

Shallow groundwater surrounding the Likeng landfill, Guangzhou, China – major ions and elements indicating the contamination sources

Jian-Ting Shi, Qianhong Liu, Yan-Rong Zou, Yinjun Peng and Yulan Cai

ABSTRACT

An investigation of groundwater contamination around the Likeng landfill, Guangzhou, was carried out. Major ions and elements of 34 groundwater samples were measured, and the Piper trilinear diagram and expanded Durov diagram were used to analyze the chemical types and hydro-geochemical processes of the groundwater. End Member Mixing Analysis was used to find the types and sources of pollutants. The results show that the hydro-geochemical process was mainly mixing and ion exchange; the shallow groundwater around the Likeng landfill was contaminated mainly by both anthropogenic/agricultural sources and leachate pollution. There are different types of major ions, hydro-chemical processes and distributions for the two pollution sources.

Key words | end member mixing analysis, groundwater, landfill, leachate, pollution

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INTRODUCTION

Before the 1950s, disposal of domestic waste was simple, without any engineering measures required to prevent the proliferation and migration of pollution originating in the dumps. Sanitary landfills were not constructed until the late 1950s in the United States and other countries. From 69% to 73% of municipal refuse has been disposed of at landfill sites in developed countries. The construction of sanitary landfills in China began in the 1980s, and so far, more than 90% of urban wastes are being disposed of to sanitary landfills (Xu & Wang 2001). However, the landfill produced leachate has caused the possible contamination of soil, groundwater and surface waters, affecting the ecosystem balance (Fatta *et al.* 1999). It is reported that almost all landfill waste compartments have had leakage events, not only polluting the groundwater but also penetrating into the soil. About 86% of the existing landfill sites in the United States are contaminated with groundwater (Zafar & Alappat 2004; Nivala *et al.* 2007; Lou *et al.* 2009). The landfill leachate has the characteristics of complex composition: large amounts of organic matter, both biodegradable and refractory to biodegradation; large amounts of toxic substances such as heavy metals; and large numbers of

micro-organisms (Fadel *et al.* 2002). Through rainfall infiltration, these organic and inorganic pollutants enter into surface waters (such as rivers) and groundwater. Many studies on landfill leachate and its adverse effect on the surrounding surface waters and groundwater have been presented (Zheng *et al.* 1991; Fatta *et al.* 1999; Renou *et al.* 2008; Singh *et al.* 2008). Even after the landfill is closed the biological decomposition process will continue for 10 to 20 years, causing additional leachate leakage (Wei 1999). Therefore, the landfill will be a long-term pollution source during and after service.

The study area of the Likeng landfill is located in the Likeng valley of Longgui, Baiyun district, in Guangzhou province, China, about 25 km away from the downtown area. The mean annual temperature is 21.8 °C and precipitation averages 1,694 mm. Mean precipitation from April to September accounts for 82.1% of the annual total. The Liuxi River is an important source of drinking water, and the water conservation district in Guangzhou and the left branch of the main river is the important agricultural irrigation water flowing through the study area. Therefore, it is important to study the impact of the landfill on the surrounding groundwater quality.

The study area has been investigated since the 1990s (Zhou *et al.* 1999; Zhang *et al.* 2003; Luo *et al.* 2009). Zhou *et al.* (1999) analyzed the water quality characteristics of landfill leachate and its influence on the groundwater and surface water. Zhang *et al.* (2003) investigated the impact of the Likeng landfill on adjacent vegetation and evaluated the quality index of six kinds of pollutants such as Zn and Cd. Luo *et al.* (2009) tried to determine the water environmental quality evaluation criteria for this landfill area based on the groundwater and surface water quality standard (GB/T 14848-93).

The objective of this study is to evaluate the hydro-geochemical characteristics of the groundwater and investigate the changes in groundwater quality of the Likeng landfill to find the source pollutants and contamination paths which, in turn, provides a scientific basis for pollution control and remediation of the Likeng landfill.

GEOLOGICAL SETTING OF STUDY AREA

The Likeng landfill was constructed and put into use in February 1992, and closed at the end of March 2004. During the operating period, it received domestic wastes from Liwan District, Yuexiu District, Baiyun District and Tianhe District, Guangzhou. During 12 years of operation, 230,000 m² of the landfill was covered by deposited wastes. The 210,000 m² pile and the actual total amount of municipal solid wastes deposited weighs about 7,500,000 t (Zhu & Yao 2011). At present, the landfill's its closure and ecological restoration have been completed, but there are still large amounts of leachate being produced. The subsurface of the Likeng landfill is anaerobic, resulting in a relatively slow digestion process. Therefore, the decomposition of the garbage will continue after the capping for at least 15 years. Leachate and gas (mainly methane) will continue to be produced during this period.

