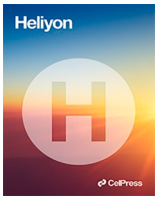
Heliyon 10 (2024) e35601

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon



Research article

Comparing roles of multiple contamination indicators in tracing groundwater pollution nearby a typical municipal solid waste (MSW) landfill

Junlun Meng [a,b], Guangli Xiao [a,b,c,*], Minghui Qi [a], Xi Han [a,b], Qili Gou [a,b], Xinyue Hao [a,b], Jianhong Ge [a,b]

[a] *Sichuan Institute of Energetical and Geological Survey, Chengdu, 610072, China*
[b] *Key Laboratory of Investigation and Monitoring, Protection and Utilization for Cultivated Land Resources, Ministry of Natural Resources, Chengdu, 610045, China*
[c] *College of Environmental Sciences, Sichuan Agricultural University, Chengdu, 611130, China*

ARTICLE INFO

Keywords:
Conservative ion
MSW landfill
Pollution tracing

ABSTRACT

Groundwater pollution resulting from leachate leakage at landfill sites has garnered significant attention. Investigating the migration of pollutants from these landfills to adjacent groundwater is crucial for understanding the diffusion patterns and extent of contamination. It is imperative to develop cost-effective yet highly efficient tracer techniques to aid landfill operators in monitoring groundwater contamination stemming from their operations. The primary objective of this research was to compare the roles of conservative tracers sodium (Na^+) and chloride (Cl^-), and conventional pollutants permanganate oxidation (COD_{Mn}), ammonium nitrogen (NH_4^+-N), lead (Pb), and zinc (Zn) in assessing pollution levels from municipal solid waste landfills to groundwater. For this purpose, a typical municipal solid landfill was selected to investigate the origin of Cl^-, groundwater quality, and spatiotemporal variations of multiple contaminations. Geochemistry analyses revealed that Na–Cl and Ca–HCO_3 were the dominant groundwater type in this study and landfill was the primary source of Cl^- in groundwater, with an average contribution of 78 %. Groundwater in proximity to the landfill (5#, 2#, 22#, 23#) exhibited elevated concentrations of Na^+ (15.6–914.0 mg/L), Cl^- (8.9–1352.0 mg/L), COD_{Mn} (0.54–95.9 mg/L), and NH_4^+-N (0.33–49.0 mg/L), yet demonstrated reduced levels of Pb (0.2–391.0 μg/L) and Zn (2.0–112.8 μg/L). In contrast, groundwater located at a considerable distance from the landfill (13#, 18#, 15#, 26#) displayed the inverse trend, with relatively low concentration of Na^+ (3.2–8.5 mg/L), Cl^- (0.1–0.7 mg/L), COD_{Mn} (0.28–4.78 mg/L), and NH_4^+-N (0.03–0.52 mg/L), but increased levels of Pb (1.2–483.0 μg/L) and Zn (1.6–357.0 μg/L). The primary determinant of groundwater quality near the landfill was NH_4^+-N, with the highest pollution index (Pi) of 492.85, whereas Pb was the predominant factor affecting water quality in areas distant from the landfill, with the highest pollution index (Pi) of 10.9. While no discernible seasonal variation was detected for all pollutants, spatial variation can be observed that pollution levels decreased progressively with increasing distance from the landfill, a trend particularly corroborated by the conservative Cl^- and Na^+ measurements. This research suggests that conservative ions, such as Cl^- and Na^+, exhibit superior efficacy in tracing the pollution range from municipal solid landfills to

* Corresponding author.
E-mail address: Gxiao267@163.com (G. Xiao).

https://doi.org/10.1016/j.heliyon.2024.e35601
Received 29 May 2024; Received in revised form 31 July 2024; Accepted 31 July 2024
Available online 3 August 2024

groundwater. Therefore, monitoring these conservative ions in groundwater can yield a more precise understanding of the extent of groundwater contamination originated from landfills.

1. Introduction

It has been estimated that approximately 95 % of the global municipal solid waste (MSW) is disposed of in landfills [1]. This proportion can even reach 100 % in many low to medium-income developing countries [2]. The majority of these landfills are characterized as simple or informal, lacking pollution prevention measures such as seepage prevention, flood prevention, and adequate coverage. Furthermore, these landfills are exposed to the atmosphere, and they come into direct contact with water and soil [3]. In China, 90 % of solid waste was disposed of in simple landfills in the early 1990s [4]. Besides simple or informal landfills, there are also many formal landfills, which must meet strict design, operation, and closure requirements. Bottom liners and surface cover are used in these landfills to isolate trash from the surrounding environment [5]. However, as these formal landfills age, they often transition into informal ones due to damages incurred from seismic events or the weathering of isolating films. Furthermore, fires that occur in improperly managed landfills can potentially lead to more severe damage to the landfill structure, accelerating the leakage of landfill leachate [6,7]. Subsequent studies suggest that leachate from waste incineration presents a greater risk to groundwater than that derived from untreated waste, due to the increased mobility of components within incinerated waste [8]. Many older landfills are situated in environmentally vulnerable areas, as historical landfill site selection seldom considered geological criteria for suitability [9]. Consequently, secondary environmental pollution caused by landfills has been a serious problem worldwide.

With the growing concern about environmental pollution caused by landfills of municipal solid waste, the threat of leachate leakage from unlined or inadequately lined landfills to the nearby environments, especially to the surface and groundwater has become an urgent problem [10,11]. Statistics indicate that approximately 70 % of landfills in China are plagued by leachate leakage issues [12,13]. Landfill leachate has been extensively documented as the primary source of groundwater and surface water pollution. Improperly collected and treated leachate can percolate through soil and rock fissures, ultimately reaching water aquifers [14–17]. The primary challenge lies in identifying and characterizing this issue, as groundwater is inherently complex and does not exhibit visible signs like surface water [18]. The threat of leachate to groundwater primarily stems from the high concentration of various contaminants, including organic matter, inorganic macro components, heavy metals, and xenobiotic organic compounds (XOCs) [19]. Once these contaminants are released into the groundwater, its quality significantly deteriorates. Furthermore, elevated concentrations of contaminants like nitrogen pollutants in groundwater near landfill sites can have adverse effects on both the ecosystem and human health due to nitrate exposure [20]. Drinking water with high concentrations of sodium may also cause renal cardiac and circulatory diseases [21], and heavy metals like lead are not considered safe at any concentration (U.S. Environmental Protection Agency, 2007).

To comprehensively characterize groundwater pollution emanating from landfills, both temporal and spatial groundwater monitoring methods are instrumental in elucidating the behaviour and trends of the contamination plume extending from the landfill to adjacent groundwater [22]. Previous research has mainly focused on the most prevalent contaminants, such as heavy metals (e.g., Pb, Cr, Zn, Hg) and inorganic macro components (e.g., NO_3^-, NH_4^+-N, SO_4^{2-}) [23–25]. However, it is challenging to assess the impact of landfills on groundwater when dealing with these traditional pollutants due to their high sensitivity to environmental conditions and propensity to transform into other substances. For instance, heavy metals have been reported to be significantly attenuated by sorption

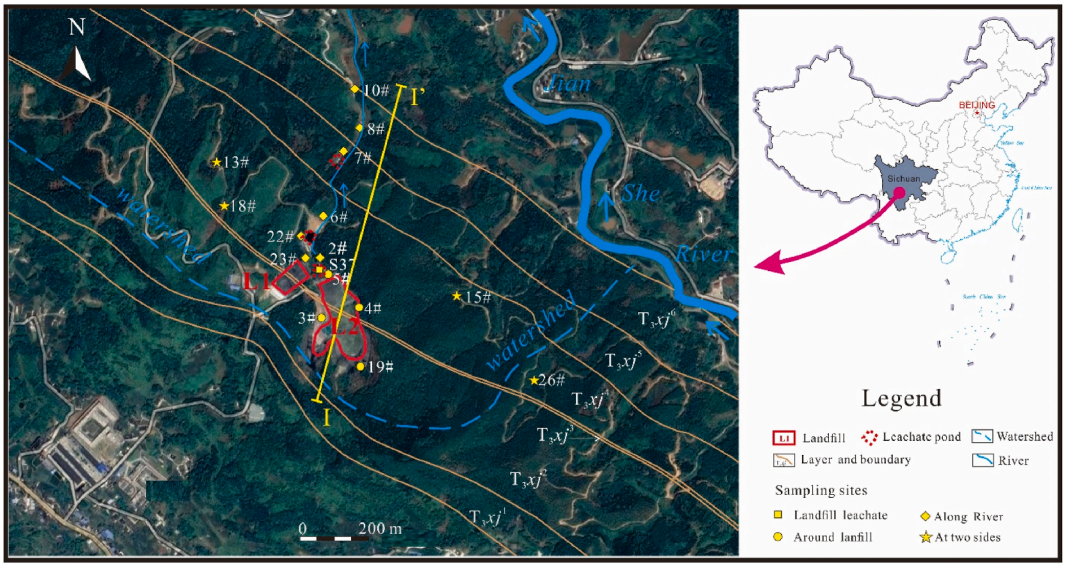


Fig. 1. Map of the study area and sampling sites.

