

Appraisal of seasonal variation of groundwater quality near an uncontrolled municipal solid waste landfill in Kolkata, India

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Abstract

The present study was aimed to evaluate the impact of leachate derived from uncontrolled municipal landfill on surrounding groundwater quality in Kolkata, India. Seasonal variation of twenty physico-chemical parameters in pre-monsoon (PRM) and post-monsoon (POM) season were analysed in forty groundwater samples around the landfill site. Groundwater pollution was identified by the spatial distribution maps of TDS, Na^+ , Cl^- , Mn and Fe along with the heavy metals like Pb, Hg and Cr in both the seasons. Hydrogeochemical characteristics of groundwater samples showed that the area was dominated by brackish water, $[\text{Ca}^{+2}-\text{Cl}^-]$, $[\text{Mg}^{+2}-\text{Cl}^-]$ and $[\text{Na}^+-\text{Cl}^-]$ type in PRM season whereas $[\text{Na}^+-\text{HCO}_3^-]$ type dominated in POM season. Hierarchical cluster analysis (HCA) was also applied to identify the source of groundwater pollution. In PRM season, groundwater samples closer to the active landfill site were physico-chemically different from upstream samples but more related to downstream samples. However, in POM season, groundwater samples closer to the active landfill site represented distinctly different physico-chemical characteristics from upstream and downstream samples as a result of high influx of leachate pollutants. In specific, the present study urges for proper pollution control measures along with landfill leachate treatment process to improve the surrounding water quality.

Keywords: Uncontrolled municipal landfill, Leachate, Groundwater quality, Hydrogeochemical characteristics, Hierarchical cluster analysis (HCA)

1. Introduction

Population growth and urbanization tends to produce high volumes of solid waste from different sources of urban society. However, lack of adequate regulatory system for proper solid waste management could result in serious ecological, environmental and health complications. Sanitary landfilling of municipal solid waste (MSW) is the most conventional management measure practiced in most of the developed countries. However, in developing countries like India, open dumping is prevalent for disposing solid wastes. In most of the cases, MSW are

directly disposed in open or uncontrolled landfills without any or little regard towards the geo-membrane liners, leachate collection systems and treatment facilities (De *et al.*, 2016). However, generation of leachate is inevitable for both the sanitary or open/uncontrolled landfills. Landfill leachates are produced as a result of rainfall percolation along with chemical, physico-chemical and microbiological processes occurring within the disposed waste mass (Li *et al.*, 2010). Leachates are the potential source of various pollutants like dissolved organic matter, inorganic macrocomponents, heavy metals and xenobiotic organic compounds (Christensen *et al.*, 1994). In India, Ministry of Environment, Forests and Climate Change (MoEFCC), has notified MSW landfill leachate discharge standards to protect the receiving waters in 2000 and amended them in 2016. As a consequence of open or uncontrolled landfilling, leachates accumulate at the base of the landfill site and percolate through the soil or flow out laterally to contaminate surrounding soil, groundwater and surface water resources (Matejczyk *et al.*, 2011). In India, several instances of groundwater pollution pertaining to uncontrolled landfilling have been reported in near past (Mor *et al.*, 2006; Kale *et al.*, 2010; Parameswari *et al.*, 2012). The majority of India's population depends on groundwater for drinking and on surface water for agricultural activities and pisciculture. Thus, water pollution not only leads to deterioration of water quality but also threatens human health. Henceforth, protection of water resources is essential to maintain social well-being and economic growth of any nation.

Until now in Kolkata, a metropolitan city of India, groundwater pollution problems related to municipal landfills have not been yet studied. Hence, assessment of groundwater quality around the uncontrolled landfill site in Kolkata is an emergency to protect the local people of the landfill site. Thus, in the present study, the objectives were to (1) assess the landfill hazard by examining leachate characteristics; (2) investigate the seasonal variation of groundwater quality evaluating the influence of landfill leachate and suitability for drinking and irrigational purposes; (3) assess the spatial distribution of physico-chemical parameters delineating the extent of groundwater pollution; (4) identify the source of

groundwater pollutants through hydrogeochemical and clustering analysis.

2. Materials and Methods

2.1. Study area

The present study was undertaken at Dhapa uncontrolled landfill site located in the extreme east of Kolkata city, India (Figure 1).

The study area lies between latitude 22° 30' 24.47" to 22° 32' 54.57" N and longitude 88° 24' 13.76" to 88° 27' 43.96"

E within East Kolkata Wetlands (EKW). The wetland comprises of intertidal marshes, ponds and shallow water bodies locally known as "jheels" and "bheries" which are used for agricultural farming and pisciculture respectively. EKW covers an area of about 10,000 ha of which Dhapa landfill site involves a portion of 24.71 ha (Hazra and Goel, 2009) with an alluvial soil type of moderate permeability 10^{-5} to 10^{-6} cm s⁻¹. About 60% of the wetland surrounding the landfill site comprises of a low-income neighborhood of rag pickers, jheels, bheries and agricultural lands.