The Likeng landfill site is located in a combination of three parts: Proterozoic metamorphic rocks, Mesozoic intrusive granitoids and Carboniferous stratigraphy (Figure 1). When the granite magmatic intrusion occurred in the Mesozoic period, the top Carboniferous cover expanded when heated and contracted after cooling, and tension cracks are well developed. In addition, the strata are located in the Guangcong fault zone and multiple tectonic movements have formed the so-called Hornfels phenomenon. The resulting fracture and joint fissure provide a channel for the downward movement of the landfill leachate.

Furthermore, the Likeng landfill construction was based on an abandoned reservoir, where the basal soil is clay with low permeability. However, the dam base is a weathered

layer with a high permeability coefficient; it had to be discarded as a reservoir for water. The curtain grouting technique was used to prevent seepage of the leachate before the landfill was constructed.

There are three types of groundwater in the study area, Quaternary pore water (Q), Bedrock fissure water (B) and Karst water (K). The Quaternary pore water is distributed in the alluvial plain, mountain valley and hilly upland, etc. The aquifer is alluvial sandy gravels and weathered sandy gravels. The hydrochemical type is dominated by HCO₃-Cl-Na.Ca, HCO₃-Na.Ca and Cl-Na.Ca, and the salinity is 140.03–618.05 mg/L. The Bedrock fissure water is distributed in the east of the Guangcong fault, restricted by fracture and joint fissure development. The aquifer of stratified rock fissure water is mainly within the clastic rocks of the Carboniferous and Tertiary, the hydrochemical types are HCO₃-Na.Ca, Cl-Na.Ca and Cl-Na, and the salinity is 46.66 to 2182.11 mg/L. The Karst water, covered by the Quaternary, is located in the northwest of the landfill. The aquifer is mainly within the limestone and dolomitic limestone of the Carboniferous Shendengzi formation. The Karst aquifer is a nearly NNE zonal distribution. The hydrochemical types is HCO₃-Ca and HCO₃-Na.Ca, and the salinity is 121.79 to 157.94 mg/L.

MATERIALS AND METHODS

Samples

Sampling sites were selected around the Likeng landfill site to trace the distribution of contamination according to the general characteristics of runoff of surface water and groundwater. The samples of landfill leachate, surface water and groundwater were obtained covering the period from December 2013 to July 2014. Over this period, 18 samples from the dry season and 18 samples from the wet season were collected, including two background samples of karst water and slate water (water occurring in karst and slate rock fissures respectively), two samples of surface water and two samples before and after treatment of landfill leachate. Sampling point distribution and sample information are presented in Figure 1 and Table 1, respectively.

The major cations, anions and elements were analyzed. The elements were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 2000DV; PerkinElmer, Inc., USA) and the major ions were detected by ICS-1500 ion-chromatograph (Dionex, USA). The concentrations of major ions and elements are presented in Table 2. The analysis of major ions was performed with

