

Understanding the Contaminant Chemistry of Water Resources at Urban Solid Waste Disposal Site, Hyderabad, India

Nageswara Rao Peddi¹, Sugriva Reddy Adlagunvan^{2*}, Ravi Kumar Gumma³

¹Central Ground Water Board, Southern Region, Hyderabad - 500 068, India. (Retd.)

²Rajiv Gandhi National Ground Water Training Institute, Raipur - 492 001, India. (Retd.)

³Central Ground Water Board, Southern Region, Hyderabad - 500 068, India

*E-mail: sugrivaadla@gmail.com

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ABSTRACT

The Hyderabad urban solid waste dump site, though located on a rocky hillock, has a highly weathered mantle apart from an interconnected network of fractures. These hydrological features favored massive dissipation of contaminants into the surface as well as sub-surface water resources. The surface water bodies in the vicinity turned into leachate pools and groundwater in the zone of influence is not fit for any use. Both surface (15) and groundwater (79) samples were collected during 2011 and 2012 hydrological cycles and tested for major parameters. A few samples (15) of 2012 were also analyzed to determine TOC, BOD, and COD. The general order of abundance of prominent ion species in groundwater was Cl^- , Ca^{2+} , Na^+ , Mg^{2+} , HCO_3^- and SO_4^{2-} . A very high and similar Cl^- concentration in surface water (37 meq/l) and contaminated groundwater (40 meq/l) establish that solid waste stockpile was the point source through leachate. The presence of high (>200 mg/l) TOC, BOD, and COD in many surface and groundwater samples supports the inference. Modified Piper plots display the Ca-Mg-Cl and Ca-Mg-HCO₃ were the dominant hydrochemical facies in groundwater, whereas many surface water and few groundwater samples belong to Na-Cl/SO₄ type. A good correlation (~0.90) between Cl^- - Ca^{2+} , TH, Na^+ , and Mg^{2+} points out that these ion species were from the same source. Gibbs plots, positive CAI-1 and 2, together with >2 ratios of $\text{Ca}^{2+}/\text{Mg}^{2+}$, Cl^-/Na^+ in many samples divulge water-rock interaction and ion exchange were also controlling the hydrochemistry. The low $\text{HCO}_3^-/\text{Cl}^-$, TA/TH and $\text{SO}_4^{2-}/\text{HCO}_3^-$ values indicate an insufficient influx of freshwater and non-lithogenic sources altered the groundwater chemistry. Favorable hydrochemistry in the form of alkaline water, high TH, Cl^- and prevailing redox conditions as well as methanogenic phase of dump yard might have spurred up ion enrichment activity within the zone of influence of point source.

INTRODUCTION

A globally growing urban population is resulting in the generation of enormous solid waste and its safe dispensation has become a challenge to municipal administrators and sanitation experts. Largely municipal solid waste (MSW) is disposed off in an unorganized manner and is rarely processed for safe disintegration, which is creating havoc on the local environment. Talalaj and Biedka (2016) shared the data from 2013 which show that in 14 countries of the European Union, the share of land-filling was over 50 %, and in 6 of these countries

even over 75 % (Greece, Croatia, Cyprus, Latvia, Malta, Romania; Eurostat 2015). In the USA, about 135 million tons of solid wastes (53.8 %) were discarded in landfills in 2012 (USEPA 2012). In 2002, in China the quantity of MSW disposed of was 74.04 million tons, 89.30% of which was land-filled, 3.72% was incinerated, and 6.98% was composted (Huang et. al., 2006). India produced 55.51 million tons of MSW in 2018-19 of which only 20.35% is treated (CPCB 2019). Dumping of solid waste either as a landfill or over-ground led to the generation of harmful compounds which propagate to the regional hydrological cycle. Water has become the first victim of solid waste mismanagement, often when surface water bodies turn to cesspools of leachate and point source of aquifer contamination (Raman and Sathiya 2008; Zhiyong et. al., 2016; Nataliaia and Oleg 2017; Vahabian et. al., 2019). Though many guidelines and environmental protection acts exist, they are more flouted than followed, especially in underdeveloped countries. Land with massive rock structures or confined layers are selected as solid waste disposal sites or the sites are engineered to prevent the percolation of pollutants. But over the years, maintenance and management of such structures did not receive the required attention, leading to the proliferation of toxic chemicals deteriorating the local aqueous system. Ample studies were carried out on landfill sites world-over which present the prevailing poor conditions along with reasons and causes for contaminants migration (Peter Kjeldsen et. al., 2002; Kola-Olusanya 2012; Daniel et. al., 2013; Akhtar and Tang 2014; Bikash Adhikari et. al., 2014; Salar Rezapour et. al., 2018; Vongdala et. al., 2019; Dan Zeng et. al., 2021). Thus far, the focus of the research was mostly limited to deciphering the extent and variability of contamination apart from discussing the physiological features and local hydrological properties that promote the propagation of pollutants. Innovations in analytical hydrochemistry and solute transport models helped in understanding contaminant kinetics. Even though regional hydrological features, as well as load and age of the solid waste, determine the extent of pollution the receptive chemical characteristics of the host aqueous environment cannot be ignored. Dan Zeng et. al., (2021) concluded that the groundwater contamination near the landfill sites was influenced by leachate, soil, climate, and hydrogeology characteristics. In this context, research on hydrogeochemistry of groundwater close to solid waste dump sites is gaining ground. It is all the more important as groundwater chemistry is governed by aquifer matrix apart from anthropogenic or external inputs. A highly contaminated hydrological environment at Jawaharnagar municipal solid waste dumpsite in Hyderabad city was

studied with the assumption that groundwater chemistry has also influenced the absorption of contaminants and contaminant chemistry of pore water altered the mineralization processes.

The infiltration rate was high (29 cm/hr) at the Madyala stream, low at Rajiv karmika Nagar (9.2 cm/hr) and Cherial village (9.6 cm/hr; Rao, 2015).