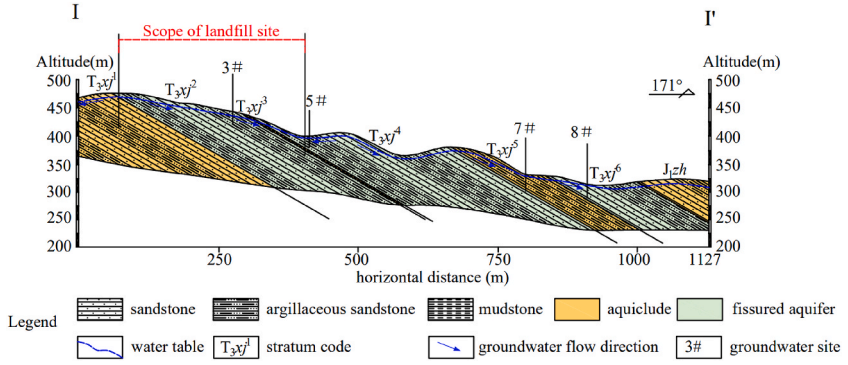


Fig. 2. Geological profile of section I–I'.

and precipitation within sedimentary aquifers [26], which will complicate the assessment of the landfill's impact on groundwater quality. Additionally, other potential sources of contamination or background influences may be overlooked when solely relying on flexible contamination methods to evaluate the impact of landfills on groundwater. In contrast to these susceptible contaminants, the conservative behaviour of Na^+ and Cl^- during transportation, combined with their minimal interactions with the surrounding substrate in most scenarios, renders these halides and their ratios(Na/Cl)particularly effective in determining groundwater movement in a majority of circumstances. Consequently, they can serve as excellent indicators for water sources and can also trace potential pollution leakage from landfill sites [27,28], as well as identify the possible pollution leaked from landfills.

For this study, we selected conventional pollutants, including heavy metals (Pb and Zn), biochemical targets (COD_{Mn} and NH_4^+-N), and conservative ions (Na^+ and Cl^-), to achieve the following objectives: a) identify the contribution of Cl^- from the landfill to nearby groundwater; b) evaluate groundwater quality by using single pollution index and Nemerow index; c) compare the migration behaviour of different pollutants and their effectiveness in tracing landfill pollution.

2. Materials and methods

2.1. Study area

This research was conducted at two adjacent landfills in Sichuan province, southwestern China (Fig. 1). One old landfill (L1) was sealed in 2008, while another relatively new landfill (L2), has been in operation since 2008. Both landfills are equipped with a base layer to prevent seepage, and flood ditches have been strategically constructed to redirect rainwater from the surrounding mountains. A concrete dam was built in the comparatively lower stratum of the terrain to inhibit the leachate discharge downstream. Methane discharge pipes were set up at the landfills to prevent possible explosions caused by methane combustion and no landfill fire events were recorded according to the landfill manager. However, the improper management of the previous L1 resulted in the disposal of both municipal solid waste and construction waste, along with other miscellaneous garbage and waste. In contrast, the newly established L2 primarily accepts municipal solid waste and has disposed of approximately 49,500 tons of waste to date. Although these landfills were initially designed with bottom impermeable membranes, the impermeability gradually degraded over time, and groundwater contamination was detected in a monitoring well near the landfill, indicating possible leachate leakage from the landfills.

2.2. Geology and hydrogeology

Typical sandstone formations of the Permian System ($T_3xj^{1\text{-}6}$) prevailed in this area. These formations consist of relatively fine and coarse sandstone layers, with both water-resistant and water-bearing layers. The two landfills were constructed atop a hill at an elevation between 430 m and 515 m above sea level. The location encompasses three distinct layers (T_3xj^2, T_3xj^3, T_3xj^4) and is upstream of a seasonal stream (Figs. 1 and 2). The landfills are located in relative aquifers, with only a thin layer of relative aquifers (T_3xj^3), so the leachate produced by landfills is likely to enter the groundwater and spread with the groundwater flow. Contaminated groundwater may spread along the strata, causing pollution on both sides of the landfill, or it may spread along the stratigraphic inclination to downstream areas through bedrock fissures.

2.3. Sampling

Given the specific local geographic and geomorphic conditions, both landfills were strategically located on the north side of the watershed. As a result, all sampling campaigns were executed from this same side. Three distinct sampling areas were established to track the migration of potential contaminants originating from landfills, including four sites adjacent to the landfill, seven sites distributed from upstream to downstream along a seasonal stream, and four sites located at two sides of the landfill in the stratigraphic direction (Fig. 1). In addition, one landfill leachate pool was monitored concurrently. Groundwater samples as well as landfill leachate samples were collected monthly from April 2021 to March 2022. These samples were then transported to the laboratory and stored at a

Table 1
Locations of samples.

Sample ID	Sample type	Latitude (E)	Longitude (N)	Height (m)	Mean groundwater table (m)	Location detail
S37	leachate	105.273	28.286	431.81	\	Leachate pond of Landfill L1
19#	groundwater	105.274	28.283	515.28	505.35	Around landfill L1: northern side
4#	groundwater	105.274	28.286	472.41	465.72	Around landfill L1: western side
3#	groundwater	105.273	28.285	481.72	473.68	Around landfill L1: eastern side
5#	groundwater	105.273	28.287	431.90	431.55	Around landfill L1: southern side
2#	groundwater	105.273	28.287	432.31	429.93	Along seasonal river: upstream
23#	groundwater	105.273	28.287	431.20	429.50	Along seasonal river: upstream
22#	groundwater	105.272	28.287	430.12	422.56	Along seasonal river: upstream
6#	groundwater	105.273	28.288	423.79	408.89	Along seasonal river: downstream
7#	groundwater	105.274	28.290	394.40	394.40	Along seasonal river: downstream
8#	groundwater	105.274	28.291	380.22	380.17	Along seasonal river: downstream
10#	groundwater	105.274	28.292	347.83	347.83	Along seasonal river: downstream
13#	groundwater	105.269	28.290	411.16	407.49	Along layers: eastern side of landfill
18#	groundwater	105.270	28.288	415.22	407.49	Along layers: eastern side of landfill
15#	groundwater	105.277	28.286	430.92	425.31	Along layers: western side of landfill
26#	groundwater	105.280	28.284	383.00	382.92	Along layers: western side of landfill

temperature of 4 °C before analysis. Detailed information on these samples is summarized in Table 1.

2.4. Sample analyses

The parameters analysed in this study include pH, organic composite indicator (COD_{Mn}), inorganic nonmetals (NH_4^+-N, Cl^-, SO_4^{2-}, HCO_3^-), major cations (K^+, Na^+, Ca^{2+} and Mg^{2+}) and heavy metals (Pb, Zn). Analytical testing of samples was conducted in the laboratory of Sichuan Keyuan Engineering Technology Testing Center Co., LTD (Chengdu, China), and analytical procedures were strictly performed according to the "Standard for groundwater quality" (GB/T 14848–2017) (General Administration of Quality Supervision, Inspection and Quarantine of the P.R. China and SAC, 2017) and recommended analytical test methods in this standard. Statistics of measured parameters are listed in Table 2 and Table S1.

2.5. Data calculation

2.5.1. Data analysis

In this study, Microsoft Excel 2019 (Microsoft Corp., Redmond, WA, USA) was employed for data collation, while Origin 2023 (OriginLab Corp., Northampton, MA, USA) was utilized for data analysis and graphical representation.

2.5.2. Water quality index

Both the single-factor pollution index (Pi, Eq. (1)) and the Nemerow index (Ni, Eq. (4)) were utilized to assess the impact of landfills on water quality [29]. The parameter standards were compared against the level III water quality categories outlined in the "Quality Standard for Ground Water" of China (GB/T14848–2017) (Table 2). Considering the sampling campaigns were conducted monthly and parameter values varied throughout the year, the average value of each parameter was selected from all sites to calculate the Pi and Ni. The general formulas for calculating Pi and Ni are expressed as follows:

$$\mathrm{Pi} = \frac{\mathrm{C_i}}{\mathrm{C_{si}}} \tag{1}$$

$$\text{For pH value, } \mathrm{Pi} = \frac{\text{7-ph}}{\text{7-pH}_{\mathrm{sd}}} \text{ when pH} \leq 7 \tag{2}$$

$$\mathrm{Pi} = \frac{\text{pH-7}}{\text{pH}_{\mathrm{su}}\text{-7}} \text{ when pH} > 7 \tag{3}$$

$$Ni = \sqrt{\frac{(P_{max})^2 + (P_{avg})^2}{2}} \tag{4}$$

$$P_{avg} = \frac{1}{n}\sum_{i=1}^{n} Pi \tag{5}$$

In Eq. (1), Pi is the pollution index for the ith parameter; *Ci* is the measured concentration of the ith parameter of each sample; Si is the standard for the ith parameter in each sample.

In Eqs. (2) and (3), pH_{sd} and pH_{su} are the lower limit and upper limit values, respectively.

In Eq. (4), Ni is the Nemerow index; P_{avg} is the average of Pi; P_{max} is the maximum value of Pi.

Table 2
Statistic of measured parameters of leachate and groundwater samples.