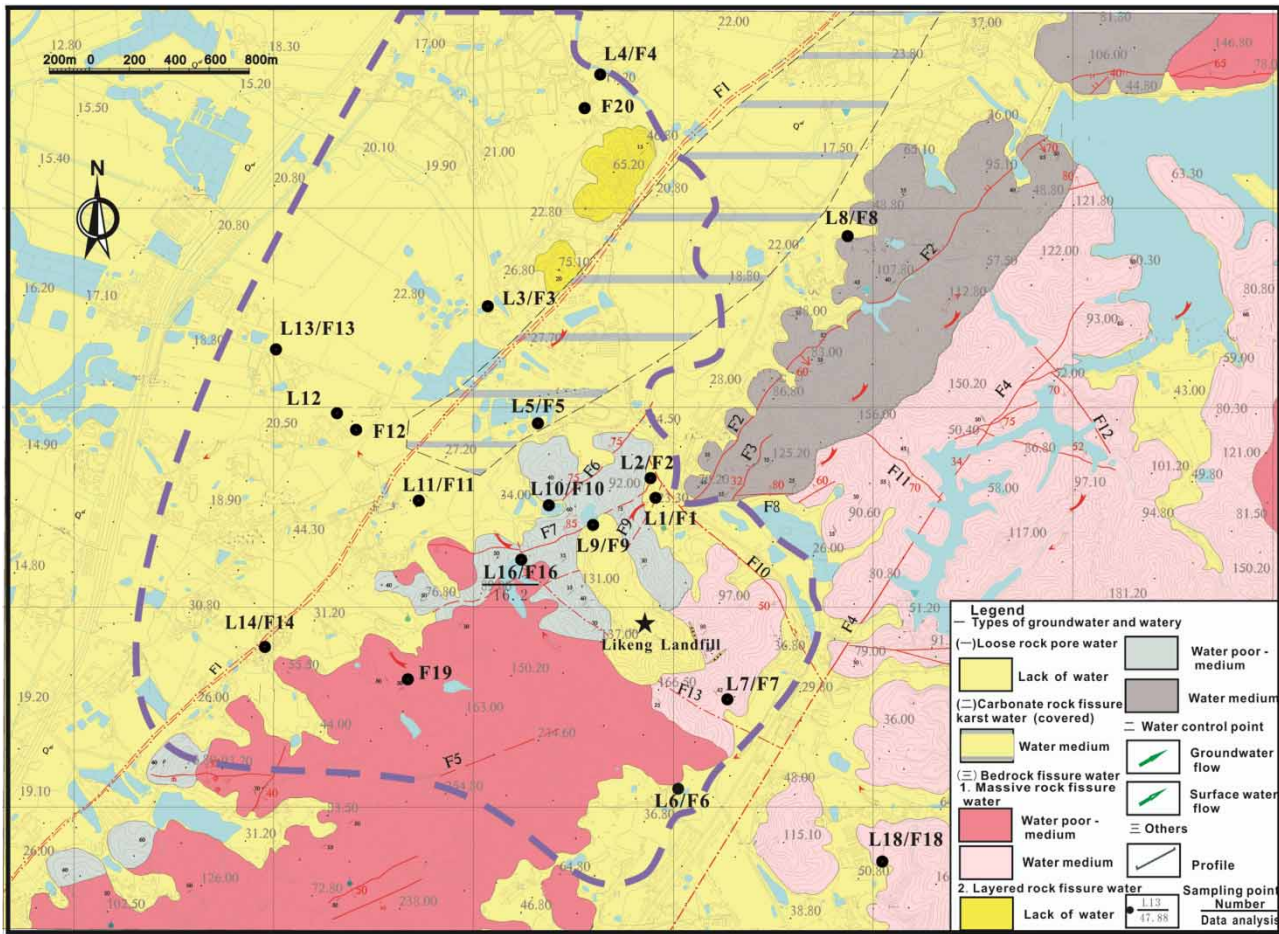


Figure 1 | Geological background and sampling sites.

reference to the natural mineral drinking water detection method (GB/T 8538-2008). All of the analyses were carried out in the Guangzhou Institute of Geologic Survey.

The major ions were used to assign chemical types and perform hydro-geochemical analysis, while these ions plus the major elements were used to carry out the statistical analysis.

Groundwater chemical types

In the study, the Piper tri-linear Diagram (Piper 1944) was used to understand and identify the water composition in different hydrochemical types (Figure 2). There are two triangles and one diamond in the plot.

Two triangles are used to plot cations and anions, respectively; the diamond is used to show a single point from the combination of cations and anions to bring out the chemical relationships among groundwater samples (Prasad et al. 2009). The graphical results not only clearly display the anion and cation concentrations of the

groundwater, but also provide clearer and more understandable information on hydrochemical types.

The analyses of cations and anions in the dry season are shown in Figure 2(a). There are three categories in the dry season: the HCO₃-Ca, HCO₃-Na + K and Cl-Na + K types. Background water samples (+), and samples L3, L5, L6 and L14 are of the HCO₃-Ca type. Karst background water L17 is close to 100% HCO₃-Ca type, while the slate background water L18 has a small amount of Mg²⁺, Cl⁻ and SO₄²⁻. Sample leachate (○) is of the HCO₃-Na + K type, in which the concentration of Ca²⁺ is low, the concentration of Na⁺ and K⁺ is up to 80% and the concentration of HCO₃⁻ almost dominates the anions. Samples L4, L7 and L8 are of the HCO₃-Na + K type, and the chemical composition of major ions in samples L7 and L8 is similar to leachate. Samples L1 and L2 are typical of the Cl-Na + K type, with the concentration of Cl⁻ dominating. Samples L1 and L2 came from the intersection of faults F7, F9 and F10 close to the landfill site, and subject to serious pollution.