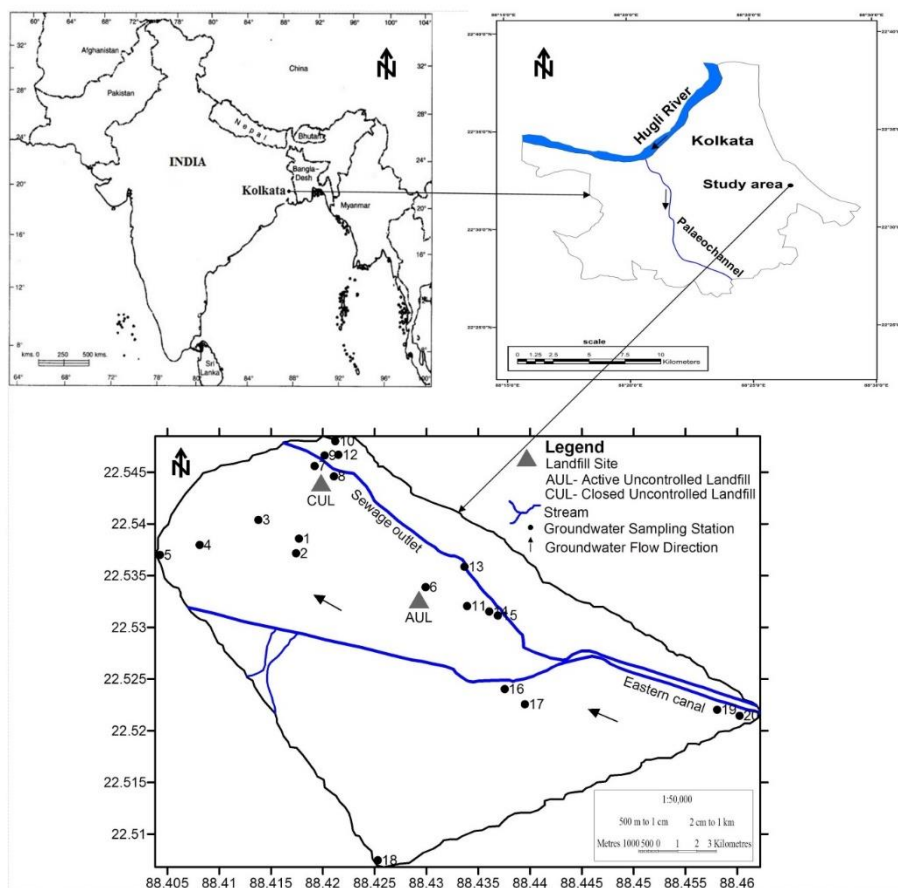


Figure 1. Location of the study area showing sampling stations around the Dhapa landfill site

The landfill site receives around 3000 tons of MSW per day from Kolkata city since 1981 (Chattopadhyay *et al.*, 2009) and devoid of any kind of groundwater protection measures and leachate collection system. Kolkata belongs to hot and humid climatic regime with the temperature varying between 12° C to 40° C. Relative humidity generally ranges between 68% in March to 85% in August with an annual average rainfall of 1650 mm receiving from northeast and southwest monsoons. Groundwater and surface water are also used to get their supply from monsoon season which generally extend from June to October. The depth of the water table in the study area is approximately 14 m below ground level (mbgl) in pre-monsoon (PRM) season and 12 mbgl in post-monsoon (POM) season. A high level of groundwater table persists in and around the study area as a consequence of percolation from the surrounding water bodies. There is also a groundwater trough near the western Kolkata (Sahu and

Sikdar, 2008). Thus, in the study area groundwater flows from east to west in direction (Sahu and Sikdar, 2008) and can transport pollutants from the landfill site located in the EKW towards the aquifer system of the central and western Kolkata.

2.2. Sampling and analysis

The topographical map (79B/6) of Kolkata of scale 1:50,000 was procured from the Survey of India (SOI) to delineate the boundary of the study area. The locations of the landfill site and groundwater sampling stations were attributed as shown in Figure 1.

Composite leachate samples were regularly collected every month (12 sampling periods from January to December) from the base of the waste dump. Composite samples were obtained by manually mixing spot leachate samples from spatially distributed sources to yield representative leachate samples. A total of forty (20×2) groundwater

water samples were collected from wells within an area of 3.5 km from the landfill site for two different seasons, PRM and POM during April 2014 and November 2014 respectively. Leachate and groundwater samples were kept in pre acid-washed polyethylene bottles at 4 °C for further laboratory analysis. 100 ml of the collected samples were filtered using 0.45 µm Millipore membrane filter papers and were acidified with 5N nitric acid to pH<2 and kept on 4 °C for the determination of the heavy metals. All the analytical reagents and chemical standards used were of Merck, analytical grade (AR) and the selected parameters were subsequently analyzed in triplicate. The analytical methods were according to the internationally accepted procedures and standard (APHA AWWA WPCF, 1999) to determine pH, EC, TDS, Ca^{+2} , Mg^{+2} , Na^{+} , K^{+} , F^{-} , Cl^{-} , HCO_3^{-} , SO_4^{2-} , PO_4^{-} , NO_3^{-} , $\text{NH}_3\text{-N}$, TKN, COD and BOD_5 . Dissolved heavy metals like As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn were detected by atomic absorption spectrometry (Perkin Elmer AAnalyst 400) equipped with graphite furnace (HGA Graphite Furnace).

The geospatial data of the sampling stations were recorded by using a Garmin GPS system and the spatial distribution maps for selected parameters of groundwater samples were prepared by kriging interpolation technique using Surfer version 8 software.

Sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and sodium percentage (Na%) were also determined for groundwater samples.

Salinity laboratory of the US Department of Agriculture has recommended SAR for analyzing irrigational water quality (Wilcox 1955) which can be calculated by the following formula (where the ions are in meq/L)

$$\text{SAR} = \frac{\text{Na}^{+}}{\sqrt{\frac{\text{Ca}^{+2} + \text{Mg}^{+2}}{2}}} \quad (1)$$

RSC can be calculated using the following formula (where the ions are in meq/L)

$$\text{RSC} = [(\text{HCO}_3^{-} + \text{CO}_3^{2-}) - (\text{Ca}^{+2} + \text{Mg}^{+2})] \quad (2)$$

Na% can be evaluated by the formula given below (where the ions are in meq/L)

$$\text{Na\%} = \frac{(\text{Na}^{+} + \text{K}^{+}) \times 100}{\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Na}^{+} + \text{K}^{+}} \quad (3)$$

2.3. Hydrogeochemical classification of groundwater

The hydrogeochemical classification of the groundwater samples was determined by plotting the concentrations of anions and cations on the Piper trilinear diagram (Piper, 1944). The dominant anion and cation in each groundwater sample can be identified from the right and left ternary diagrams respectively. $[\text{SO}_4^{2-}]$, $[\text{HCO}_3^{-}]$ and $[\text{Cl}^{-}]$ are the anionic constituents of the right ternary diagram while $[\text{Ca}^{+2}]$, $[\text{Mg}^{+2}]$, and $[\text{Na}^{+}]$ are the cationic constituents of the left ternary diagram. The hydrogeochemical characteristics of the groundwater sample can be

determined by combining the predominant ions at each sampling station (Nguyen *et al.*, 2014).