Parameter		s37	19#	4#	3#	5#	2#	23#	22#	6#	7#	8#	10#	13#	18#	15#	26#
Ref		Leachate	Sites around landfill							Sites along river					Sites along layer		
	Min	7.37	5.74	5.35	6.03	6.4	5.49	5.83	6.12	4.39	6.22	6.83	6.34	5.77	5.82	5.69	6.19
pH	Max	8.28	6.51	6.45	6.67	6.91	6.07	6.62	6.71	6.92	7.62	7.54	6.98	7.46	7.52	6.66	6.96
6.5~8.5	Mean	7.87	6.16	6.02	6.29	6.72	5.81	6.19	6.36	5.46	7.15	7.24	6.62	6.35	6.31	6.10	6.57
	CV	0.03	0.04	0.06	0.03	0.02	0.03	0.04	0.04	0.13	0.05	0.03	0.03	0.07	0.08	0.04	0.04
	Min	1200.0	1.3	3.0	1.8	482.9	15.6	22.7	49.7	2.9	5.0	2.3	6.1	3.8	3.2	4.3	4.1
Na^+	Max	3835.0	3.7	4.4	35.0	914.0	29.0	39.9	77.3	4.1	7.5	2.8	7.1	4.6	3.8	8.5	5.7
200 mg/L	Mean	2870.5	2.0	3.7	10.0	618.7	19.9	33.1	62.9	3.5	6.6	2.6	6.7	4.2	3.5	6.1	4.6
	CV	0.30	0.34	0.11	1.16	0.25	0.23	0.14	0.13	0.12	0.11	0.06	0.05	0.06	0.07	0.16	0.11
	Min	2653.7	0.2	0.0	1.4	790.7	25.0	41.5	8.9	1.3	0.0	0.1	0.3	0.1	0.0	0.1	0.0
Cl^-	Max	4825.0	1.8	2.1	11.9	1352.0	41.8	47.3	100.2	1.9	1.8	0.4	0.7	0.5	0.2	0.7	0.5
250 mg/L	Mean	3654.1	1.0	0.5	4.3	1013.1	32.1	44.9	70.5	1.6	1.1	0.3	0.6	0.2	0.1	0.3	0.2
	CV	0.16	0.43	1.20	0.90	0.20	0.17	0.04	0.34	0.11	0.41	0.32	0.18	0.69	0.35	0.85	0.68
	Min	233.00	0.67	0.36	1.48	7.88	0.54	0.84	1.10	0.36	0.49	0.44	0.28	0.28	0.32	0.53	0.51
COD	Max	1200.00	2.28	41.10	106.00	95.90	7.79	2.42	4.96	2.00	1.74	1.84	2.00	1.52	4.78	1.92	0.64
3.00 mg/L	Mean	723.34	1.29	4.82	32.14	50.00	2.00	1.48	3.16	0.90	0.91	0.93	0.87	0.87	1.63	0.97	0.57
	CV	0.38	0.42	2.64	1.00	0.49	1.09	0.31	0.33	0.49	0.50	0.55	0.65	0.45	1.30	0.52	0.12
	Min	819.00	0.08	0.04	0.63	2.52	0.33	1.72	1.61	0.03	0.07	0.06	0.05	0.03	0.04	0.03	0.03
NH_4^+-N	Max	1938.36	0.30	0.24	32.50	499.00	5.72	14.80	9.02	0.52	0.42	0.49	0.78	0.52	0.17	0.28	0.11
0.50 mg/L	Mean	1441.89	0.16	0.10	11.10	246.43	1.65	6.68	5.97	0.14	0.27	0.20	0.23	0.13	0.07	0.14	0.06
	CV	0.26	0.42	0.57	1.05	0.79	0.87	0.45	0.31	1.19	0.47	0.61	0.88	1.29	0.60	0.67	0.56
Pb	Min	8.1	53.0	0.5	3.3	0.2	6.9	79.3	18.5	4.1	1.6	2.2	0.4	1.2	12.8	11.2	58.3
10 μg/L	Max	54.8	168.0	12.2	63.2	11.4	35.3	391.0	233.9	31.7	407.0	28.6	2.7	483.0	325.0	170.0	138.0
Parameter		s37	19#	4#	3#	5#	2#	23#	22#	6#	7#	8#	10#	13#	18#	15#	26#
Ref		Leachate	Sites around landfill							Sites along river					Sites along layer		
	Mean	25.8	108.2	3.6	20.6	4.0	14.6	207.6	138.1	10.7	54.1	13.6	1.4	98.9	100.9	87.2	107.9
	CV	0.62	0.27	0.97	1.01	1.33	0.57	0.42	0.35	0.79	2.33	0.75	0.54	1.34	0.94	0.54	0.24
	Min	12.9	20.3	4.0	1.0	2.0	9.5	3.3	11.8	5.7	3.7	1.5	4.7	1.6	6.0	10.6	9.3
Zn	Max	2269.5	353.0	114.0	92.2	112.8	38.4	53.8	71.9	204.0	21.8	57.4	18.9	357.0	131.0	84.2	52.9
1000 μg/L	Mean	787.2	77.0	24.2	49.3	22.0	21.6	20.8	30.1	33.1	8.4	12.5	10.7	44.0	21.9	32.0	28.5
	CV	0.78	1.20	1.40	0.67	1.37	0.47	0.62	0.62	1.67	0.71	1.31	0.42	2.37	1.88	0.86	0.54

Table 3
Grading method for Nemerow index [10,30].

Nemerow index (Ni)	Water quality
Ni ≤ 0.7	No pollution
0.7 < Ni ≤ 1.0	Small pollution loading
1.0 < Ni ≤ 2.0	Lesser pollution loading
2.0 < Ni ≤ 3.0	Moderate pollution loading
3.0 < Ni	Heavy pollution loading

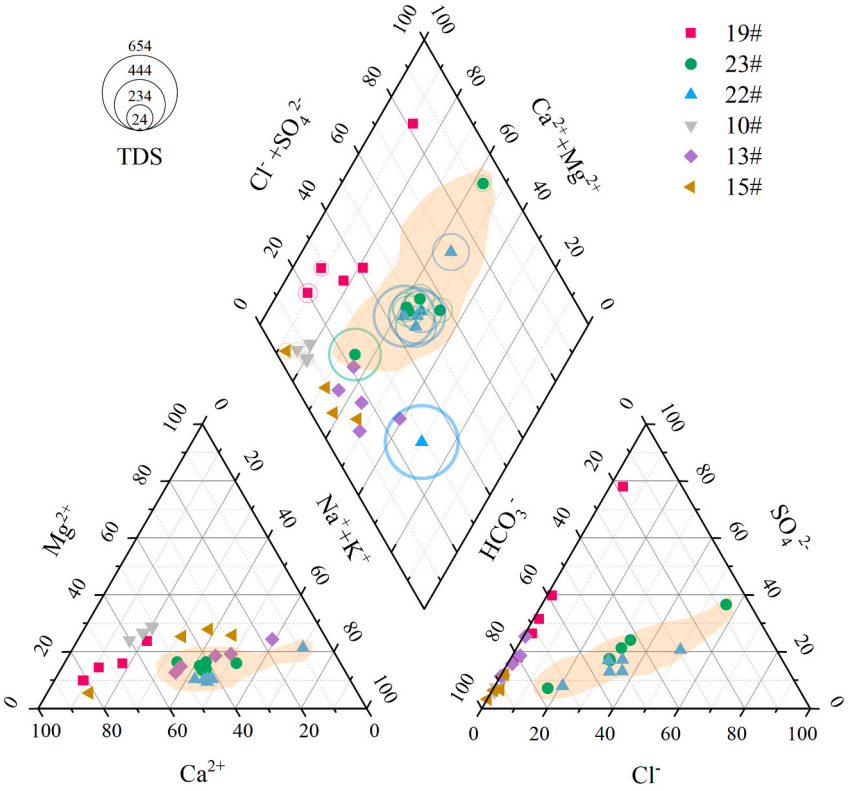


Fig. 3. Piper diagram of the groundwater samples (TDS = $[Ca^{2+}+Mg^{2+}+Na^{+}+K^{+}]+[HCO_3^- + SO_4^{2-} + Cl^-]$).

Grading method for Nemerow index are listed in Table 3.

2.5.3. *ANOVA test*

One-way ANOVA test provides a way to assess the difference between different groups [31,32]. In this study, based on the calculated monthly single-factor pollution index (Pi) and Nemerow index (Ni) of landfill leachate samples and groundwater samples, we compared the difference between the water quality of leachate samples and the quality of groundwater samples by ANOVA test. This is proceeded on the statistical analysis software (SPSS: 20.0), and a significance level of 0.05 ($p < 0.05$) was set as the threshold for determining statistical significance. For statistical purposes, the values of selected pollutants below detection limits were replaced by LOD/2 to calculate the Nemerow index [33].

2.5.4. *Cluster classification for groundwaters*

Hierarchical cluster analysis is commonly applied to categorize objects into distinct clusters based on their inherent similarities [34]. Consequently, it is also extensively employed for classifying water quality [35,36]. In this study, a hierarchical cluster analysis based on groundwater's mean six chemical measurements was conducted by using IBM SPSS Statistic 20. All data were standardized by using z-score calculation and Ward's method with Euclidean distance was used for the cluster analysis [37]. A dendrogram was illustrated to reflect the linkage distance during the history of cluster merging (Fig. 9). The number of clusters depends on the phenon line, and the different phenon lines yield disparate outcomes in cluster classifications and interpretations.

3. Results

3.1. Values of pH

The pH values of the leachate were slightly alkaline, ranging from 7.37 to 8.28, with a mean value of 7.87. This finding is consistent with previous studies conducted by Abd et al. (2015) and Tränkler et al. (2005) [14,38], suggesting a brief acidic phase followed by an early methanogenic phase in the landfill [38]. Groundwaters from 7# and 8# had average pH values of 7.15 and 7.24, respectively. The rest of the groundwater samples had mean pH values of faintly acidic, varied from 5.46 to 6.72. Groundwater samples of 6# had the lowest mean pH value among all groundwater samples in this study, ranging from 4.39 to 6.92, with a mean value of 5.46.