Table 1 | Sample information in the study area

| No. | Laboratory label | | Location | Water type |
|-----|------------------|------------|---|--|
| | Dry season | Wet season | | |
| 1 | L01 | F01 | Doorway of Huaweida glass factory | Bedrock fissure water |
| 2 | L02 | F02 | Huaweida glass factory | Bedrock fissure water |
| 3 | L03 | F03 | 7th community, Shihu Village | Quaternary pore water |
| 4 | L04 | F04 | Committee of Shihu Village | Quaternary pore water |
| 5 | L05 | F05 | Vehicle factory of Highway Bureau | Karst water |
| 6 | L06 | F06 | No. 6, 1st South Lane, Dayuan Village | Quaternary pore water |
| 7 | L07 | F07 | Guangzhou International Economics College | Bedrock fissure water |
| 8 | L08 | F08 | No. 115 secondary school of Guangzhou | Bedrock fissure water |
| 9 | L09 | F09 | Likeng waste treatment plant | Leachate |
| 10 | L10 | F10 | Likeng waste treatment plant | Treated leachate |
| 11 | L11 | F11 | No. 17, Yongsheng Street | Quaternary pore water |
| 12 | L12 | F12 | No. 6, 9th East Lane, Shuiniupu, Yongxing village 9th East Lane, Shuiniupu, Yongxing village | Quaternary pore water Quaternary pore water |
| 13 | L13 | F13 | No. 83, North Lane, Niugang west street | Quaternary pore water |
| 14 | L14 | F14 | No. 31, Shikeng Street | Quaternary pore water |
| 15 | L15 | F15 | Lake on the top of Maofengshan hill | Surface water |
| 16 | L16 | F16 | Hulian reservoir | Surface water |
| 17 | L17 | F17 | Well, Chentian Garden | Karst water (background) |
| 18 | L18 | F18 | Deep well, Julong holiday village | Slate water (background) |
| 19 | - | F19 | Hulian, Shikeng | Bedrock fissure water |
| 20 | - | F20 | No. 2, 5th East Lane, Shihu south road, Shihu Village | Quaternary pore water |

There are some changes to the chemical composition in the wet season. In [Figure 2\(b\)](#), although the water's chemical classification remains of the $\text{HCO}_3\text{-Ca}$, $\text{HCO}_3\text{-Na + K}$ and Cl-Na + K types, some samples have obviously changed. For example, the concentration of Ca^{2+} in samples F3 and F5 has decreased and the concentration of Na + K has increased gradually to make the type change from $\text{HCO}_3\text{-Ca}$ to $\text{HCO}_3\text{-Na + K}$, which may be affected by sewage. Moreover, the major cations of sample F7 changed from Na + K to Mg , possibly related to the rainfall. In sample 13, the major cations changed to Ca , and may be affected by the impact of rainfall or sewage infiltration.

Hydro-geochemical analysis

An expanded Durov diagram was used to identify the hydrochemical processes. The major cations and anions were presented to help understand its hydrochemical evolution, grouping and regional distribution ([Al-Bassam & Khalil 2012](#)). The method was developed by Burdon and Mazloum

to identify the hydrochemical processes and reaction paths such as mixing, ion exchange and dissolution that affect groundwater composition ([Burdon & Mazloum 1958](#)). On the Durov diagrams, horizontally from left to right, the exchanges of cations Ca^{2+} , Mg^{2+} and Na^{+} are reflected, vertically, from top to bottom, the diagrams reveal the changes of anions HCO_3^- , SO_4^{2-} and Cl^- , which relate to the degree of contamination. The cation and anion triangles are recognized and are separated along the 25% axes to divide the square into nine fields.

In order to compare changes to the major ions between the dry season and the wet season, the samples are plotted together in [Figure 3](#). The three hydrochemical processes were revealed, i.e. mixing, ion-exchange and reverse ion-exchange, which provided the clues about the water quality changes. In [Figure 3](#), there are nine fields: fields I, V, and IX show dissolution or mixing of sample concentration; fields I, II and III (from left to right) show ion exchange, and fields IX, VIII and VII (from right to left) show reverse ion exchange. Sample 17 is of the $\text{HCO}_3\text{-Ca}$ type, which is

Table 2 | The concentration of major ions and elements (mg/L)