2.4. Hierarchical Cluster Analysis (HCA)

HCA was applied to identify the source of groundwater pollutants in PRM and POM seasons by using Statistical Package for Social Sciences (SPSS) version 20. In the present study, the interval of Euclidean distance was used for clustering the groundwater samples and the clustering method of ward linkage was applied to associate the clusters. To achieve the cluster analysis normal distribution and homogeneity of the variances were assumed and the data were standardized to their corresponding z scores (Yidana *et al.*, 2010). In HCA, standardization of data is crucial as Euclidean distance is largely influenced by the high variances of the data (Li *et al.*, 2012). For the computation of HCA, the data of the parameters were represented with detection limit values when the concentrations were found below the detection limit of the applied technique.

3. Results and Discussion

3.1. Leachate characterisation

Table 1 summarizes the leachate analysis results and were compared with the leachate discharge standards for inland surface water as specified by MoEFCC (2016).

Dhapa landfill site was in the methanogenic phase as the leachate was characterized by alkaline pH (8.2), low value of COD (4933.50 mg L⁻¹), intermediate BOD_5/COD ratio (0.47) and high value of $\text{NH}_3\text{-N}$ (1596.57 mg L⁻¹). BOD_5/COD ratio of 0.47 indicated that the landfill leachate is at the intermediate level of biodegradability as the process of waste deposition still continues in the landfill site. However, acidogenic leachate was not observed due to the presence of high bicarbonate concentration (29317.44 mg L⁻¹) along with the high ratio of the old disposed waste to the newly deposited waste (Demirbilek *et al.*, 2013). Landfill leachate under study may act as a potential source of groundwater pollution due to the presence of high values of TDS (9007.50 mg L⁻¹) along with the conservative pollutants like Cl^{-} (3973.11 mg L⁻¹), Na^{+} (2267.91 mg L⁻¹) and K^{+} (1688.19 mg L⁻¹). High concentrations of $\text{NH}_3\text{-N}$ indicate the occurrence of reducing environment in leachate which leads to high levels of soluble Fe (3.89 mg L⁻¹) and Mn (1.89 mg L⁻¹). Methanogenic leachates are usually associated with low concentrations of heavy metals (Kjeldsen *et al.*, 2002) due to the sorption and precipitation reactions with sulphides, carbonates and hydroxides (Lo, 1996). However, in the current study, some of the heavy metals like Cr (2.54 mg L⁻¹), Hg (0.98 mg L⁻¹), Pb (0.63 mg L⁻¹) and Zn (6.16 mg L⁻¹) were present in high concentrations exceeding the permissible discharge limits. Maiti *et al.* (2016) also reported similar trend of heavy metal contamination from the Dhapa landfill site, Kolkata. This may be due to the insufficient or low-availability of the sorption and precipitation reactants.

3.2. Groundwater quality for drinking

Table 2 depicts the statistical summary of groundwater analysis results for PRM and POM seasons. The suitability

of groundwater samples for drinking purposes was analysed by comparing with WHO (1971, 1993, 2002, 2004, and 2011) drinking water quality standards.

Table 1. Leachate characteristics of the Dhapa uncontrolled landfill site in Kolkata, India

Parameters ^a	Mean \pm SD ^b	Range	No. of samples	Leachate discharge standards ^c	
				Inland surface water	
pH	8.20 \pm 0.17	7.8 – 8.6	12	5.5 – 9	
EC	27364.88 \pm 11960	9557.14 – 52600	12	–	
TDS	9007.50 \pm 3571	2320 – 15700	12	2100	
Na ⁺	2267.91 \pm 1375	292.11 – 5342	12	–	
K ⁺	1688.19 \pm 996	168.37 – 3375	12	–	
F ⁻	1.06 \pm 1.11	0.20 – 2.53	12	2	
Cl ⁻	3973.11 \pm 1446	2103 – 6735	12	1000	
HCO ₃ ⁻	29317.44 \pm 29357	5319.20 – 127032	12	–	
SO ₄ ²⁻	1721.20 \pm 1670	52.50 – 5730	12	–	
PO ₄ ³⁻	33.27 \pm 45.72	1.20 – 156	12	–	
NO ₃ ⁻	28.50 \pm 13.30	9.45 – 59.20	12	–	
NH ₄ ⁺	1596.57 \pm 1288	168 – 4210	12	50	
TKN	4455.93 \pm 3214	631 – 9139	12	100	
COD	4933.50 \pm 3189	1200 – 13200	12	250	
BOD ₅	2317.00 \pm 1702	525 – 6440	12	30	
As	0.10 \pm 0.19	0.0045 – 0.5610	12	0.2	
Cd	0.66 \pm 0.94	0.006 – 2.11	12	2.0	
Cr	2.54 \pm 3.25	0.104 – 10.43	12	2.0	
Cu	0.30 \pm 0.14	0.14 – 0.68	12	3.0	
Fe	3.89 \pm 3.52	0.80 – 11.25	12	–	
Hg	0.98 \pm 0.99	0.16 – 2.65	12	0.01	
Mn	1.89 \pm 0.91	0.68 – 3.90	12	–	
Ni	0.48 \pm 0.20	0.20 – 0.77	12	3.0	
Pb	0.63 \pm 0.25	0.37 – 1.14	12	0.1	
Zn	6.16 \pm 6.66	1 – 25.14	12	5.0	

^aAll concentrations are given in mg L⁻¹ except pH and EC (μ S/cm), ^bStandard deviation, ^cMoEFCC 2016

Table 2. Physico-chemical parameters and heavy metal content for groundwater around Dhapa uncontrolled landfill, Kolkata, India in PRM and POM season