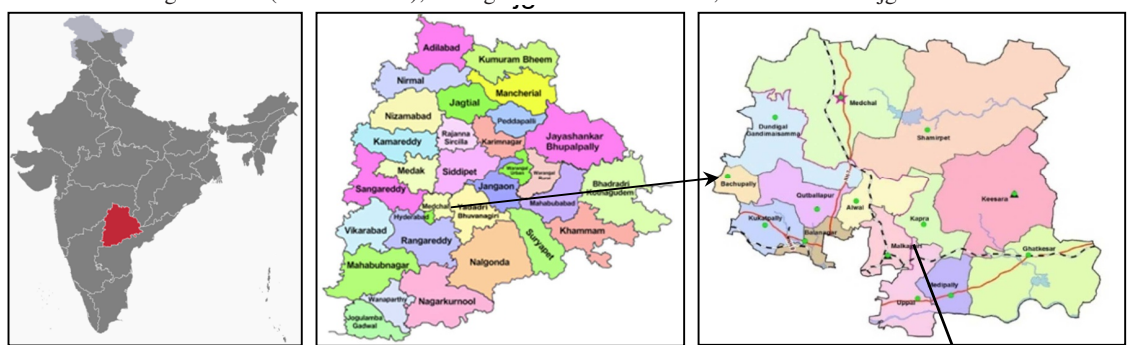
STUDY AREA

The study area comprising a solid waste dumping site and its surroundings spread over nearly 5 sq km at Jawaharnagar village, Medchal-Malkajiri district, Telangana State, India (Fig. 1). The area falls between 17° 30' to 17° 32' N latitude and 78° 35' to 78° 38' E longitude, its general topographic elevation ranges from 510 to 560 m. The climate in the area is semi-arid and receives a normal annual rainfall of 753 mm. The study area belongs to the Madyala stream watershed and Dammaiguda mini watershed of the Musi river which is part of the Krishna river basin. The drainage pattern is dendritic to sub-dendritic. The area is underlain by the gray granite gneisses and massive granites of the Archaean age. The thickness of weathering extends down to 18 m, while the fractures are recorded down to 106 m. Water table elevation contour ranges from 500 to 560 m with a gradient of 10 m/km. The groundwater flow is towards the southeast.

METHODS AND METHODOLOGY

Hydrogeological studies were carried out in May 2011 and water sampling sources were identified. A varied sampling pattern was followed to have a wide representation of contaminated as well as normal areas. Both surface (15 nos) and groundwater (79 nos) samples were collected in pre and post-monsoon seasons of 2011 and 2012 to cover two hydrological cycles. All the samples were tested for 13 parameters in the chemical laboratory of Central Ground Water Board, Southern Region, Hyderabad following standard procedures of APHA (2017) and 15 samples for TOC, COD, and BOD in Centre for Environment JNTU (H). The pH was measured by using the digital pH meter and EC by the EC/TDS analyzer, CM 183 model. The classical methods of analysis were applied for the estimation of Ca²⁺, Mg²⁺, CO₃²⁻, HCO₃⁻ and Cl⁻. Na⁺ and K⁺ were analyzed using the flame photometry method using the CL-345 model. SO₄²⁻ was

India with Telangana State (marked in red); Telangana State with districts, Medchal-Malkajiri district with mandals



Jawaharnagar GHMC dumping yard.

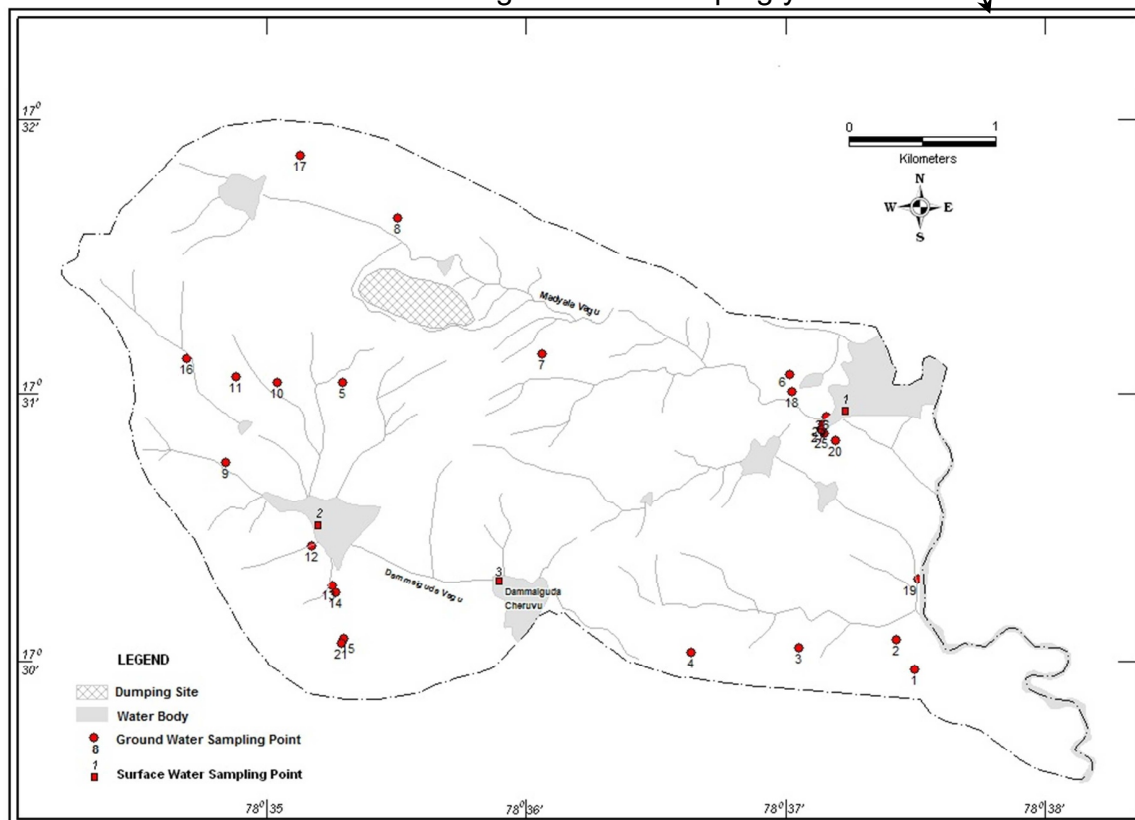


Fig.1. Key map with study area and sample locations

estimated by the turbidity method with the digital Nephelo-Turbidity meter 132 model. NO_3^- was estimated by applying the UV-Vis screen method with UV- visible spectro-photometer UV-1201 model. F^- was tested by the ion-selective electrode method using the Orion 290A+ model. The total hardness (TH) and total dissolved solids (TDS) were estimated by the calculation method (Hem, 1991). The obtained results were tested for accuracy by calculating the normalized inorganic charge balance (Huh et al., 1998). All of the analyzed samples had ionic charge balances of $< \pm 3\%$.