| Sample | K ⁺ | Na ⁺ | Ca ²⁺ | Mg ²⁺ | NH ₄ ⁺ | HCO ₃ ⁻ | Cl ⁻ | SO ₄ ²⁻ | F ⁻ | NO ₃ ⁻ | Total Fe | Mn | Al | TDS | Total hardness ^a |
|----------|----------------|-----------------|------------------|------------------|------------------------------|-------------------------------|-----------------|-------------------------------|----------------|------------------------------|----------|--------|---------|----------|-----------------------------|
| L01 | 22.23 | 673.6 | 94.63 | 1.91 | 56 | 101.7 | 1,134.4 | 113.49 | 0.24 | 16.44 | 5.91 | 6.12 | 0.59 | 2,182.11 | 244.1 |
| L02 | 7.42 | 108.67 | 39.43 | 0.48 | 6.6 | 37.58 | 234.98 | 4.1 | 0.22 | 16.36 | 0.04 | 2.43 | 0.23 | 453.1 | 100.42 |
| L03 | 5.39 | 21.52 | 41.01 | 0.48 | 1 | 99.49 | 39.5 | 26.9 | 0.34 | 0 | 1.04 | 0.49 | 0.022 | 197.63 | 104.36 |
| L04 | 7.65 | 55.95 | 28.39 | 0.48 | 1.36 | 101.7 | 40.51 | 32.36 | 0.11 | 49.16 | 0.04 | 0.067 | 0.053 | 273.07 | 72.86 |
| L05 | 1.49 | 13.6 | 13.41 | 0.48 | 0 | 61.9 | 7.09 | 4.31 | 1.3 | 1.28 | 0.05 | 0.0086 | 0.001 | 121.79 | 35.44 |
| L06 | 2.04 | 14.24 | 20.9 | 0.72 | 0 | 55.27 | 13.17 | 4.73 | 0.33 | 26.3 | 0.02 | 0.0001 | 0.006 | 156.47 | 55.13 |
| L07 | 7.52 | 14.75 | 14.98 | 0.48 | 0 | 44.22 | 16.21 | 3.68 | 0.26 | 26.06 | 0.03 | 0.027 | 0.001 | 123.27 | 39.38 |
| L08 | 1.85 | 13.88 | 7.89 | 0.96 | 0 | 59.69 | 5.06 | 3.26 | 0.28 | 0 | 0.51 | 0.17 | 0.004 | 107.43 | 23.63 |
| L11 | 20.29 | 51.63 | 124.6 | 0.96 | 0 | 145.92 | 126.61 | 79.43 | 0.27 | 119.49 | 0.05 | 0.008 | <0.001 | 618.05 | 315.06 |
| L12 | 13.36 | 50 | 34.3 | 0.72 | 0 | 70.75 | 67.86 | 30.89 | 0.11 | 40.76 | 0.15 | 0.11 | 0.01 | 285.11 | 88.61 |
| L13 | 6.71 | 24.29 | 24.45 | 0.48 | 0 | 37.58 | 31.4 | 23.22 | 0.18 | 37.38 | 0.04 | 0.022 | 0.24 | 180.48 | 63.01 |
| L14 | 26.31 | 31.64 | 87.53 | 5.74 | 0 | 271.94 | 34.44 | 46.65 | 0.55 | 36.67 | 0.02 | 0.015 | 0.15 | 429.27 | 242.2 |
| L17 | 0.67 | 1.91 | 46.13 | 0.72 | 0 | 145.92 | 4.05 | 3.89 | 0.17 | 0 | 0.38 | 0.091 | 0.001 | 142.41 | 118.15 |
| L18 | 2.85 | 6.22 | 11.08 | 2.92 | 0 | 57.48 | 4.05 | 6.94 | 0.24 | 0 | 0.64 | 0.065 | 0.001 | 109.4 | 39.71 |