Parameters ^a	PRM		POM		WHO standard	
	Mean \pm SD ^b	Range	Mean \pm SD ^b	Range	Desirable limit	Permissible limit
pH	7.30 \pm 0.14	7.1 – 7.6	7.20 \pm 0.26	7 – 7.8	7 – 8.5	9.2
TDS	1148.00 \pm 295	711 – 1820	1045.00 \pm 742	400 – 3390	500	1500
Ca ²⁺	147.47 \pm 45	24.02 – 248.25	147.84 \pm 67	26.02 – 320.32	75	200
Mg ²⁺	80.71 \pm 16	51.94 – 120.48	95.19 \pm 66	41.20 – 328.01	50	150
Na ⁺	139.32 \pm 48	85.23 – 281.91	287.14 \pm 127	173.91 – 739.13	–	200
K ⁺	2.46 \pm 0.83	1.27 – 3.92	3.44 \pm 0.81	1.47 – 5.16	–	12
Cl ⁻	435.26 \pm 135	156.55 – 715.83	480.86 \pm 263	141.80 – 1264.09	200	600
HCO ₃ ⁻	376.78 \pm 67	259.25 – 535.75	1449.94 \pm 456	881.45 – 2825.83	–	500
SO ₄ ²⁻	21.18 \pm 13	12 – 65.75	22.99 \pm 11	4.15 – 51.55	200	400
NO ₃ ⁻	1.7 \pm 0.42	0.71 – 2.38	1.3 \pm 0.81	0.54 – 4.38	–	50
As	0.0031 \pm 0.003	BDL ^c – 0.009	0.0036 \pm 0.003	BDL ^c – 0.0088	–	0.01
Cd	0.01 \pm 0.0019	0.0097 – 0.017	0.02 \pm 0.001	0.016 – 0.022	–	0.003
Cr	0.04 \pm 0.03	BDL ^d – 0.08	0.05 \pm 0.02	0.03 – 0.14	–	0.05
Cu	0.0047 \pm 0.001	0.0029 – 0.0079	0.0060 \pm 0.002	0.0028 – 0.0094	–	2.0
Fe	0.53 \pm 0.39	0.02 – 1.73	2.29 \pm 2.19	0.067 – 9.57	–	0.3
Hg	0.22 \pm 0.1	0.02 – 0.36	0.23 \pm 0.05	0.15 – 0.3	–	0.006
Mn	0.30 \pm 0.08	0.15 – 0.45	0.26 \pm 0.09	0.09 – 0.47	–	0.5
Ni	0.04 \pm 0.02	0.01 – 0.08	0.02 \pm 0.01	0.0076 – 0.05	–	0.07
Pb	0.02 \pm 0.01	0.005 – 0.05	0.06 \pm 0.05	0.008 – 0.2	–	0.01
Zn	1.29 \pm 0.51	0.42 – 2.11	0.22 \pm 0.13	0.0056 – 0.54	–	5.0

^aAll concentrations are given in mg L⁻¹ except pH, ^bStandard deviation, ^cBDL– Below Detection Limit of 0.0002 mg L⁻¹, ^dBDL– Below Detection Limit of 0.00003 mg L⁻¹

3.2.1. Physico-chemical characteristics of groundwater

The pH of all groundwater samples was neutral and within the desirable limits of WHO standards during PRM and POM seasons respectively. TDS of majority of groundwater samples exceeded the WHO desirable limit of 500 mg L⁻¹ indicating its unsuitability for drinking purposes. Higher TDS values were observed in both the seasons in GW6, GW11, GW14 and GW15 which were in the close vicinity of

the active landfill site indicating the presence of leachate contamination (Fig. 2). Similar trend of TDS was also observed by Mor *et al.* (2006). These high values of TDS may be due to the leaching of various inorganic pollutants into the ground water. The results showed a gradual decrease in TDS concentration as the distance of groundwater samples increases from the active landfill site attributing to the effect of leachate infiltration in the nearby groundwater (Fig. 3a and a').

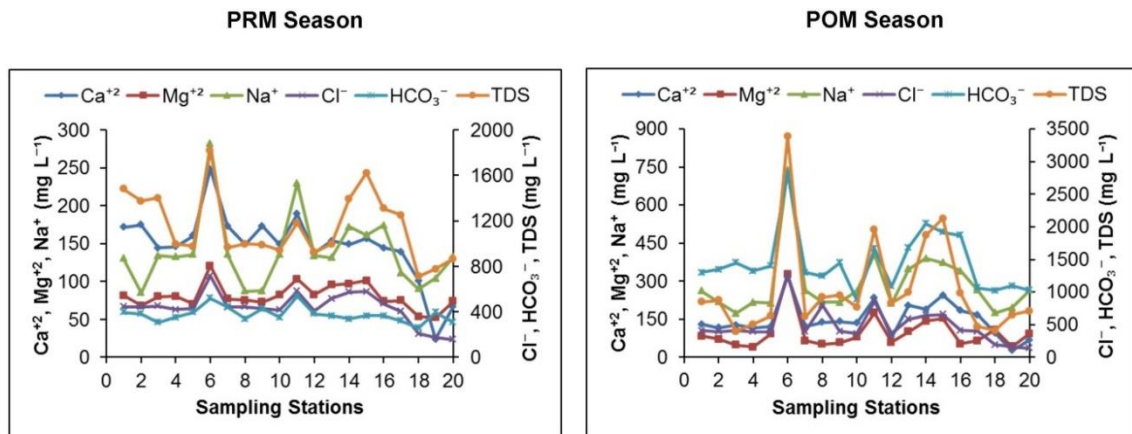


Figure 2. Seasonal variation of physico-chemical parameters in groundwater samples