RESULTS AND DISCUSSION

Surface Water Chemistry

The results of all the tested inorganic parameters exhibit that the surface water of tanks close to Hyderabad integrated municipal solid waste dump site (HIMSWDS) turned into pools of leachate (Supplemental material 1). The mean pH was about 8.00, EC 13000 $\mu\text{S}/\text{cm}$, TH 753, Ca^{2+} 107, Mg^{2+} 118 and SO_4^{2-} 291, Na^+ 813, K^+ 530, HCO_3^- 978, Cl^- 1304, and NO_3^- 262 (all in mg/l ; Table 1). Many tested parameters of water samples from Irlagutta, Haridaspalli, Cherial, and Dammaiguda tanks (in order of contaminant abundance) were abnormally high and very much above the MoEF benchmark for leachate or effluent land discharge (MoEF, 2016).

Groundwater Chemistry

The mean of the tested results of the entire groundwater sample belonging to four monitoring episodes (79) indicates the influence of solid waste dumps on the hydrochemistry of the area. Though concentration of few parameters (pH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} and F^-) were found within the background values of granitic terrain, the EC (2062 $\mu\text{S}/\text{cm}$), HCO_3^- (268 mg/l), Cl^- (474 mg/l), NO_3^- (58 mg/l) were very high (Table 1). The samples represent the core area as well as periphery beyond the zone of influence of dumpsite thus the average values do not exhibit prevailing chemical quality scenario. To have keen insight into contaminant chemistry, the samples having EC > 3000 $\mu\text{S}/\text{cm}$ were segregated and their chemistry was deliberated in conjunction with other samples. All the groundwater samples (79) belonging to four monitoring sessions were classified into two groups based on EC as normal groundwater (designated for discussion purpose only) with $< \text{EC } 3000$ $\mu\text{S}/\text{cm}$ which were 62 samples and those with EC > 3000 $\mu\text{S}/\text{cm}$ as contaminated groundwater which were 17 samples. Normal groundwater samples also have certain parameters in high concentration and none of them are suitable for drinking uses

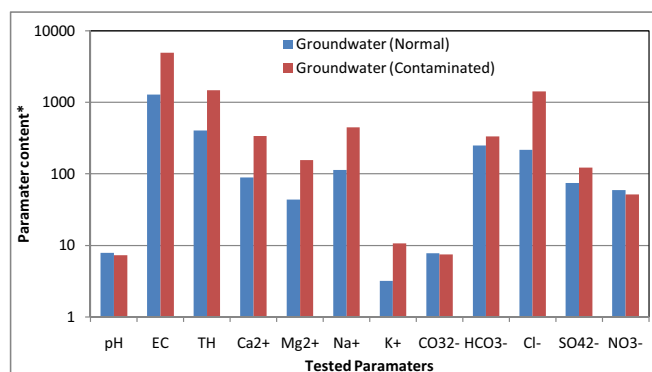


Fig. 2. Mean content of parameters for Good and Contaminated samples. *(Units - EC: $\mu\text{S}/\text{cm}$; others mg/l)

when compared with acceptable criteria of Indian drinking water standards. The mean concentration of all the parameters except pH and NO_3^- were very high in contaminated samples than normal ones (Supplemental material 2 and Table 1). It is obvious, but most of the parameters were higher by $> 250\%$ and Cl^- by 528% than normal samples. A small variation in HCO_3^- (32%) concentration is noticed among two sets of samples and pH and NO_3^- were marginally less (-0.56 and -6.68 mg/l respectively) in contaminated samples. Minimum and maximum values of pH and NO_3^- were distinctly different (low and high) in normal samples from those contaminated (Fig. 2). Elevated mean content of Ca^{2+} (337 mg/l), Na^+ (444 mg/l) and Cl^- (1414 mg/l) together with normal pH and low NO_3^- in contaminated samples confirm the dumpsite as the pollution source. Spatial distribution plots of TDS, TH, Cl^- substantiate MSW as the point source and migration of pollutants (to south) through preferred path ways controlled by local hydrogeological conditions (Fig. 3a-f). Nonexistence of other contamination source like industries in and around the area supports the contention. The mean EC was about 5000 $\mu\text{S}/\text{cm}$ in contaminated samples, but more than half of the samples (9nos) have it from 3000 to 4000 $\mu\text{S}/\text{cm}$ range and five samples fall in 4000 to 5000 $\mu\text{S}/\text{cm}$ range. Only two samples have very abnormal conductivity (> 9000 $\mu\text{S}/\text{cm}$) which could be due to local contamination. In the other group of samples (normal) most of the tested wells (76%) had an EC of 1000 to 2000 $\mu\text{S}/\text{cm}$ (Supplemental material 3 and Table 1). Presence of high organic compounds like TOC - 154 mg/l , COD - 176 mg/l , and BOD - 117 mg/l (average of 15 groundwater samples of pre-monsoon 2012) support the presence of biomass in waste

Table 1. Summary results of chemical analysis of all water samples belonging to 2011 and 2012 hydrological cycles

	pH	EC $\mu\text{S}/\text{cm}$	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^{2-} mg/L	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-
Surface water (n=15)													
Minimum	7.50	1220	350	56.1	49	117	1.04	0.00	43	305	4.80	7.00	0.13
Maximum	9.06	17640	1440	257	316	2128	2151	120	5368	2907	1440	2000	2.10
Mean	7.95	6251	753	107	118	813	530	15	978.3	1304	291	262	1.07
All Groundwater (n=79)													
Minimum	6.44	400	108	14	2.43	19	0.24	0	12.2	17.7	0.5	3.72	0.12
Maximum	9.24	10540	4040	1174	729	1725	119	72	1232	3205	392	200	2.10
Mean	7.78	2062	635	143	68	184	4.82	7.77	267.5	474	85	58	0.96
Contaminated Groundwater (n=17)													
Minimum	6.44	3014	560	76	10	179	1.17	0.00	49	652	10	10	0.12
Maximum	8.51	10540	4040	1174	729	1725	20	48	1232	3205	330	120	1.00
Mean	7.30	4890	1478	337	155	444	10.69	7.50	332	1414	123	52	0.45
Normal Groundwater (n=62)													
Minimum	6.90	400	108	14	2.43	19	0.24	0.00	12	18	0.50	3.72	0.23
Maximum	9.24	2510	890	253	136	322	86	72	653	737	205	200	2.10
Mean	7.91	1287	404	90	44	113	3.21	7.84	250	216	75	59	1.10