| F01 | 17.17 | 419.35 | 112.77 | 102.58 | 68 | 138.31 | 1,154.66 | 112.96 | 0.23 | 9.52 | 0.1 | 6.3 | 0.57 | 2,083.15 | 703.96 |
| F02 | 4.52 | 113.5 | 30.84 | 26.01 | 7 | 30.51 | 303.86 | 5.65 | 0.14 | 10.5 | 0.04 | 3.73 | 0.21 | 531.97 | 184.11 |
| F03 | 14.22 | 27.55 | 12.53 | 0.29 | 0 | 67.12 | 25.32 | 18.3 | 2.03 | 0.81 | 0.05 | 0.11 | 1.27 | 140.03 | 32.49 |
| F04 | 7.03 | 55.85 | 37.59 | 2.34 | 4.8 | 122.04 | 32.41 | 68.06 | 0.07 | 32.77 | 0.04 | 0.14 | <0.0001 | 305.46 | 103.49 |
| F05 | 1.26 | 17.47 | 14.46 | 3.21 | 0 | 73.22 | 9.12 | 6.08 | 1.41 | 2.78 | 0.01 | 0.01 | <0.0001 | 139.18 | 49.34 |
| F06 | 1.6 | 18.43 | 21.2 | 3.21 | 0 | 69.16 | 13.17 | 6.29 | 0.27 | 26.86 | 0.01 | 0.001 | 0.011 | 171.17 | 66.18 |
| F07 | 2.33 | 9.45 | 8.67 | 6.43 | 0 | 48.82 | 8.1 | 4.79 | 0.19 | 17.7 | 0.02 | 0.025 | 0.3 | 100.73 | 48.13 |
| F08 | 0.65 | 5.2 | 4.82 | 0.58 | 0 | 24.41 | 2.03 | 3.08 | 0.04 | 0.43 | 0.08 | 0.14 | 0.091 | 46.66 | 14.44 |
| F11 | 14.44 | 43.57 | 97.35 | 11.69 | 0 | 120.01 | 104.32 | 71.06 | 0.19 | 89.55 | 0.02 | 0.052 | 0.0051 | 515.84 | 291.21 |
| F12 | 24.95 | 50.85 | 24.13 | 2.64 | 0 | 54.92 | 81.09 | 20.58 | 0.05 | 41.11 | 0.001 | 0.056 | 0.012 | 282.07 | 71.13 |
| F13 | 7.65 | 25.4 | 28.49 | 2.64 | 0 | 54.92 | 34.75 | 20.2 | 0.23 | 37.92 | 0.03 | 0.031 | 0.21 | 195.86 | 81.99 |
| F14 | 30.1 | 30.35 | 77.54 | 7.68 | 0.02 | 237.98 | 30.12 | 80.58 | 0.69 | 27.19 | 0.01 | 0.0035 | 0.059 | 424.2 | 225.24 |
| F16 | 19.35 | 31.85 | 26.11 | 4.56 | 11 | 88.48 | 46.34 | 29.13 | 0.27 | 23.53 | 0.1 | 0.11 | 0.15 | 261.47 | 83.97 |
| F17 | 0.8 | 2.31 | 45.1 | 4.8 | 0.02 | 152.55 | 8.11 | 10.9 | 0.05 | 0.14 | 0.44 | 0.087 | <0.0001 | 157.94 | 132.38 |
| F18 | 3.36 | 7.17 | 12.05 | 2.34 | 0 | 57.48 | 4.05 | 7.72 | 0.1 | 0 | 0.02 | 0.11 | 0.01 | 138.63 | - |
| F19 | 2.02 | 5.64 | 6.33 | 1.2 | 0 | 33.56 | 3.48 | 4.58 | 0.11 | 4.79 | 0.1 | 0.029 | 0.03 | 66.15 | 20.75 |
| F20 | 6.91 | 31.1 | 56.97 | 4.32 | 0 | 103.73 | 41.71 | 50.82 | 0.05 | 57.21 | 0 | 0.0009 | <0.0001 | 306.84 | 160.04 |
| Leachate | 687.3 | 989.2 | 123.6 | 40.4 | 950 | 2,764 | 2,024 | 615.8 | 1.4 | 72.2 | 1.6 | 0.46 | 0.4 | 8,480 | 476 |