3.2. Major elements of representative groundwater

Major elements (K^+, Na^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and HCO_3^-) of representative groundwater were measured to analyse the overall groundwater chemistry in this region (Table S2, Fig. 3). The total dissolved solids (TDS) ranged from 29.81 to 701.39 mg/L, indicating huge variations in groundwater chemical signatures. Correspondingly, significant changes in the concentrations of ions such as K^+ (0.64–20.00 mg/L), Na^+ (1.40–77.30 mg/L), Ca^{2+} (1.20–86.00 mg/L), Mg^{2+} (1.04–11.40 mg/L), Cl^- (0.05–100.15 mg/L), SO_4^{2-} (2.13–49.22 mg/L), and HCO_3^- (6.88–495.00 mg/L) can also be observed. Higher TDS and higher concentrations of major elements were detected at sites near the landfill (22#, 23#), but lower values were found at sites far from the landfill (10#, 13#, 15#) or sites located at the upstream of the groundwater flow (4#, 19#). These results indicated potential influences of landfill activity on groundwater geochemistry [39,40], and a claim would be further substantiated by Piper analysis (Fig. 3).

3.3. Concentrations of Na^+ and Cl^- in all samples

The concentrations of Na^+ in leachate samples were consistently an order of magnitude higher than the standard value for Class III (200 mg/L), ranging from 1200 mg/L to 3835 mg/l. In the groundwater surrounding landfills, only samples from 5# exceeded a concentration of 200 mg/L, with values ranging from 483 mg/L to 914 mg/L. The remaining samples around the landfills (19#, 4#, 3#) had mean concentrations below 10 mg/L. Samples collected along the seasonal river revealed that groundwater at the upstream locations (2#, 23#, 22#), which were also proximate to the landfill, exhibited higher Na^+ concentrations, ranging from 15.6 mg/L to 77.3 mg/L. In contrast, samples collected from downstream (6#, 7#, 8#, 10#) and sites along the layers (13#, 18#, 15#, 26#) demonstrated mean Na^+ contents below 10 mg/L. A similar high Na^+ concentration (321.70 mg/L) for polluted groundwater and a relatively low Na^+ concentration (25.40 mg/L) for unpolluted groundwater around a landfill was also reported by Şimşek et al. (2008) [41].

The concentrations of Cl^- in the leachate were found to be the highest, ranging between 2653.7 mg/L and 4825.0 mg/L, significantly higher than the value for Class III of 250 mg/L. Despite the considerable fluctuation of Cl^- concentration in landfill leachate (825–4000 mg/L), it predominantly displays traits of elevated concentration [42,43]. For groundwater samples, most of them exhibited relatively low Cl^- values of less than 100 mg/L. However, these samples from location 5# showed notably higher Cl^- concentration, ranging between 790.7 mg/L and 1352.0 mg/L, three to four times greater than the standard value of 250 mg/L. Samples from upstream of the seasonal stream (2#, 23#, 22#) had higher Cl^- concentrations than the downstream (6#, 7#, 8#, 10#), with average values of 49.17 mg/L and 0.90 mg/L, respectively. Samples from sites along the layer (13#, 18#, 15#, 26#) had the lowest Cl^- concentration, with an average value of 0.2 mg/L.

By comparing the results of Na^+ and Cl^- for all sample sites, it was evident that these two ions exhibited identical spatial variation. Both ions were found in higher concentrations at site 5#, subsequently decreasing from upstream to downstream or with increasing distance from the landfills. The lowest concentrations were observed at sites located along layers.

3.4. NH_4^+-N and COD_{Mn}

NH_4^+-N and COD_{Mn} are prevalent pollutants in groundwater surrounding municipal solid waste landfills. They come from the degradation of domestic waste, particularly organic materials such as unclassified kitchen scraps, plant and animal decomposition remains, food products, and excreta [44]. Leachate serves as the primary conduit for discharging degraded materials from landfills into adjacent groundwater, resulting in elevated concentrations of NH_4^+-N and COD_{Mn}. In the leachate, the concentrations of NH_4^+-N varied between 819.00 mg/L and 1938.36 mg/L, with a mean value of 1441.89 mg/L. Site 5# had a significant decrease in concentration, dropping below 499.00 mg/L with an average value of 246.43 mg/L. However, this concentration was still much higher than the Chinese standard for Class III (0.5 mg/L). Sites around landfills (19#, 4#, 3#) had lower NH_4^+-N concentrations, with mean values ranging between 0.10 mg/L and 11.10 mg/L, and some of them satisfied the Chinese standard for Class III. For these groundwaters sampled along the river and layers, only these sites from upstream (2#, 23# and 22#) had slightly higher NH_4^+-N concentrations than 0.5 mg/L, with a mean value of 1.65 mg/L, 6.68 mg/L, and 5.97 mg/L, respectively. The majority of the groundwater samples had ammonia concentrations below 0.5 mg/L.

The COD_{Mn} values in the leachate were also highest and ranged from 233.00 mg/L to 1200.00 mg/L, with an average value of 723.34 mg/L, significantly higher than the standard value of 3.00 mg/L. Groundwater samples from 5# exhibited a secondary high value of COD_{Mn}, varied from 7.88 to 95.90 mg/L, with a mean value of 50 mg/L. This value subsequently decreased from upstream (mean value of 2.21 mg/L) to downstream (mean value of 0.91 mg/L), with no significant differences observed among the

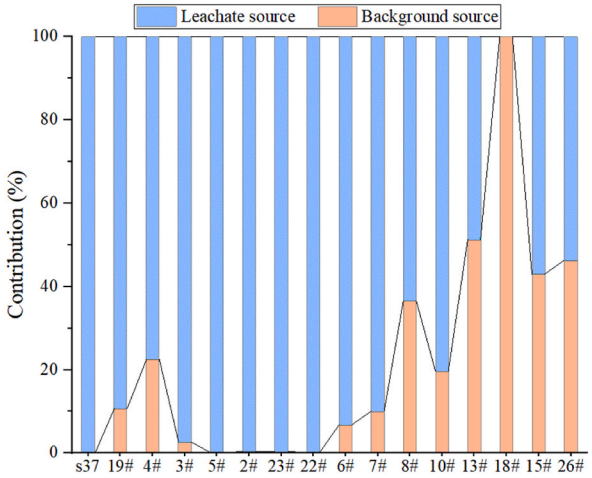


Fig. 4. Contributions of Cl^- in groundwater from leachate and background.

groundwater samples collected along layers (mean value of 1.01 mg/L).

3.5. Heavy metals of Pb and Zn

The leachate discharged from L1 exhibited Pb concentrations with an average value of 25.8 μg/L, exceeding the Chinese groundwater standard for Class III (10 μg/L). However, elevated Pb concentrations were not detected in the leachate but rather in samples 19#, 23#, 22#, 13#, 18#, 15#, and 26#, which were situated at considerable distances from the landfills. The highest concentration of Pb, at 207.6 μg/L, was found in sample 23#. Groundwater from both sides of the landfill (13#, 18#, 15#, 26#) exhibited relatively stable and elevated Pb levels across different layers, ranging between 87.2 μg/L and 107.9 μg/L, with an average value of 98.7 μg/L.

The concentration of Zn in the leachate was 2269.5 μg/L, exceeding the groundwater standard of class III(1000 μg/L). Among these sites around landfill I, 19# had the highest Zn content (353.0 μg/L), but still met the groundwater standard of class III. In the cases of groundwater from sites along the river and at two sides, only sites 6# and 13# exhibited relatively high Zn content, with mean values of 33.1 μg/L and 44.0 μg/L, respectively. However, the values were consistently lower, averaging around 25 μg/L, in samples from other sites. In general, the Zn concentration was relatively low at sites far away from the landfill.

4. Discussion

4.1. Groundwater geochemistry

4.1.1. Piper diagram

A Piper Plot was applied here to identify the dominant water facies [45]. According to the Piper diagram (Fig. 3), most groundwaters tended to be Ca·Mg - HCO_3 type, but a few of them, especially groundwaters from 23# and 22# were plotted as Na–Cl type, characterized by high portions of Cl^- and Na^+. In this study area, sandstone formations prevailed, and dissolution of the highly soluble calcite mineral serves as the primary source of Ca^{2+}, Mg^{2+} and HCO_3^- [46,47]. Consequently, the background geochemistry of groundwater is supposed to be of the Ca·Mg–HCO_3 type, reflecting the outcomes of local water-rock reactions. Groundwater of the Na–Cl type is consistently attributed to seawater intrusion or weathering of Na–Cl halite [48–50]. Additionally, previous studies have identified that groundwater near MSW landfills also exhibits a Na–Cl type due to the leakage of high concentrations of Na^+ and Cl^- in leachate [51,52]. It is worth noting that the study area is located inland in China, far from the seacoast, so the impact of the seacoast on groundwater can be ruled out. Therefore, landfills are the main cause of Na–Cl type groundwater, as further evidenced by the significant contrition of Cl^- to groundwater from landfill (Fig. 3). When comparing these groundwater samples collected away from the landfill (10#, 13#, 15#) with those collected near the landfill (23# and 22#), it was evident that there might be contamination from landfill. However, sample 19#, despite being located near the landfill, had a low Cl^- concentration, indicating that the north side of the landfill seemed to be unaffected by the landfill due to its elevated position.