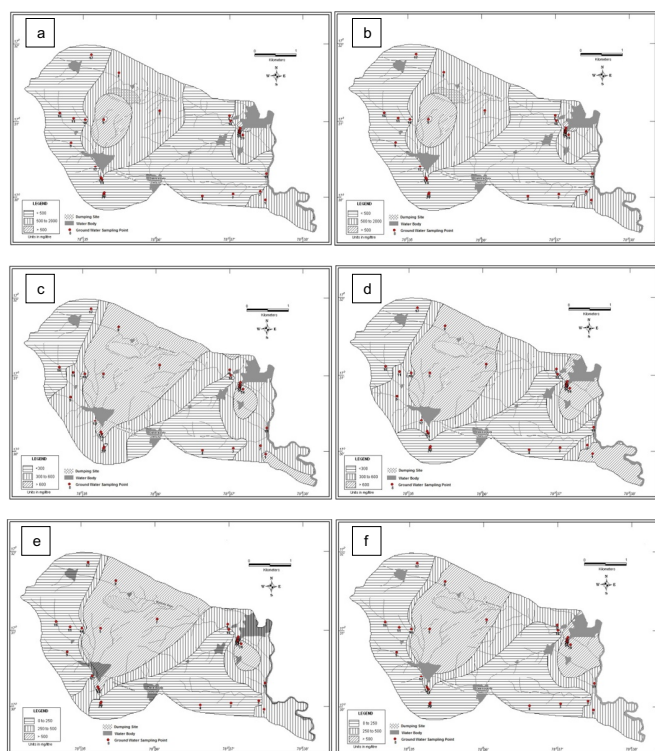


Fig. 3a-f. Spatial distribution of TDS, TH, Cl for pre and post-monsoon seasons, displaying the impact of contamination as well as pollution path ways.

dumps. Moderate mean HCO_3^- (332 mg/l) suggests the aquifer received limited freshwater influx but was replenished with the base flow or unnatural sources which enriched the ion content of groundwater. The pH might be balanced by alkalinity as reflected by the basic nature of the water (pH is >7.00 in most samples).

Hydrogeochemistry

Ion dominance pattern: The ion dominance pattern (IDP) for cations was $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ in 2011 pre-monsoon and both good as well as contaminated samples. The IDP varied in rest of the sampling sessions. Ca^{2+} , Mg^{2+} , Na^+ respectively was the most dominating cation in other sampling sessions. Na^+ was second and third positions in 2011 post-monsoon and 2012 pre-monsoon (Table 2). Among the anions $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$ was the most dominating pattern in three sampling sessions and both types of samples. In post-monsoon 2012 SO_4^{2-} replaced HCO_3^- in second position. In 2012, molar content of Mg^{2+} gained significantly reaching the second position in pre-monsoon and third in post-monsoon replacing Na^+ and Ca^{2+} . Another notable change in 2012 was bicarbonate concentration reduced considerably ranking in fifth and sixth positions in pre and post-monsoon seasons respectively. Predominance of Na^+ and Cl^- in groundwater chemistry points out prevalence of contamination. The variable number of samples and sampling points in 2011 and 2012 could be one of the reasons for changes in IDP. It also validates the assumption of mineralization processes were influenced by multiple sources and external factors.

Water type: Water speciation was studied plotting the data in Chadha's modified Piper plot (Chadha 1999). In all the sampling episodes, the groundwater samples were mostly of Ca-Mg-Cl type with permanent hardness. They were 53% in pre-monsoon 2011, 33% in post-monsoon, 60% in pre-monsoon 2012, and 68% in post-monsoon (Fig. 4a and b). Even most of the highly contaminated groundwater and some of the surface water belong to Ca-Mg-Cl facies

Table 2. Ion dominance pattern and % content of tested ions of groundwater

2011					
Pre-monsoon (n=17)			Post-monsoon (n=12)		
meq/l concentration	meq/l in % content	Ion dominance	meq/l concentration	meq/l in % content	Ion dominance
12.22	27.51	Cl^-	11.65	28.90	Cl^-
11.24	25.30	Na^+	9.78	24.26	Ca^{2+}
7.58	17.07	Ca^{2+}	8.08	20.05	Na^+
7.52	16.93	HCO_3^-	6.35	15.75	HCO_3^-
3.39	7.63	Mg^{2+}	2.31	5.73	Mg^{2+}
1.18	2.66	SO_4^{2-}	1.31	3.24	SO_4^{2-}
1.14	2.57	NO_3^-	0.73	1.81	NO_3^-
0.10	0.22	K^+	0.06	0.15	F^-
0.05	0.11	F^-	0.04	0.10	K^+
0.00	0.00	CO_3^{2-}	0.00	0.00	CO_3^{2-}

2012					
Pre-monsoon (n=25)			Post-monsoon (n=25)		
meq/l concentration	meq/l in % content	Ion dominance	meq/l concentration	meq/l in % content	Ion dominance
14.88	35.58	Cl^-	13.47	33.57	Cl^-
7.98	19.09	Mg^{2+}	7.48	18.63	Na^+
6.60	15.78	Ca^{2+}	6.21	15.47	Mg^{2+}
6.32	15.10	Na^+	6.12	15.24	Ca^{2+}
3.90	9.32	HCO_3^-	2.87	7.15	SO_4^{2-}
1.32	3.16	SO_4^{2-}	1.80	4.48	HCO_3^-
0.72	1.72	NO_3^-	1.09	2.72	NO_3^-
0.05	0.12	K^+	0.81	2.01	CO_3^{2-}
0.05	0.12	F^-	0.25	0.63	K^+
0.00	0.00	CO_3^{2-}	0.04	0.11	F^-

(Fig. 4c and d). This indicates the mixing of high salinity water caused by surface sources, such as liquid and solid waste discharged into nearby land and channels (Jeyaraj et. al., 2016). Another dominant water type was Ca-Mg- HCO_3^- ; about 30% of samples of all but the last sampling episode belong to this facies. Many surface water samples and very few groundwater samples from all the sampling sessions were of Na-Cl/ SO_4 type. It confirms that surface water bodies were cesspools for groundwater contamination. Water is more contaminated in Cherial catchment, which forms discharge area for Madyalavagu water shed, than Dammalguda catchment. Dump site, being the recharge zone, immensely contribute ions which get altered in solute transport process impacting the chemical makeup of water. Water facies further support the contention that natural mineralization processes, as well as anthropogenic activity, were operating in the mineralization of water. (Emmanuel et. al., 2019).