^aAs CaCO₃.

-, not determined.

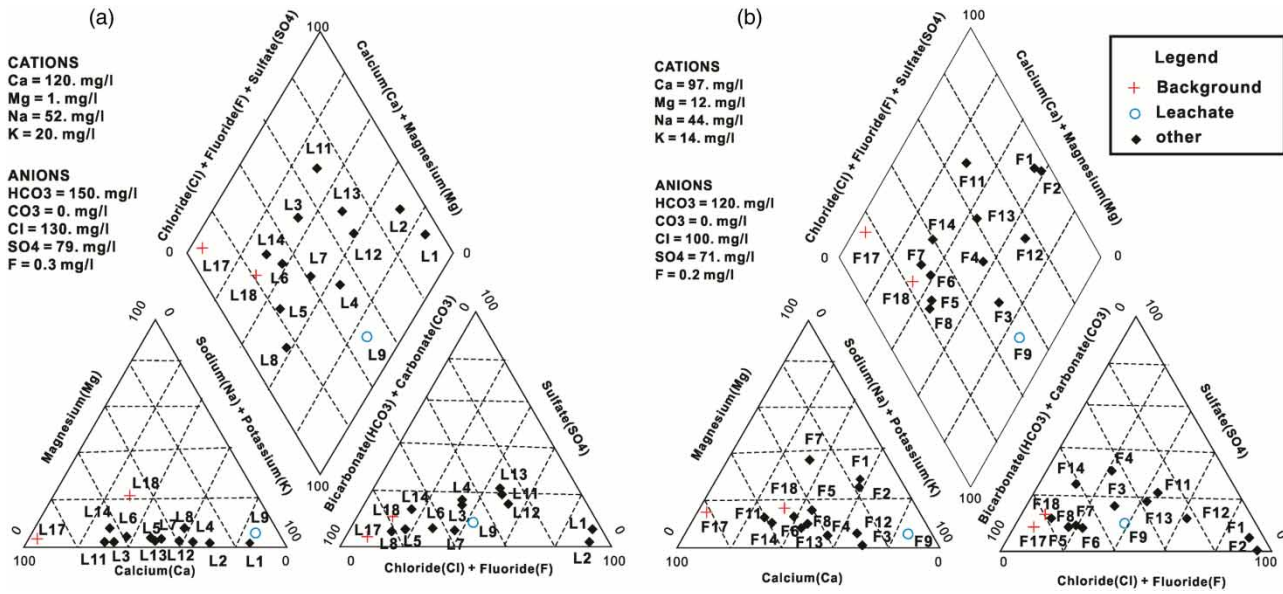


Figure 2 | Piper trilinear diagram of groundwater in the dry season (a) and wet season (b).

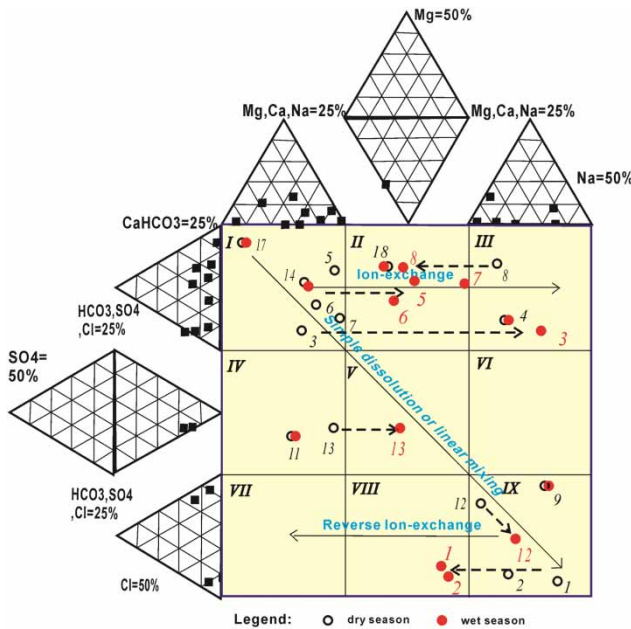


Figure 3 | Durov diagram of major ions in the dry season and wet season.

fresh and clean water. Sample 18 is of the HCO₃-Na/Ca type with a particular ion exchange likely related to the slate background. Samples 1 and 2, located in the Huaweida glass factory, are seriously polluted in the dry season, while the concentration of Na⁺ decreased a little in the wet season, which appears to be related to the high concentration of polluted water being diluted by the rainfall. Sample 3, located in the 7th community Shihu Village, with a sharp increase in

Na⁺, showed the characteristics of strong cation exchange, which may be associated with the rainfall bringing pollutants from urban road into the wells. Directly affected by rainfall, the water qualities of Samples 5, 6, 7 and 13 deteriorated in the wet season; it is likely this is related to the water level rising and the sewage in the water. Sample 8 may be relatively closed and a change in water quality is unusual, creating a high concentration of Na⁺ in the dry season and showing the characteristics of being contaminated, while the concentration of Na⁺ decreased in the wet season, which may be related to dilution by the rainfall.

Statistical analysis

The major ions were used in water chemical and hydro-chemical analysis, while the ions and elements related to contamination, e.g. NO₃⁻ and NH₄⁺, were not used. All the data can be further analyzed by statistical methods. The concentration of major ions and elements (Table 2) was subjected to multivariate analytical techniques such as principal component analysis (PCA). The relative variables were extracted to infer the controlling water chemistry process by principal component (PC) analysis (Brahim *et al.* 2013). Eigenvalues and eigenvectors obtained from PCA performance were used to determine the number of end members in end-member mixing analysis (EMMA).

EMMA has been used previously to identify the characteristics of mixed groundwater with different end members (e.g., Christopherson & Hooper 1992). Groundwater data

were standardized and a series of PCs were performed to best explain the variability in the entire dataset (Garrett et al. 2010). The statistical and EMMA analyses were performed using Pirouette[®] software (Infometrix Inc., USA).

RESULTS AND DISCUSSION

PC analysis

PCA, as a multivariate method of data analysis, is effective in processing with large multidimensional data sets. The use of PCA allows a large number of variables (such as the major anions and cations in water samples) to be reduced to a small number of variables called the PCs. PCA constructs a new set of coordinates that are a linear combination of all the variables, and takes advantage of

the correlation in the data. More concisely, PCA is used to extract related variables by combining two or more correlated variables into one variable. The eigenvalues of the PCs are a measure of their associated variance. Each eigenvalue corresponds to a factor, and a factor is a linear combination of the initial variables. The eigenvalues and the corresponding factors are sorted by descending order of how much of the initial variability they represent (converted to %), which can be more easily explained in terms of the hydro-geochemical processes of groundwater.