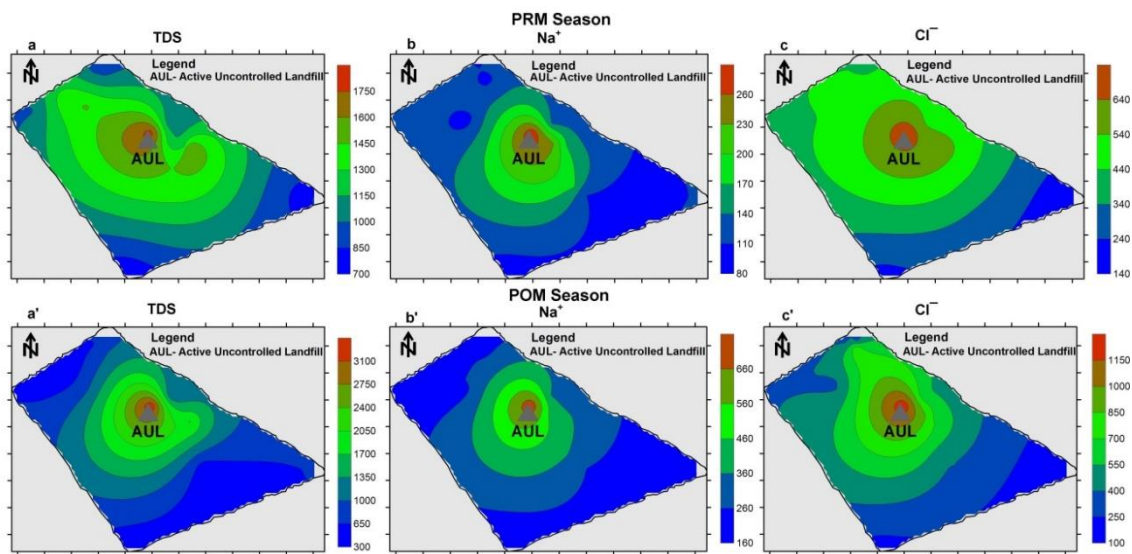


Figure 3. Spatial distribution maps of TDS, Na⁺ and Cl⁻ of groundwater samples (Concentrations are in mg L⁻¹)

In the PRM season, Ca²⁺ and Mg²⁺ concentrations were found to be higher than the WHO desirable limits in 90% and 100% of groundwater samples respectively. In terms of meq L⁻¹, percentage of Ca²⁺, Mg²⁺, Na⁺ and K⁺ ions in PRM season were 36.96, 32.28, 30.44 and 0.32 respectively. Thus the decreasing hierarchy of major cations was Ca²⁺ > Mg²⁺ > Na⁺ > K⁺ in PRM season. Whereas, in the POM season, Ca²⁺ concentrations were found to surpass the WHO desirable limit in 90% of groundwater samples whereas Mg²⁺ and Na⁺ were above the WHO limit in 85% of samples. In terms of meq L⁻¹, percentage of Ca²⁺, Mg²⁺, Na⁺ and K⁺ ions in POM season were 26.55, 28.18, 44.95 and 0.32 respectively. Thus the decreasing hierarchy of major cations was Na⁺ > Mg²⁺ > Ca²⁺ > K⁺ in POM season.

The concentrations and hierarchy of cations changed as a result of seasonal effect with leachate percolation in groundwater. Likewise in the PRM season, Cl⁻ was present in higher concentrations in 90% of groundwater samples exceeding the WHO desirable limit for drinking. In terms of meq L⁻¹, percentage of Cl⁻, HCO₃⁻, SO₄²⁻ and NO₃⁻ ions in PRM season were 64.89, 32.64, 2.33 and 0.14 respectively. Thus the decreasing hierarchy of major anions was Cl⁻ > HCO₃⁻ > SO₄²⁻ > NO₃⁻ in PRM season. But in the POM season, Cl⁻ and HCO₃⁻ concentrations were found to be higher than the WHO prescribed limit in 90% and 100% of groundwater samples respectively. In terms of meq L⁻¹, percentage of Cl⁻, HCO₃⁻, SO₄²⁻ and NO₃⁻ ions in POM season were 35.86, 62.82, 1.27 and 0.06 respectively. Thus

the decreasing hierarchy of major anions was $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^-$ in POM season. Seasonal effect also changed the concentrations of anions indicating the recharge of groundwater along with the admixing of landfill leachate within the aquifer matrix. Higher concentrations of Ca^{+2} , Mg^{+2} , Na^+ , Cl^- and HCO_3^- were found in GW6, GW11, GW13, GW14 and GW15 which were closest to the active landfill site (Fig. 2). Moreover, in both the seasons, Na^+ and Cl^- , the characteristic pollutants of landfill leachate

represented a gradual decrease in concentration in groundwater samples as the distance increases from the active landfill site implicating the influence of leachate on groundwater (Fig. 3b, b', c and c'). Thus, in this study, the presence of high concentrations of TDS, Ca^{+2} , Mg^{+2} , Na^+ , Cl^- and HCO_3^- ions can be attributed to the landfill leachate as the concentration of these elements were much higher than their natural background values in Kolkata (Supplementary Table 1) (WBPCB, 2014).

Supplementary Table 1. Natural background values of physico-chemical parameters of groundwater of Kolkata in 2014

Parameters ^a	Min	Max	Mean
pH	7.50	7.80	7.60
TDS	494	694	614.67
Ca^{+2}	72.00	104.00	85.33
Mg^{+2}	19.44	53.46	38.07
Na^+	72.90	154.30	123.80
K^+	3.00	5.00	3.67
Cl^-	107.63	136.98	121.48
HCO_3^-	190.00	370.00	300.00
SO_4^{2-}	BDL ^b	29	14.19
NO_3^-	0.01	0.55	0.26
As	-	-	BDL
Cd	-	-	BDL
Total Cr	BDL	0.0063	0.0027
Cu	-	-	BDL
Fe	0.10	0.45	0.32
Hg	BDL	0.0013	0.00085
Ni	-	-	BDL
Pb	-	-	BDL
Zn	0.11	0.64	0.37

^aAll concentrations are given in mg L^{-1} except pH, ^bBDL– Below Detection Limit, Source: WBPCB, 2014

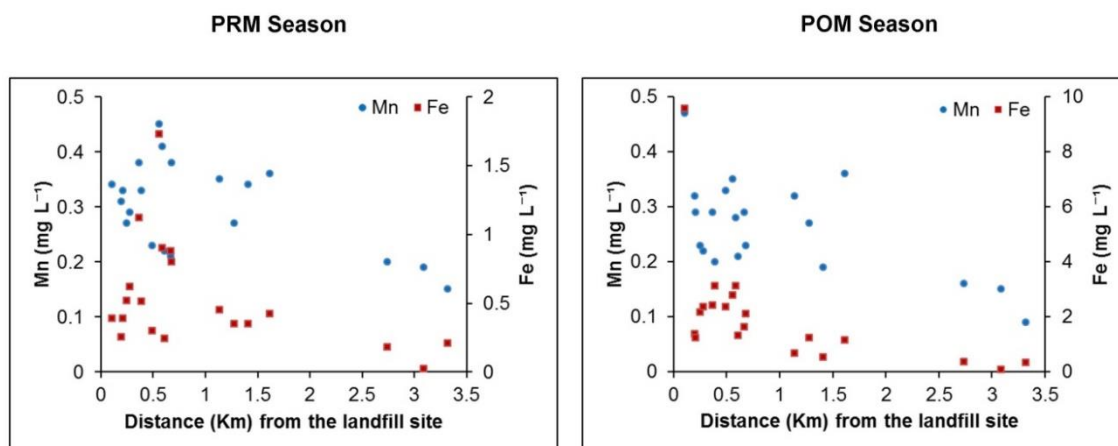


Figure 4. Spatial variation of Mn and Fe with increasing distance from the landfill site