Ionization processes: Abnormal increase and decrease of certain chemical constituents among different sampling sessions suggest that multiple processes were active in the evolution of hydrochemistry. The mechanism controlling the mineralization process was studied using the Gibbs (1970) plots. In Na+K:(Na+K+Ca) vs TDS plot, most of the data points of both the seasons of two years fall close to rock-dominance (Fig. 5a and b). The Cl:(Cl+ HCO_3^-) vs TDS plots exhibit that in pre-monsoon evaporation process whereas in post-monsoon water-rock interaction was dominant in mineralization of groundwater (Fig. 5c and d). $\text{Ca}^{2+}/\text{Mg}^{2+}$ (meq/l) ratio of >2 (mean value vary between 1 and 14) in the majority of the samples in both the seasons (pre and post-monsoon) of 2011 (71%, 75%) and few samples in 2012 (28%, 16%) demonstrate alkali earths were contributed by silicate weathering.

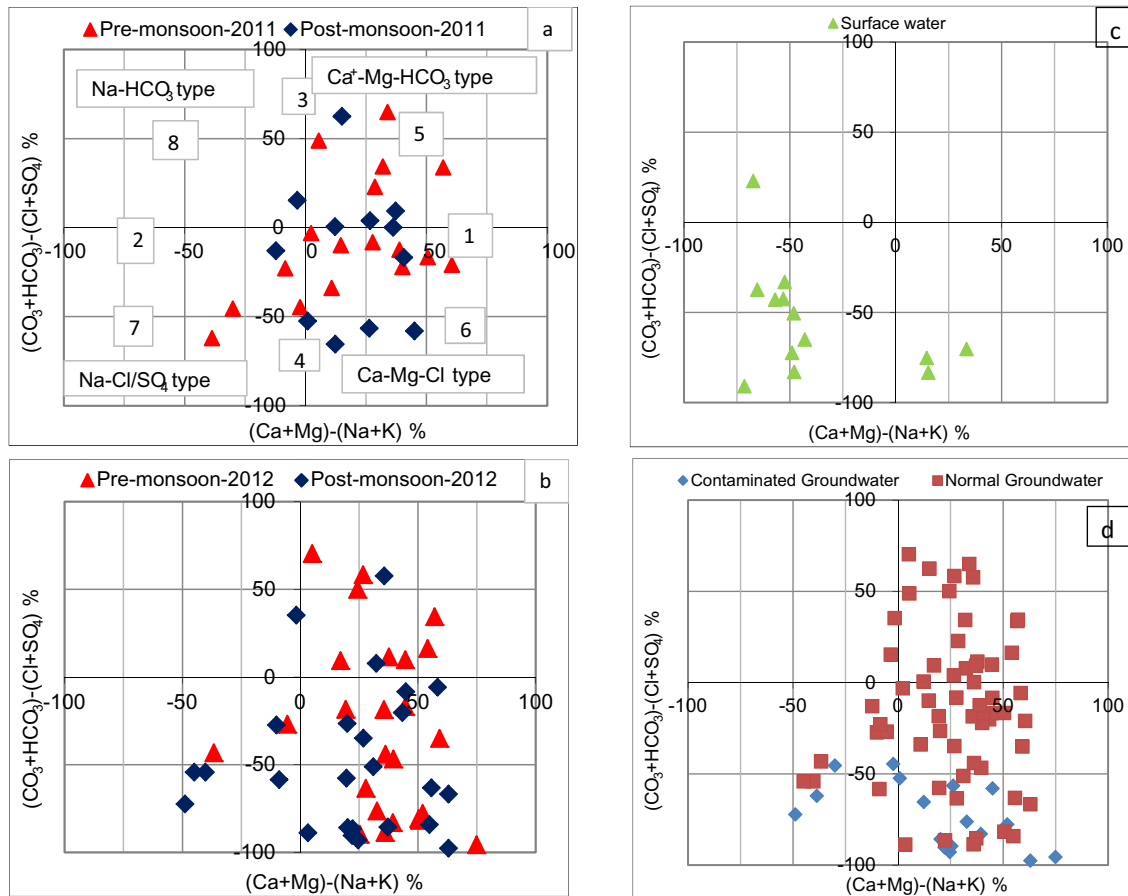


Fig.4. (a-b) Modified Piper Diagrams for Pre and Post-monsoon 2011, 2012. (c-d) Modified Piper Diagrams for surface water and groundwater.

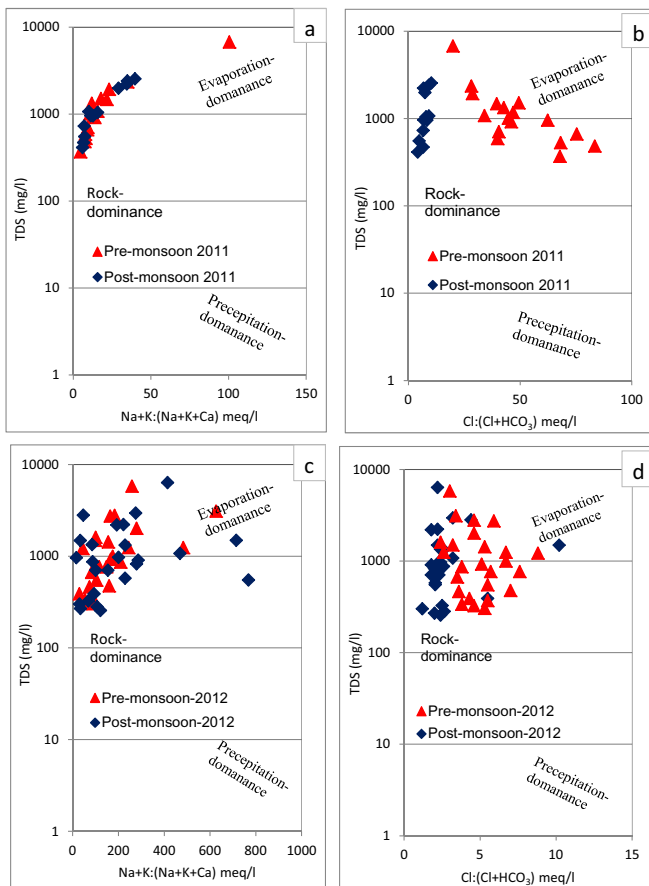


Fig. 5a-d. Gibbs plots for pre and post-monsoon-2011 & 2012.

The high molar ratio of Cl/HCO_3^- (mean for contaminated groundwater samples vary from 3 to 32 and 1 to 5 in normal samples), the ratio has increased tremendously in 2012 (Table 3), it validates insufficient influx of freshwater and non-lithogenic sources altered the groundwater chemistry (Tahoora et al., 2014). Atun Roy Choudhury et. al., (2021) in their study of Jawahar Nagar dump site noted legacy dump largely composed of degraded material and wood, plastic, cloth, rubber etc. They also observed that chlorides as Cl^- are very high in leachate (10826 mg/l), groundwater (1838 mg/l) and surface water (684 mg/l).