4.1.2. Source of Cl^-

Generally, in groundwater without salt rock deposition and human activities such as landfills, Cl^- ions in groundwater mainly come from atmospheric precipitation [53]. The study area is primarily composed of sandstone strata, which naturally have a low Cl^- content. Consequently, atmospheric precipitation is generally considered to be the main natural source of Cl^- in the water bodies of this region [54]. Since no rainfall samples were collected in this study area, 18# with the lowest Cl^- content (0.1 mg/L) was selected as the background value of groundwater. Assuming that Cl-was neither absorbed by plants nor chemically reacted with aquifer materials,

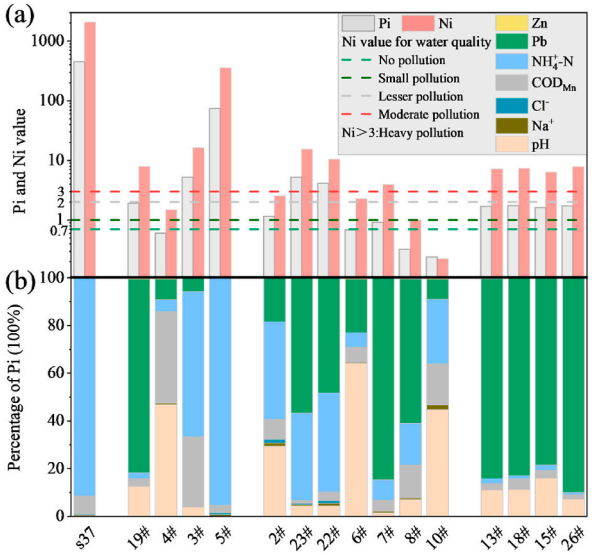


Fig. 5. Groundwater quality indicators of average single pollution index (Pi), Nemerow index (Ni) (a) for all sampling sites and percentage of Pi (b) showed the contribution of each pollutant to groundwater quality.

the Cl^- concentration of 18# (0.1 mg/L) and the mean Cl^- concentration of landfill leachate (3654.1 mg/L) can be considered as two mixed end-elements: one representing the geological background source and the other the landfill leachate source. Then, the contribution of the two end-elements to the groundwater Cl^- concentration was estimated. Results showed that the Cl^- in the groundwater of the study area mainly derived from the pollution of landfill leachate, with an average value of 78 %. For groundwater near the landfill site, almost all Cl^- came from landfill leachate. Conversely, only approximately 50 % of the Cl^- in the groundwater located further away from the landfill site originated from landfill leachate (Fig. 4). Atmospheric precipitation significantly affected the Cl^- content of groundwater in remote areas, where human activities had minimal impact. Given that atmospheric precipitation exhibits certain variations [55], changes in the Cl^- content of groundwater distant from landfills may mirror these atmospheric fluctuations. Consequently, the contribution of leachate from landfills to the Cl^- content of groundwater from remote regions might be overestimated.

4.2. Groundwater quality assessment

Results of the groundwater quality index, including the mean pollution index (P_{avg}) and Nemerow index (Ni), were presented in Table S2 and Fig. 5. Generally, almost all groundwater samples in this study area were contaminated with Ni values ranged from 0.98 to 2063.94, averaging at 6.34, which excluded the values of leachate (Ni = 2063.94) and most polluted 5# (352.40). Leachate samples (s37) had the highest values of P_{avg} (451.12) and Ni (2063.94), indicating a significant environmental threat. Groundwater closest to the landfill (5#) had the secondary high P_{avg} (73.95) and Ni (352.40), which were apparently affected by the leachate. Other groundwater samples near the landfill (3#, 23#, 22#) also showed heavy pollution, with an average P_{avg} of 4.85 and Ni of 13.82. For samples around the landfill, all groundwaters were polluted, but groundwater quality of 19# (P_{avg} = 1.90, Ni = 7.77) and 4# (P_{avg} = 0.6, Ni = 1.45) were not worse than 3# and 5#. For samples along the river, upstream of 2#, 23# and 22# had higher values of Ni (mean value of 9.27), indicating heavy pollution, and downstream of 6#, 7#, 8# 10# had much lower values of Ni (mean value of 1.82), but still revealed small pollution of groundwater. This might suggest that the impact of the landfill had significantly diminished with increasing distance. Samples collected along different layers (13#, 18#, 15#, 26#) also exhibited signs of heavy pollution, with mean P_{avg} of 1.69 and Ni of 7.08.

A comparative analysis of pollution indexes (Pi) for each parameter showed that NH4⁺-N, Pb, and pH were the primary contaminants (Table S2, Fig. 5). NH_4^+-N was predominant in samples of leachate (s37) and groundwaters surrounding the landfill (samples 3#, 5#, 2#). Conversely, pH played a significant role in samples 6# and 10#. Lead (Pb) contamination was found to be more severe than other pollutants in groundwater samples 7#, 8#, 13#, 15#, and 18#, which were located at a considerable distance from the landfill. The site 19#, situated near the landfill, exhibited the highest Pi value for Pb. The influence of Na^+ and Cl^- on Ni value was minimal, resulting in low Pi values. However, it was noteworthy that the Pi values for Na^+ and Cl^- were closely aligned, particularly at sites proximate to the landfill, indicating similar behaviour of these ions. By comparing the results of groundwater quality, it was observed that all groundwaters in the study area were contaminated due to various causes. Near the landfills, particularly the newer ones, biochemical-related contaminants like NH_4^+-N were more prevalent, while heavy metal Pb was a major concern farther from the landfills.

To further confirm the water quality between the leachate samples and groundwater samples, a one-way ANOVA test was applied here at a significant level of 0.05 (95 %). Results showed that the homogeneity of variances was not verified, the Tamhane post hoc test

Table 4
Results of multiple comparisons (Tamhane post hoc test).

Leachate	Groundwater	Mean Difference	Std.Error	Sig.	Mean Difference	Std.Error	Sig.
			Pi			Ni	
S37	19#	449.78394*	33.86655	1.34E-05	2060.88568*	167.27584	2.73E-05
	4#	450.99455*	33.86668	1.31E-05	2066.65727*	167.27382	2.66E-05
	3#	446.76227*	33.90662	1.38E-05	2052.38390*	167.42450	2.77E-05
	5#	371.34455*	37.54328	1.03E-05	1683.84000*	185.53737	2.98E-05
	2#	450.49455*	33.86640	1.32E-05	2065.67000*	167.27485	2.68E-05
	23#	446.57227*	33.87049	1.43E-05	2054.02818*	167.28651	2.82E-05
	22#	447.44061*	33.86679	1.41E-05	2057.80902*	167.27640	2.77E-05
	6#	450.91545*	33.86618	1.31E-05	2065.91364	167.27402	2.67E-05
	7#	450.67636*	33.87002	1.31E-05	2064.56091*	167.29388	2.68E-05
	8#	451.26000*	33.86614	1.30E-05	2067.27091*	167.27383	2.66E-05
	10#	451.30394*	33.86611	1.30E-05	2067.50318*	167.27369	2.65E-05
	13#	449.85811*	33.87063	1.34E-05	2060.91735*	167.29593	2.72E-05
	18#	449.82827*	33.86862	1.34E-05	2060.79118*	167.28725	2.73E-05
	15#	450.17727*	33.86698	1.33E-05	2062.77152*	167.27735	2.71E-05
	26#	449.83727*	33.86633	1.34E-05	2060.30318*	167.27499	2.74E-05

* The significance level of the mean difference is 0.05.

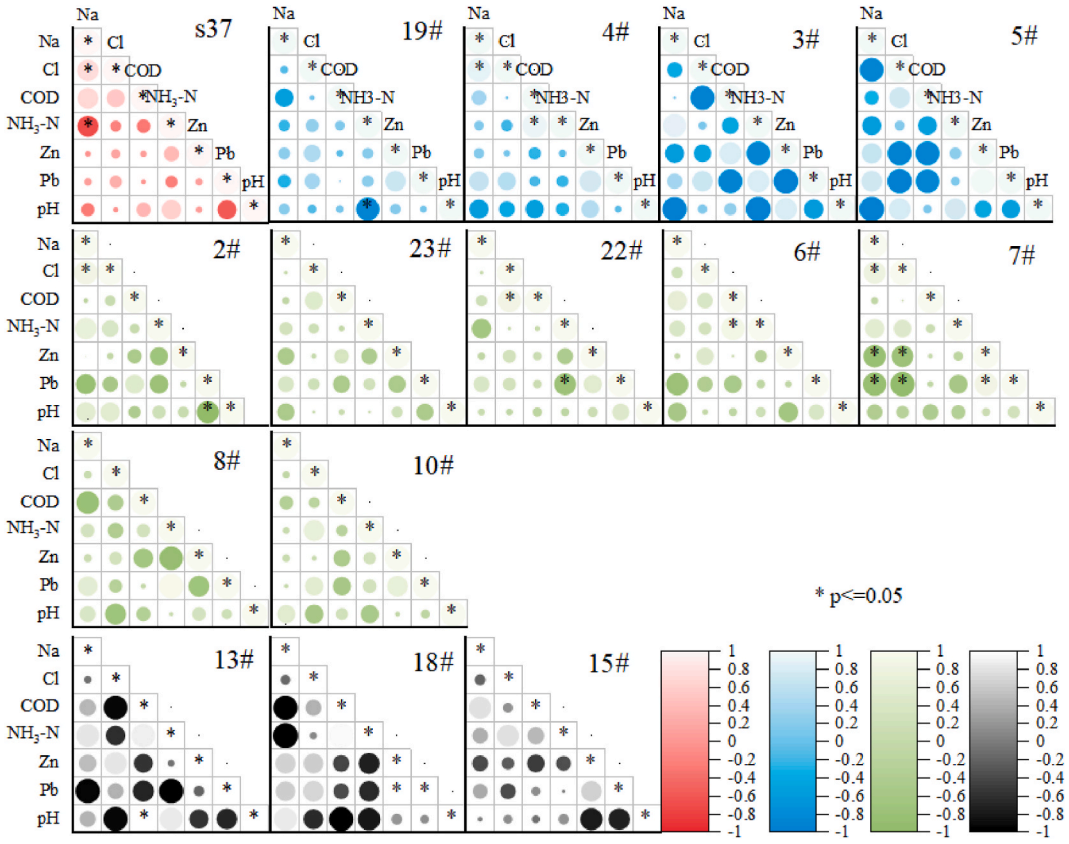


Fig. 6. Correlation heatmap among contaminations at different sites.