3.2.2. Mn and Fe

Landfill leachate is a reducing effluent which solubilizes the adsorbed Mn and Fe after infiltrating into the groundwater aquifer (Mor et al., 2006). Although Mn concentration of all groundwater samples was within the WHO permissible limit in both the seasons, Fe concentration exceeded the WHO permissible limit in 70% and 90% of groundwater samples in PRM and POM season respectively. High concentration of Fe was also reported in groundwater surrounding landfill site of erode city, Tamil Nadu, India (Nagarajan et al., 2012). However, Mn and Fe sourced from landfill leachate can be identified as Mn and Fe values in

groundwater samples gradually decreases as the distance increases from the active landfill site (Fig. 4). The lower values of Mn and Fe at the distant sampling stations from the landfill site indicated the prevalence of oxidizing condition as Mn and Fe precipitates in the range of neutral pH under oxidizing environment.

3.2.3. Heavy metals

Leachate plume of Dhapa landfill site showed relatively high concentrations of heavy metals. Thus groundwater in the studied area was highly contaminated with heavy metals like Cd, Cr, Hg, Ni and Pb in both the seasons as a result of very little effect of redox control on the heavy

metal transport. However, the concentrations of As, Cu and Zn in both the seasons were within the WHO stipulated standard in all the sampling stations. Pb, Hg and Cd in both the seasons were detected above the WHO permissible limit in all the sampling stations (Table 2). Pb and Hg showed a declining trend in concentration as the distance of sampling stations increases from the active landfill site implicating the direct mixing of leachate in groundwater (Fig. 5a, a', b and b'). However, Pb was also high at remote sampling stations like GW19 and GW20 upstream to the active landfill site may be due to some geogenic sources. In

PRM season, Cd with highest concentration was found at GW18 (0.017 mg L^{-1}) away from active landfill site and in POM season, GW16 (0.022 mg L^{-1}) showed highest concentration which indicated some local anthropogenic activities. During PRM and POM season, Cr was found to be higher than the WHO permissible limit in 35% and 70% of groundwater samples respectively. Cr showed the highest concentration in GW6 closest to the active landfill site and its concentration gradually decreases from the active landfill (Fig. 5c and c').

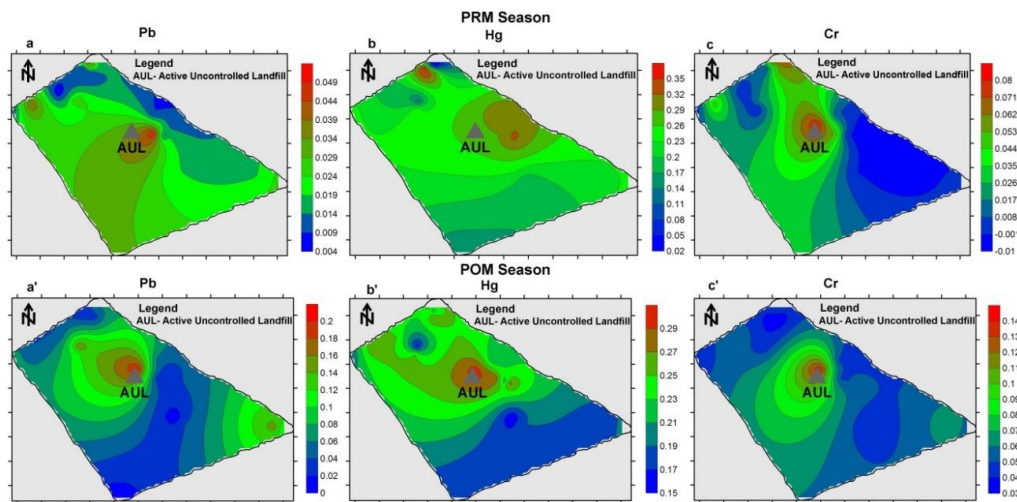


Figure 5. Spatial distribution maps of Pb, Hg and Cr of groundwater samples (Concentrations are in mg L^{-1})

In PRM season high values of Ni were present in GW6 (0.07 mg L^{-1}), GW11 (0.08 mg L^{-1}) and GW14 (0.07 mg L^{-1}). Apart from these sampling stations, Ni in both the seasons was below the stipulated standards. Generally, attenuation processes like sorption and precipitation delimit the extent of heavy metal pollution in groundwater surrounding landfills. However in this study, heavy metals in leachate significantly affected the groundwater despite cation exchange capacity of the soil column and attenuation mechanisms. These high values of heavy metals can be attributed to the deficient or unavailable sorption and precipitation reactants within the aquifer matrix. Similarly, like the major ions, the high concentration of Cd, Cr, Hg, Ni and Pb in the study area can be imputed to the landfill leachate as the concentration of these elements were much higher than their natural background values in Kolkata (Supplementary Table 1) (WBPCB, 2014).

3.3. Groundwater suitability for Irrigation

Groundwater analysis results of the study area based on SAR, RSC and Na% were also determined to compare with irrigational water quality standards in PRM and POM seasons.

3.3.1. Sodium Adsorption Ratio (SAR)

SAR is one of the important parameters to assess irrigational water quality as it signifies alkali or sodium hazard to vegetation (Ramesh and Elango, 2012). SAR varied from 1.39 to 3.67 in PRM season and 2.89 to 6.94 in POM season which indicated that all groundwater samples

were suitable for irrigational purposes. Irrigation water causes permeability hazards when SAR values are more than 10. In both the season, GW6 closest to the active landfill site showed the highest SAR value implicating the mixing of landfill leachate into the groundwater. Moreover, all groundwater samples exhibited higher SAR values in POM season in comparison to PRM season as a result of dissolution of Na^+ with the leachate flowing out from the landfill site.