The role of aquifer material in evolution of groundwater chemical composition can be probed by determining chloro alkali indices (CAI). CAI are developed by Schoeller (1967) relates the ion exchange process between groundwater and aquifer material. CAI is determined applying the following formulae.

$$\text{Chloroalkali indices (CAI-1): } (\text{Cl}^- - \text{Na}^+ + \text{K}^+) / (\text{meq/l})$$

$$\text{Chloroalkali indices (CAI-2): } \text{Cl}^- - \text{Na}^+ + \text{K}^+ / (\text{SO}_4^{2-} + (\text{HCO}_3^- + \text{CO}_3^- + \text{NO}_3^-)) \text{ (meq/l)}$$

Most of the surface water and groundwater samples in all the sampling sessions had positive chloroalkaline indices-1 and 2 (CAI-1; CAI-2). This supports the assumption that direct base (cation-anion) exchange reactions were dominant, which involves the exchange of Na^+ and K^+ from the pore water with Ca^{2+} and Mg^{2+} of the aquifer material. Negative CAI ratios observed in many samples of 2011 demonstrate the exchange was of indirect base indicating chloro-alkaline disequilibrium, where replacement of Ca^{2+} and Mg^{2+} in groundwater occurs with Na^+ and K^+ of the host rock (Schoeller 1965, 1967; Al-Ahmadi 2013). The high temporal fluctuation of Na^+ and Ca^{2+} content, as well as the abundance of certain ion concentrations and water facies, support that both direct and reverse exchange

Table 3. Mean of various ionic ratios (all in meq/l)

Ratios	Surface water	Contaminated Groundwater	Normal Groundwater
Ca ²⁺ /Mg ²⁺	0.70	4.34	2.86
Ca ²⁺ /Na ⁺	0.27	1.09	1.16
Ca ²⁺ /Cl ⁻	1.22	0.44	0.18
Ca ²⁺ +Mg ²⁺ /Na ⁺ +K ⁺	0.59	2.01	1.99
Mg ²⁺ /Na ⁺	0.39	0.93	0.85
Na ⁺ +K ⁺ /TZ ⁺	0.69	0.41	0.37
Na ⁺ /Cl ⁻	0.88	0.53	1.21
Na ⁺ +K ⁺ /Cl ⁻ +SO ₄ ²⁻	1.03	0.50	0.86
HCO ₃ ⁻ /Cl ⁻	0.36	0.17	1.52
SO ₄ ²⁻ /HCO ₃ ⁻	1.35	1.40	0.84
Cl ⁻ /SO ₄ ²⁻	74.32	45.49	7.52
Cl ⁻ /NO ₃ ⁻	32.49	90.41	23.96
TA/TH (mg/l)	0.91	0.27	0.64
Cl⁻/Na⁺			
Pre-monsoon 2011	0.96	1.15	1.03
Post-monsoon 2011	1.40	1.94	0.85
Pre-monsoon 2012	1.50	3.80	1.38
Post-monsoon 2012	1.52	2.43	1.30
Ca²⁺/Mg²⁺			
Pre-monsoon 2011	0.86	2.68	6.34
Post-monsoon 2011	0.53	13.82	4.32
Pre-monsoon 2012	0.74	1.05	1.63
Post-monsoon 2012	0.51	1.04	1.01
Cl⁻/HCO₃⁻			
Pre-monsoon 2011	1.88	3.12	0.87
Post-monsoon 2011	6.04	3.65	0.71
Pre-monsoon 2012	10.06	17.32	2.64
Post-monsoon 2012	10.92	31.53	4.80

processes, though on a variable scale, were governing the cation content of the groundwater. The inference was further strengthened by about 2 (mean, meq/l) ratios of Ca²⁺+Mg²⁺/Na⁺+K⁺ in both normal and contaminated groundwater samples, whereas it was 0.6 in surface water samples (Table 3). The <0.50 ratio of Ca²⁺/Na⁺, Mg²⁺/Na⁺, Na⁺+K⁺/TZ⁺, >2.0 Ca²⁺/Mg²⁺ in many samples and the data points plotted along

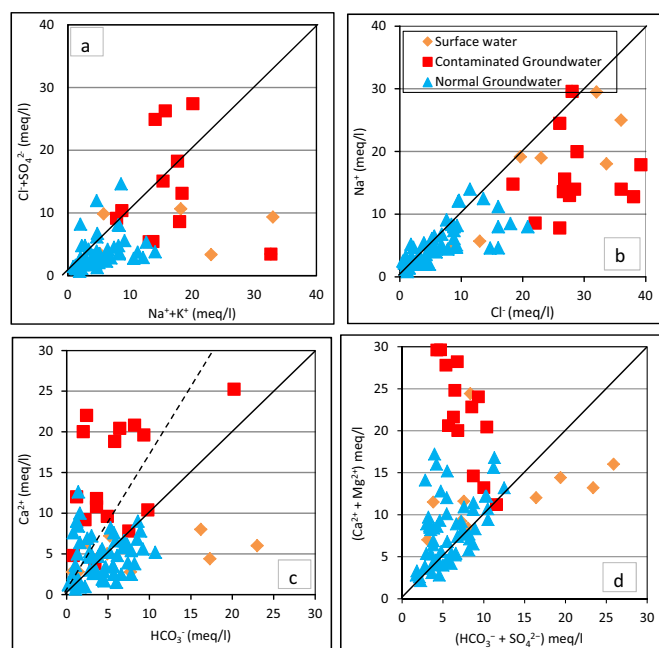


Fig. 6a-d. Cross plot of (a) Na+K vs Cl⁻+SO₄²⁻; (b) Cl⁻ vs Na⁺; (c) HCO₃⁻ vs Ca²⁺; (d) HCO₃⁻+SO₄²⁻ vs Ca+Mg.

the 1:1 line in Fig. 6a (Na⁺+K⁺ vs Cl⁻+SO₄²⁻) suggest the silicate weathering could be responsible for cation contribution in groundwater apart from the dissolution of leachate. The 1:2 ratio of Na⁺:Cl⁻ in contaminated groundwater unequivocally proves that Cl⁻ was sourced from effluents generated from the domestic waste of MDY together with local habitations. The samples plotted close to the 1:1 line could have undergone evaporation for Na⁺ enrichment (Fig. 6b). The predominance of Ca²⁺ over Mg²⁺, Na⁺, HCO₃⁻ in many groundwater samples depicts that weathering of carbonate minerals could be responsible for the input of Ca²⁺ and Mg²⁺ (Table 3; Fig. 6c). The assumption was substantiated by the (Ca²⁺ + Mg²⁺) versus (HCO₃⁻ + SO₄²⁻) scatter diagram in which most of the normal groundwater and few sample points of other categories aligned along the equiline (Fig. 6d).