was subsequently applied for mean comparison. According to the results of multiple comparisons (Table 4), both the single-factor pollution index (Pi) and the Nemerow index (Ni) showed significant differences between landfill leachate and groundwater ($P < 0.05$).

4.3. Relations among contaminations and sampling sites

4.3.1. Relations revealed by contaminations

Correlation heatmap among contaminations at different sites suggested that no specific relationship was found for the entire study

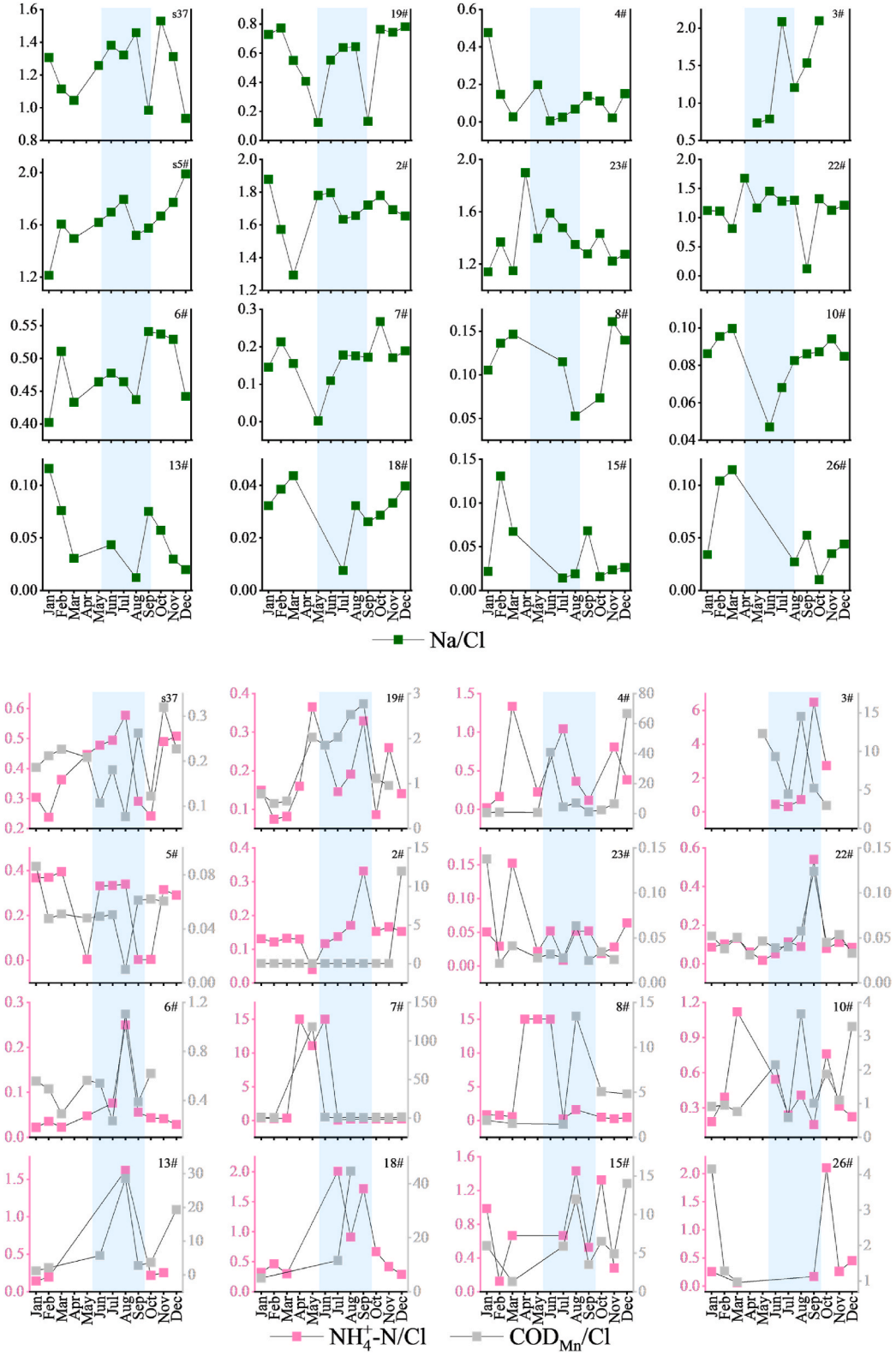


Fig. 7. Seasonal variations of Na/Cl, COD_{Mn}/Cl, NH_4^+-N/Cl, Pb/Cl and Zn/Cl ratios at different sampling sites

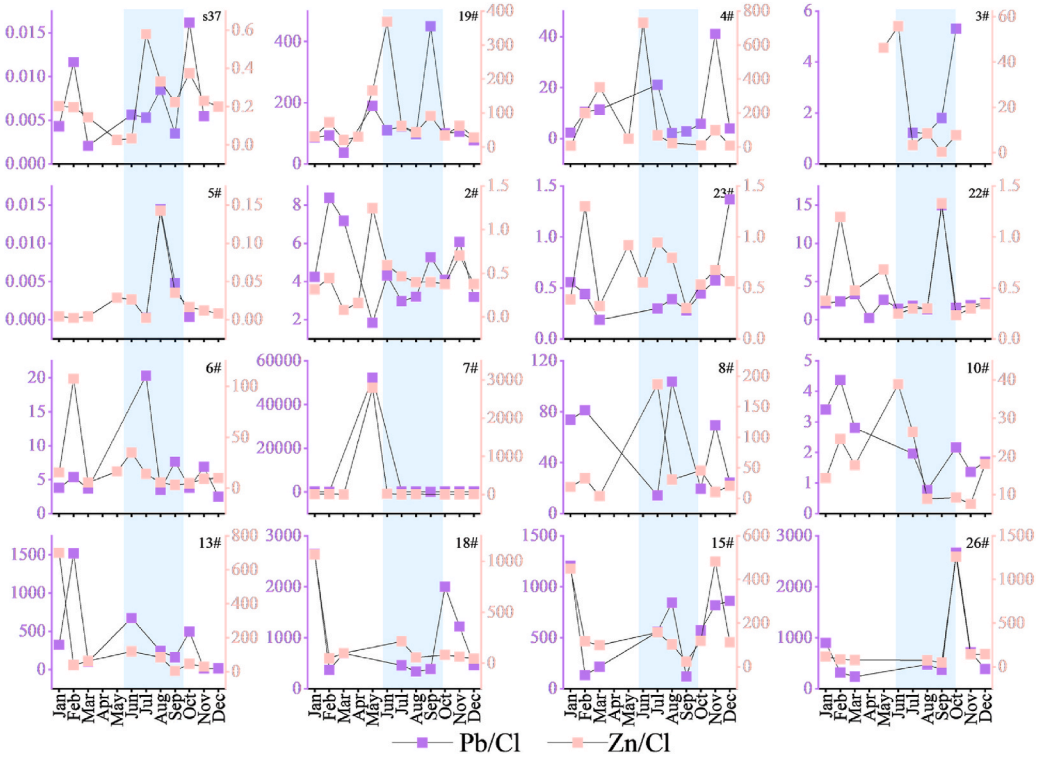


Fig. 7. (*continued*).

area (Fig. 6). However, in the leachate samples (S37), there existed a significant positive correlation ($p \leq 0.05$) between Na^+ and Cl^- and a negative correlation ($p \leq 0.05$) between Cl^- and NH_4^+-N. A negative correlation between pH and Pb was observed, indicating that higher pH levels decrease Pb concentration. Conversely, there was a positive correlation between pH and Zn, indicating that higher pH levels increased concentrations of Zn. Previous research has demonstrated that most heavy metals like Pb tend to precipitate or solidify under alkaline conditions [56]. The negative correlation between pH and Pb could also be found at sites far from the landfill, with low pH but relatively high Pb concentration.

4.3.2. *Relations revealed by spatiotemporal variation*

Previous studies have indicated that contamination levels in landfill leachate and adjacent groundwater show significant seasonal variations, influenced by water level fluctuations and vertical hydraulic gradients [29,57,58]. Rainfall affects the leaching process, increasing or decreasing leachate volume [38], and the dilution effect reduces pollutant concentrations [59,60]. To counteract dilution effects, contaminant molar ratios to Cl^- concentration (Na/Cl, COD_{Mn}/Cl, NH_4^+-N/Cl, Pb/Cl, Zn/Cl) were used to represent seasonal variations across sampling sites (Figs. S1–S4, Fig. 7).