3.3.2. Residual Sodium Carbonate

Suitability as irrigation water can also be identified by evaluating RSC (Siddiqui *et al.*, 2005). According to USEPA (1999), irrigation waters are safe when $\text{RSC} < 1.25$ and becomes unsuitable as RSC exceeds 2.5. RSC in groundwater ranged from -13.78 to 1.05 meq L^{-1} in PRM season and 1.29 to 17.14 meq L^{-1} in POM season. Negative RSC indicated that excess concentrations of Ca^{+2} and Mg^{+2} were present in PRM season. Thus on the basis of RSC, groundwater samples in PRM season were suitable for irrigation. However, in POM season, 85% of samples exceeded the RSC limit implying the dissolution of landfill leachate in groundwater.

3.3.3. Sodium Percentage

Percentage of sodium (Na%) is another vital parameter to assess suitability of irrigation water (Wilcox 1948). Water samples for irrigation is suitable when $\text{Na\%} < 35 \text{ meq L}^{-1}$ (Vasanthavigar *et al.*, 2010). Na% in groundwater varied between 20.99 to 45.97 meq L^{-1} in PRM season and 35.75

to 64.11 meq L⁻¹ in POM season. In PRM season, 10% of samples (GW6 and GW11) closest to the active landfill site showed Na% exceeding 35 meq/L. However, in POM season, all of the groundwater samples exhibited higher Na% making it unsuitable for irrigation. These higher values can be attributed to the mixing of pollutants from leachate and also may be due to the intrusion of chemical fertilizers from the nearby agricultural fields.

3.4. Hydrogeochemical classification of groundwater

The hydrogeochemical characteristics of the groundwater samples in the studied area were observed through the Piper trilinear diagrams. Distribution of water types in the Quaternary aquifer underlying the study area shows that the aquifer has 4 water types during PRM season and 2 water types during POM season (Fig. 6). 90% of groundwater samples collected during PRM season were characterized as brackish type (65% as [Ca²⁺-Cl⁻] type, 15% [Mg²⁺-Cl⁻] and 10% [Na⁺-Cl⁻] type), which can be

attributed to the intrusion of landfill leachate into the groundwater as Cl⁻ is one of the major characteristic pollutant of landfill leachate. [Na⁺-Cl⁻] type characteristic of saline water was found in GW6 and GW11, closest to the active landfill site clearly showing the input of Na⁺ and Cl⁻ ions from landfill leachate. Rest 10% of groundwater samples (GW19 and GW20) upstream to active landfill site were characterized as [Mg²⁺-HCO₃⁻] type which represents background water quality of the study area. During POM season, 95% of groundwater samples were identified as [Na⁺-HCO₃⁻] type and 5% as [Mg²⁺-HCO₃⁻] type. [Na⁺-HCO₃⁻] type was observed may be as a result of aquifer recharge along with the cation exchange with Ca²⁺ implying the mixing of Na⁺ from landfill leachate. GW18 far away from active landfill site showed [Mg²⁺-HCO₃⁻] type. But GW19 and GW20 showed [Na⁺-HCO₃⁻] type which can be attributed to the agricultural return flow as the area is highly used for cultivation.

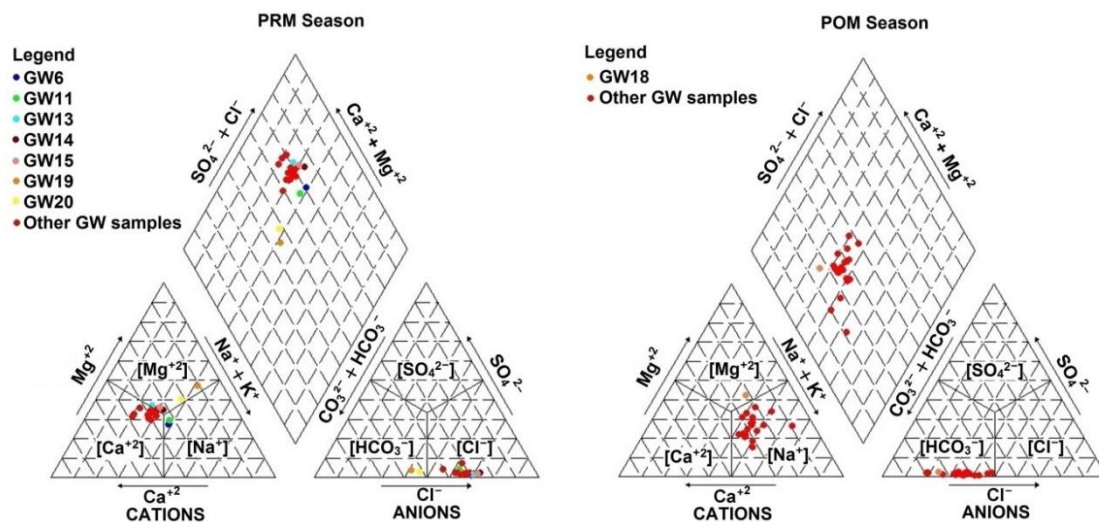


Figure 6. Piper diagram for groundwater samples in PRM and POM season

3.5. Hierarchical Cluster Analysis (HCA)

In order to better understand the sources of groundwater pollutants, HCA was performed on the groundwater samples in PRM and POM seasons for clustering the physico-chemically similar groundwater samples. In PRM season, 6 clusters named C1–C6 were identified by drawing an imaginary phenon line across the dendrogram at a linkage distance of 10 (Fig. 7).