Inter-relationship of ions: Correlation (r) of all tested parameters of each sampling session shows that a strong relationship exists between Ca²⁺ and Cl⁻ which was 0.97, 0.98, 0.86, and 0.92. Both were largely contributed from different sources, Ca²⁺ from the host environment and Cl⁻ from non-lithogenic sources. Similarly, r for TH:Cl⁻ was unusually high (average 0.96) in all the sampling sessions. The unusual relation can be attributed to anthropogenic activity in the vicinity. The strong correlation of Cl⁻:Na⁺ in both the seasons of 2011 (>0.90) suggests evapotranspiration process played crucial role in increasing mineralization of the water. The wastewater discharge from solid waste dumps could be contributing the ions to the aquatic environment. Weakening of relation (0.71) between Cl⁻ and Na⁺ in 2012 samples indicates altered the mineralization process (Table 4).

The surface water displays strong relationship (>0.70) among many parameters like EC, TH, Mg²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻ and NO₃⁻ which indicates heterogeneous anthropogenic source for ions (Supplemental material 4). Contaminated groundwater exhibit strong correlation among limited parameters viz. pH:SO₄²⁻; EC:TH, Cl⁻; TH:Ca²⁺, Mg²⁺, Cl⁻; CO₃²⁻:K and HCO₃⁻:Na⁺. Unusual relation among some parameters point out that multiple contamination processes were operating. Few parameters show inter-relationship (EC:TH, Na⁺, Cl⁻; TH:Ca²⁺, Mg²⁺, Cl⁻) in Normal groundwater which can be accounted for dynamic recharge - discharge condition together with interflow among different hydrological units. It can be inferred from correlation of three categories of water that surface water turned leachate was contributing contaminants to groundwater by different hydrochemical processes.

Contaminant Chemistry

Contaminated water displays distinct chemistry, the surface water, which forms the reservoir of pollutants, has highly reactive chemical characteristics like about (mean) 8.00 pH, 750 TH, and 800 mg/l Alkalinity (Table 1). These physicochemical properties promote absorption of ions from the inflow of leachate at an incipient stage which was visible in TDS being 4000 mg/l. Higher content of Na⁺, K⁺, HCO₃⁻ and SO₄²⁻ in leachate than groundwater suggests the influence of external influx together with the conductive hydrochemical environment on surface water quality. The chemical makeup of contaminated groundwater was unique by having low pH (7.30) and high TH (1478 mg/l) in comparison with surface water and normal groundwater, which confirm host water chemistry facilitated ion enrichment rather than physical features like hydraulics and thermodynamics. A mean TDS of about 3100 mg/l indicates high mineralization. The mean meq/l contents of alkali earths, and Cl⁻ were higher whereas alkali metals, HCO₃⁻, SO₄²⁻ and NO₃⁻ were lower in contaminated groundwater than other categories of water samples. Very high and near similar Cl⁻ concentration in surface water (37 meq/l) and contaminated groundwater (40 meq/l) indicate intermixing of these

Table 4. Correlation matrix for groundwater samples of each sampling session

Pre-monsoon-2011												
	pH	EC	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻
pH	1.00											
EC	-0.71	1.00										
TH	-0.63	0.96	1.00									
Ca ²⁺	-0.64	0.96	0.90	1.00								
Mg ²⁺	-0.34	0.53	0.73	0.35	1.00							
Na ⁺	-0.73	0.99	0.92	0.96	0.45	1.00						
K ⁺	-0.24	0.40	0.46	0.24	0.62	0.37	1.00					
HCO ₃ ⁻	-0.47	0.91	0.91	0.84	0.62	0.90	0.42	1.00				
Cl ⁻	-0.75	1.00	0.93	0.97	0.48	0.99	0.36	0.88	1.00			
SO ₄ ²⁻	0.30	-0.21	0.03	-0.26	0.48	-0.29	0.06	-0.07	-0.27	1.00		
NO ₃ ⁻	-0.24	0.25	0.29	0.13	0.42	0.23	0.61	0.20	0.21	0.08	1.00	
F ⁻	0.35	-0.60	-0.58	-0.64	-0.25	-0.60	-0.01	-0.55	-0.59	0.19	-0.20	1.00
Post-monsoon-2011												
	pH	EC	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻
pH	1.00											
EC	-0.79	1.00										
TH	-0.77	0.96	1.00									
Ca ²⁺	-0.81	0.96	0.97	1.00								
Mg ²⁺	0.16	-0.01	0.13	-0.14	1.00							
Na ⁺	-0.72	0.93	0.80	0.85	-0.18	1.00						
K ⁺	-0.55	0.53	0.50	0.41	0.34	0.51	1.00					
HCO ₃ ⁻	-0.38	0.67	0.59	0.50	0.34	0.68	0.46	1.00				
Cl ⁻	-0.81	0.99	0.96	0.98	-0.11	0.92	0.48	0.56	1.00			
SO ₄ ²⁻	0.03	0.18	0.30	0.11	0.75	-0.01	0.36	0.45	0.08	1.00		
NO ₃ ⁻	-0.13	0.31	0.24	0.21	0.14	0.38	0.53	0.02	0.31	0.00	1.00	
F ⁻	0.59	-0.76	-0.66	-0.70	0.16	-0.82	-0.40	-0.72	-0.73	-0.08	-0.13	1.00
Pre-monsoon-2012												
	pH	EC	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻
pH	1.00											
EC	-0.81	1.00										
TH	-0.75	0.98	1.00									
Ca ²⁺	-0.86	0.85	0.81	1.00								
Mg ²⁺	-0.61	0.92	0.96	0.62	1.00							
Na ⁺	-0.67	0.74	0.59	0.65	0.49	1.00						
K ⁺	-0.09	0.17	0.13	0.01	0.17	0.27	1.00					
HCO ₃ ⁻	0.54	-0.27	-0.32	-0.60	-0.15	0.05	0.37	1.00				
Cl ⁻	-0.82	1.00	0.98	0.86	0.92	0.71	0.13	-0.33	1.00			
SO ₄ ²⁻	-0.14	0.09	0.00	0.20	-0.09	0.40	0.23	0.11	0.05	1.00		
NO ₃ ⁻	0.15	-0.18	-0.13	-0.06	-0.14	-0.30	-0.05	-0.15	-0.21	0.10	1.00	
F ⁻	0.74	-0.63	-0.58	-0.65	-0.48	-0.57	-0.18	0.22	-0.62	-0.15	-0.13	1.00
Post-monsoon-2012												
	pH	EC	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻
pH	1.00											
EC	-0.59	1.00										
TH	-0.68	0.95	1.00									
Ca ²⁺	-0.67	0.89	0.96	1.00								
Mg ²⁺	-0.54	0.86	0.85	0.68	1.00							
Na ⁺	-0.22	0.76	0.52	0.42	0.61	1.00						
K ⁺	0.16	0.19	-0.06	-0.07	-0.01	0.58	1.00					
HCO ₃ ⁻	-0.38	0.07	0.02	-0.05	0.17	0.12	0.19	1.00				
Cl ⁻	-0.58	0.99	0.97	0.92	0.85	0.71	0.11	-0.02	1.00			
SO ₄ ²⁻	-0.32	0.82	0.63	0.54	0.66	0.94	0.50	-0.03	0.77	1.00		
NO ₃ ⁻	-0.23	-0.09	-0.07	-0.06	-0.09	-0.10	0.02	0.25	-0.17	0.00	1.00	
F ⁻	0.34	-0.60	-0.48	-0.40	-0.51	-0.65	-0.32	0.01	-0.58	-0.65	-0.01	1.00

