dumping the waste in Perungudi started in the year 1987 and continues till now. The life time of a landfill is generally twenty years, but Perungudi dumping yard has been used for more than 28 years. The leaching of heavy metals into the groundwater table increases as years pass and leads to bioaccumulation.

Since Chennai is already heavily populated, cramping for residential space, it is also hard to find an alternative place to be used as municipal land fill site. The improper maintenance of drainage system as well as unchecked sewage drains released into the newly constructed storm water drains around Pallikaranai are also the contributing factors for the intrusion of heavy metal pollutants into the groundwater.

Since toxic heavy metals tend to cause chronic and often irreparable damage to humans as well as the wildlife. Though this problem has to be addressed immediately with the highest priority, it is often overlooked by environmentalists. Unless and until awareness on heavy metal pollution is spread to reach the common men and women, our ecosystem continues to get polluted by toxic heavy metals.

RECOMMENDATIONS

- The Perungudi dumping yard should no longer be used as a municipal waste dump site in future.
- The pre-existing garbage in the dumping yard can be eliminated from the site by bio-remediation technologies to prevent further leaching of heavy metals.
- The Chennai corporation can implement various existing groundwater remediation technologies which are being practiced by many countries.

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Corresponding author: J. Ranjitha, Research Scholar, Department of Advanced Zoology and Biotechnology, Guru Nanak College, Guru Nanak Salai, Velachery, Chennai-600042, Tamil Nadu, India
Email: ranjee2011@gmail.com