More or less number of clusters could be specified by sliding the phenon line through the dendrogram to obtain significant clusters of samples (Li et al., 2012). C1 linked to other clusters at the highest linkage distance indicating lowest similarity among C1 with other clusters. Groundwater samples of C1 (GW16, GW18, GW19 and GW20) were distinctly different from other clusters since C1 samples were comparatively unpolluted as located upstream to the active landfill site. C2 (GW6 and GW11) represented the highly polluted groundwater samples which were closest to the active landfill site and linked to C3–C4 and C5–C6 at a lower linkage distance indicating groundwater samples of C2 were physico-chemically

similar to C3–C4 and C5–C6. C3 and C4 along with C5 and C6 are linked to each other at the lowest linkage distance indicating higher similarity among them. C3 (GW13, GW14 and GW15) represented the groundwater samples closer to the active landfill site whereas C4 (GW1, GW2, GW3 and GW8) represented the groundwater samples closer to the closed landfill site. Since the rate of dispersion of leachate pollutants was restricted in PRM season, C3 and C4 showed higher degree of similarity. C5 (GW4, GW9, GW10 and GW12) and C6 (GW5 and GW7) showed similarity as these groundwater samples were located downstream to the active landfill site.

In POM season, 3 clusters named C1–C3 were identified by drawing phenon line across the dendrogram at a linkage distance of about 8 (Fig. 7). C1 (GW6, GW11, GW13, GW14 and GW15) represented the highly polluted groundwater samples which were closer to the active landfill site. Within C1, GW6 was linked to other samples at a higher linkage distance as GW6 (closest to the active landfill site) was most polluted indicating the high infiltration of landfill leachate in groundwater. C2 (GW16, GW18, GW19 and

GW20) and C3 (GW1, GW2, GW3, GW4, GW5, GW7, GW8, GW9, GW10 and GW12) represented the groundwater samples which were located upstream and downstream to the active landfill site respectively. C1 linked to C2–C3 at a higher linkage distance representing C1 samples as physico-chemically different from other clusters signifying

the influence of landfill leachate in nearby groundwater. GW17 which was located upstream to the active landfill site clustered in C6 in PRM season and C3 in POM season of downstream samples may be due to some geogenic sources.

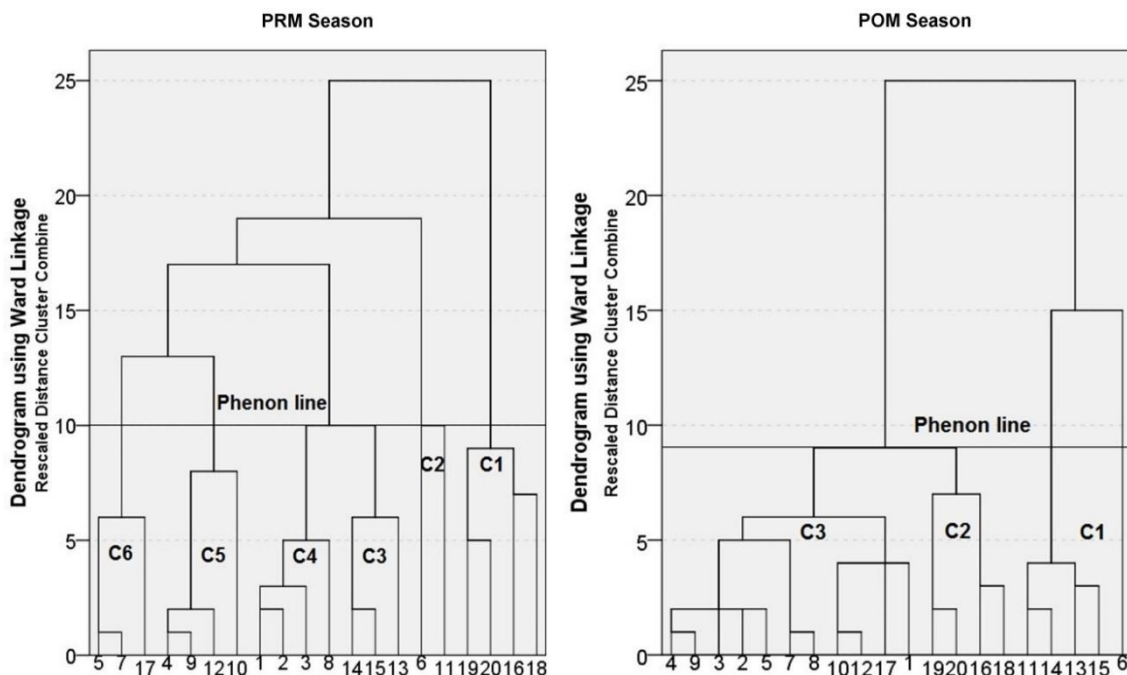


Figure 7. Dendrogram for groundwater samples in PRM and POM season

4. Conclusions

The major environmental concern in the present study indicated the toxic effect of uncontrolled landfill leachate on the surrounding groundwater quality. The impact of leachate percolation on the surrounding groundwater was evidenced from the reducing environment along with higher concentrations of pollutants closer to the active landfill site. In terms of hydrogeochemical classification, majority of groundwater samples in PRM season were characterized as brackish ($\text{Ca}^{+2}\text{-Cl}^-$, $\text{Mg}^{+2}\text{-Cl}^-$ and $\text{Na}^+\text{-Cl}^-$ type) and specifically [$\text{Na}^+\text{-Cl}^-$] type was observed closest to the active landfill site as a result of landfill leachate intrusion. However in POM season, majority of the groundwater samples were characterized as [$\text{Na}^+\text{-HCO}_3^-$] type indicating the recharge of the groundwater aquifer along with the admixing of landfill leachate. Moreover, the hierarchical cluster analysis demonstrated that in PRM season, highly contaminated samples of C2 (closest to the active landfill site) were physico-chemically different from C1 (upstream samples) but more similar to other clusters (C3, C4, C5 and C6) which were located closer and downstream to the active landfill site. However in POM, highly contaminated samples of C1 (closest to the active landfill site) became physico-chemically distinct to C2 (upstream) and C3 (downstream) clusters as an effect of dissolution of high concentration of leachate pollutants. Moreover on the basis of WHO drinking water quality standards, groundwater in this area is not at all suitable for drinking and would be toxic to health. Nevertheless, on the

basis of irrigational water quality standards, RSC and $\text{Na}\%$ indicated that groundwater samples were suitable for irrigation only in PRM season. The SAR values were found to be high in POM season. Therefore, the present study indicated the need for pre-treatment process on landfill leachate before draining in to surrounding wheels and bheries. Moreover, immediate attention is required towards the continuous monitoring and remediation of the groundwater around the Dhapa landfill site to prevent further deterioration of the water quality.

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