Note: Ions having strong positive relation (>0.70) are marked in bold (e.g. **0.71**)

waters. Similarly, low Na (19 meq/l) and high Cl⁻ (40 meq/l) confirm they were from dissimilar sources as well as processes. It can be deduced from low concentrations of Ca²⁺, Mg²⁺, Na⁺, and Cl⁻ in normal groundwater that unaffected water still exists in the area even though the MWD has attained a stable methanogenic phase (Peter Kjeldsen

et. al., 2002). Close range in the concentration of SO₄²⁻ (2 to 6 meq/l) and NO₃⁻ (1 to 4 meq/l) in surface water, as well as both the types of groundwaters, point out the prevalence of redox conditions. Moderate NO₃⁻ content (50 to 60 mg/l) in groundwater can be accounted for denitrification process. Disproportionate content of Cl⁻ and NO₃⁻ in

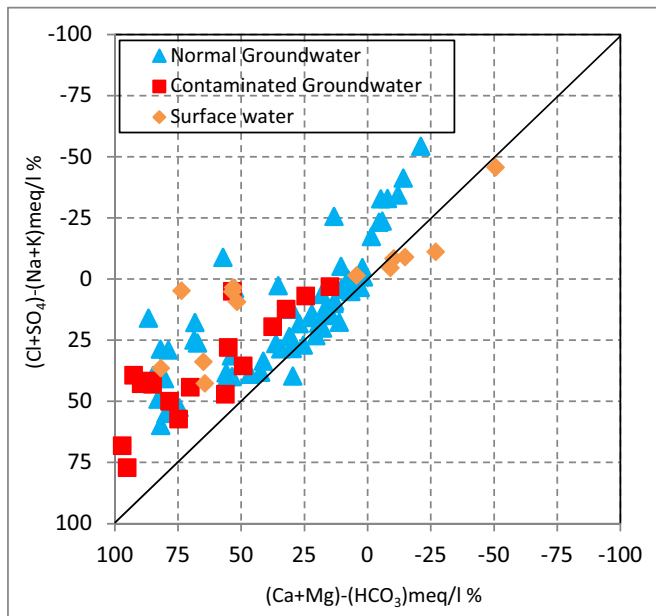


Fig. 7. Langelier and Ludwig plot (modified).

most of the samples as evident from their ratios of 1:0.12 for surface water, 1:0.02 for contaminated samples and 1:0.16 for normal groundwater (mean; meq/l) indicate different sources and exponential concentration of Cl^- in all samples can be attributed to huge solid waste dumps. High content of chlorine in legacy dump (2.4% in RDF sourced from the legacy dump; Atun Roy Choudhury et. al., 2021) as well as Cl^- in surface water close to dump site (about 2000 mg/l) and groundwater (1414 mg/l in Contaminated samples and 216 mg/l in Normal samples) link the dump with the surface water and subsequently to groundwater. Field conditions prove that there is no other source for high salinity and such critical parameters. More than 5 meq/l of Cl^- content and 1 to 3 meq/l of NO_3^- in half of the normal groundwater samples (largely gathered from the non-core area) could be due to multiple sources including poor disposal of sewerage from rapidly developed unplanned colonies. Sequential reduction in the content of certain ions from surface water to contaminated groundwater and normal groundwater indicates the flow path of pollutants from source to sink (e.g. Fig. 6b). The contamination process could be dissipation of contaminants from legacy dump to leachate (surface water pools) by leaching and disintegration followed by percolation down to sub-surface domain through feebly fractured bed rock by diffusion (Fig. 7).

CONCLUSIONS

Ion content of both surface and subsurface waters unambiguously establishes the municipal solid waste dumpsite as a point source for widespread contamination at Jawaharnagar dump yard. Local physiographic features and un-engineered disposal sites, together with favorable hydrological conditions, triggered the mass movement of leachate from dumpsites to surface water bodies and in the form of the plume propagation into aquifers through preferred pathways. It can be inferred from the high molar content of Cl^- , Ca^{2+} or Na^+ , dominant Ca-Mg-Cl water type, and Gibbs plots that mineralization of water resource can be contemplated to anthropogenic source apart from geogenic processes. Favorable host water environment in the form of high content of strong acids and alkaline earths facilitated absorption of contaminants by groundwater. Dynamic hydrochemical conditions due to continuous mass flux resulted in rapid reactions in the aquifer leading to high mineralization of pore water. Unique correlation of Cl^- with Ca^{2+} , TH, and Na^+ as well as low ratios of Na^+/Cl^- , $\text{Ca}^{2+}/\text{Cl}^-$,

$\text{HCO}_3^-/\text{Cl}^-$, TA/TH, and high Ca^{2+}/Mg , $\text{Cl}^-/\text{NO}_3^-$ values support the contention. Contamination-induced mineralization led to rapid variations in the chemical makeup of pore water which created the disequilibrium resulting in ion-exchange or base exchange. Contaminants complement natural mineralization processes and vice versa.

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