For single contamination, substantial seasonal variation was noted, but no discernible pattern was observed for each element or month (Figs. S1–S4). During the wet season (from June to September), Na^+, Cl^-, NH_4^+-N and Zn tended to be higher, especially in July, while COD_{Mn} and Pb had no similar regulation. It was worth noting that the highest concentrations of Na^+, Cl^-, NH_4^+-N, COD_{Mn} and Zn were found in leachate compared to these groundwaters, while the highest concentrations of Pb were not found in the leachates. Relatively high Pb were observed in groundwater at 18# and 2#, respectively. Results indicated that Pb in groundwater may not originated from leakage of landfill I due to lower concentration of Pb in leachate. In the case of leachates with the highest Na^+, Cl^-, NH_4^+-N, Pb and Zn concentration, only samples of 5#, 2#, 22# and 23# were found to have similar seasonal variation with S37, which were all situated in proximity to the landfill.

For molar ratio, results showed no specific regulation for the whole study area (Fig. 7). However, these groundwaters sampled near the landfill (5#, 2#, 22#, 23#) seemed to have similar seasonal behaviours with leachate, indicating these groundwaters might have a hydraulic connection and have the same groundwater sources. High COD_{Mn}/Cl, NH_4^+-N/Cl, Pb/Cl and Zn/Cl were found at sites (13#, 18#, 15#, 26#, 7#, 8#, 10#) located far from the landfill due to lower Cl^- concentration. Relatively high Na/Cl ratios were found at sites located near the landfill due to both high Na^+ and Cl^- concentrations. In natural environments, sodium ion (Na^+) in groundwater primarily originates from the weathering of silicates or halite [61]. However, no halite was detected in this study area. Consequently, the Na^+ levels in groundwater at locations 13#, 18#, 15#, 26#, 7#, 8#, and 10# were representative of background values with relatively low concentrations. In groundwater proximate to the landfill, elevated levels of Na^+ in leachate originating from solid wastes would contribute to high concentrations in adjacent groundwater.

The spatial variation indicated that the concentrations of Na^+ and Cl^- were highest in groundwater sample 5# (Fig. 8). In contrast,

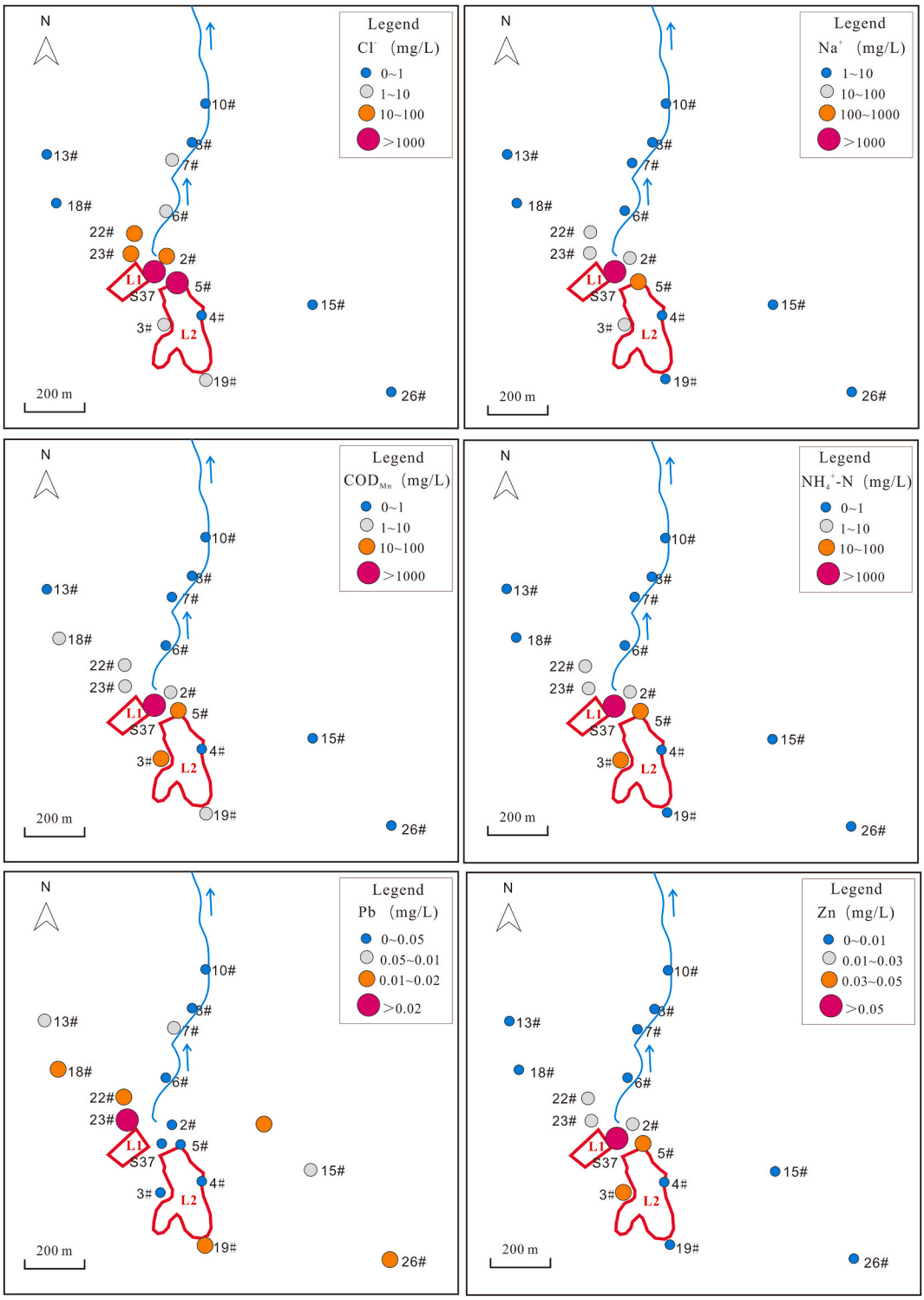


Fig. 8. Spatial variation of contaminations content (Cl^-, Na^+, COD_{Mn}, NH_4^+-N, Pb and Zn) in groundwater. Sample sites were divided into three groups: groundwater near the landfills, groundwater along the river and groundwater along layers.

the values for other groundwaters surrounding the landfill were significantly lower, akin to those from the two sides of the landfill which exhibited the lowest concentration. The concentrations of Na^+ and Cl^- in the groundwater along the river exhibited a decrease from upstream to downstream. Based on these variations, it could be inferred that only the groundwater at the 5# location near the

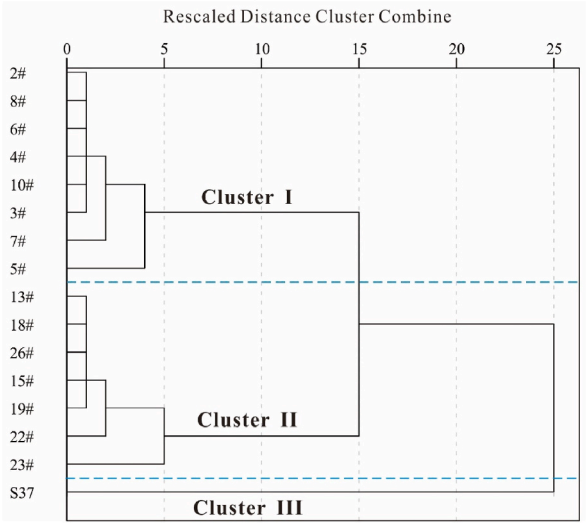


Fig. 9. Dendrogram of hierarchical cluster analysis for the groundwater samples. Three clusters are determined by the phenon line at a linkage distance of 6.

landfill and the upstream was contaminated. A similar spatial trend was observed for both COD_{Mn} and NH_4^+-N. However, site 3# exhibited significant pollution levels, surpassing those of the upstream groundwater.

The highest Pb and Zn concentrations were not found in 5# but in 19#. The Pb and Zn levels in groundwater from sample 5# were comparatively low across the entire study area, suggesting that heavy metal pollution in this region is unlikely to be attributed to the landfill. Heavy metals in groundwater might originate from either natural background levels or agricultural activities [62,63]. In this study area, no significant heavy metal pollution was observed in groundwater proximate to the landfill compared to that located further away. Consequently, a relatively high concentration of heavy metals necessitates the identification of alternative sources.

The movement of groundwater is the main pathway for pollutants to spread in groundwater [64,65]. The velocity of groundwater flow significantly influences the rate and extent of pollutant dispersion. A reduced water flow rate diminishes the migration velocity of pollutants within the groundwater stratum, consequently limiting the diffusion rate of these contaminants into the groundwater. High and low permeability with significant differences in hydraulic conductivity can also have a great impact on groundwater flow [66]. In this study area, prevailed sandstone formations were supposed to have high permeability, which was conducive to the diffusion of pollutants. Additionally, soluble pollutants are more likely to migrate within groundwater, while volatile pollutants can enter the atmosphere through evaporation. Simultaneously, adsorbable pollutants will be absorbed by underground media, leading to a slower migration speed [67]. These factors collectively affect the diffusion process of landfill pollutants in groundwater. Conservative ions like Cl^- can serve as a more accurate indicator of groundwater direction and flow rate. Conversely, non-conservative ions such as heavy metals, ammonia nitrogen, and COD_{MN} are prone to adsorption or material transformations, resulting in slower diffusion speeds and smaller diffusion ranges compared to Cl^-, which explain the spatial variation of pollutants at different sampling sites (Fig. 8).

4.3.3. Relation revealed by hierarchical cluster analysis (HCA)

Utilizing Ward's linkage method, coupled with z-score standardization to eliminate bias in parameter values, three distinct clusters were identified at a linkage distance of 6 based on the phenon line (Fig. 9). Cluster I corresponded to sites located along the river from upstream to downstream, which had proved to be polluted according to the relatively high concentration of Na^+, Cl^-, COD_{Mn}, and NH_4^+-N, particularly in the groundwater at the upstream location (5#, 3#). Cluster II responded to sites at two sides of the landfill, which exhibited low-level contamination of Na^+, Cl^-, COD_{Mn}, and NH_4^+-N, but high-level contamination of Pb. Cluster III exclusively incorporated the leachate samples (S37), which were distinguished by the highest levels of Na^+, Cl^-, COD_{Mn}, and NH_4^+-N, but reduced concentrations of Pb and Zn. Compared to the spatial variation analysis results, it could be inferred that pollution originating from the landfill was confined to a relatively limited area. In particular, only site 5#, which was close to the landfill, and sites 2#, 23#, and 22# situated upstream, were affected by pollution associated with the landfill. Hierarchical cluster analysis effectively distinguished between polluted and unpolluted regions.

4.4. Implication for tracing groundwater pollution near MSW landfill

Unlike traditional contaminants, geochemical indicators like sodium (Na), chlorine (Cl), and their ratio (Na/Cl) are more stable, offering a reliable assessment of landfill impacts. Using the Na/Cl ratio to trace the diffusion process of leachate assumed that fluctuations in the concentrations of Na^+ and Cl^- leached from the geological components of the aquifer are either disregarded or the Na/Cl ratio remains relatively consistent within a relatively confined study area. The concentrations of Na^+ and Cl^- are only diluted by groundwater and the Na/Cl ratio can avoid the influence of dilution. Consequently, when groundwater has mixed leachate with a

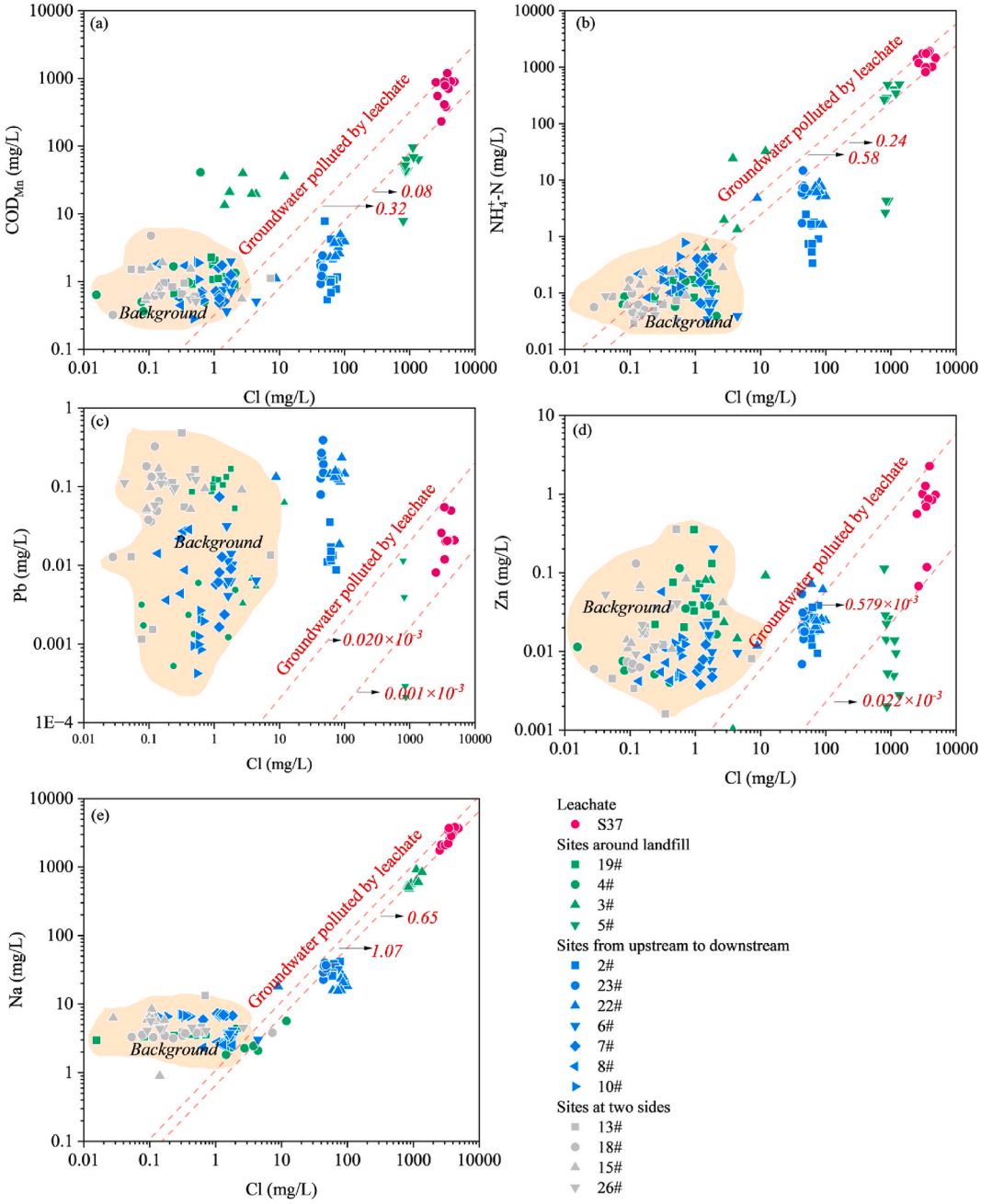


Fig. 10. Plot of COD_{Mn} (a), NH_4^+-N (b), Pb(c), Zn(d), Na(e) and Cl concentration in leachate and groundwater. Red dash lines present the range of contamination/Cl ratio of leachate (s37).

specific Na/Cl ratio, this value of groundwater from monitoring wells will be affected by the landfill and is supposed to have a similar trend as leachate.

For all samples, leachate exhibited the highest concentrations of Na^+ and Cl^-, as well as the highest Na/Cl ratio. The observed Na/Cl ratios varied between 0.94 and 1.53. Sodium (Na) and chloride (Cl), as conservative elements, exhibit increased leachability when atmospheric precipitation infiltrates solid wastes buried in landfills. This phenomenon provides a plausible explanation for the observed high concentrations of Na^+ and Cl^-.

For other elements with Cl, the leachate samples could be plotted to a narrow range but exhibited significant variations at other sites, particularly those situated distant from the landfill. The samples from 5# and a subset of samples from 2#, 23# and 22# were constrained by both COD_{Mn} and NH_4^+-N. However, Pb only constrained the 5# sample, while Zn could constrain the 5#, 2#, 23#, and 22# samples. Consequently, it can be inferred that the ability of contaminants to constrain leachate pollution from landfills varies,

decreased in the order of Na^+ and Cl^- > COD_{Mn} > NH_4^+-N > Zn > Pb (Fig. 10).

5. Conclusion

In this study, traditional concerned contaminations (COD_{Mn}, NH_4^+-N, Pb, Zn) as well as conservative ions (Na^+ and Cl^-) in leachates from a typical municipal solid waste landfill and nearby groundwaters were studied. Results indicated different geochemistry behaviours of these pollutants, where COD_{Mn}, NH_4^+-N, Na^+ and Cl^- closed to the landfill were higher, while heavy metals of Pb and Zn show the opposite trend, indicating contamination of Pb and Zn in groundwater was not derived from the landfill. Leachate under alkaline conditions was not in favour of heavy metals leaching from solid waste, leading to a low heavy metal pollution risk to groundwater near the landfill. Consequently, employing traditional pollutants such as heavy metals to monitor groundwater contamination from landfills might present certain constraints. In this study, conservative Na^+ and Cl^-, and the molar ratio of traditional contamination to Cl^- had a better performance in tracing the landfill pollution, which could distinguish the polluted and unpolluted area well. Using the conservative indicators to trace groundwater pollution near landfills is essential, and Na^+ and Cl^- were supposed to be available and cost-effective to study groundwater pollution caused by MSW landfills.

Funding

This work was financially supported by the Sichuan Institute of Energetical and Geological Survey Independent Research Project (No. 202208001) and Sichuan Institute of Geological Survey Supported Financial Research Project (No.SCIGSY-CYBXM-2023011). The authors would like to thank the anonymous reviewers for their valuable comments and suggestions.

Data availability statement

The data is available on request from the corresponding author.

Ethics declarations

Not applicable.

CRediT authorship contribution statement

Junlun Meng: Writing – original draft. **Guangli Xiao:** Project administration, Funding acquisition. **Minghui Qi:** Supervision. **Xi Han:** Methodology, Investigation. **Qili Gou:** Methodology, Investigation. **Xinyue Hao:** Data curation. **Jianhong Ge:** Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2024.e35601.

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