In the study, PCA was applied to a 13 variable dataset, consisting of HCO_3^- , Cl^- , SO_4^{2-} , F^- , NO_3^- , K^+ , Na^+ , Ca^{2+} , Total Fe, Mg^{2+} , NH_4^+ , Mn and Al, as shown in Table 2. PCA procedures are as follows. Firstly, groundwater data were standardized by subtracting the mean from each variable and dividing it by its standard deviation so that each variable has unit variance and zero mean. Secondly, the

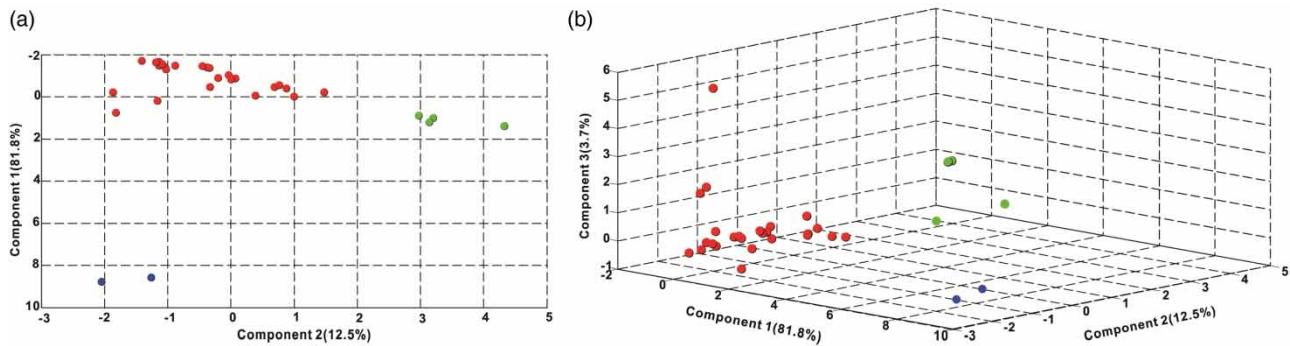


Figure 4 | The 2D and 3D PCA score plots.

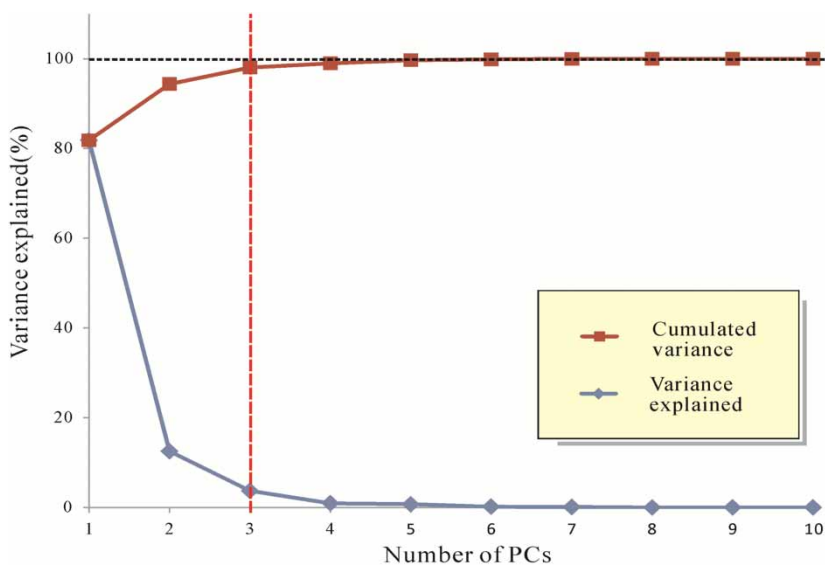


Figure 5 | Variance in principal components and the choice of end-member numbers.

Table 3 | Principal component loadings of major ions and elements

| Variables | Principal components | | |
|-------------------------------|----------------------|---------|--------|
| | PC1 | PC2 | PC3 |
| HCO ₃ ⁻ | 0.746 | -0.584 | -0.245 |
| Cl ⁻ | 0.374 | 0.731 | -0.368 |
| SO ₄ ²⁻ | 0.219 | 0.077 | 0.299 |
| F ⁻ | 0.004 | -0.005 | -0.009 |
| NO ₃ ⁻ | 0.284 | 0.197 | 0.754 |
| K ⁺ | 0.077 | 0.039 | 0.034 |
| Na ⁺ | 0.278 | 0.275 | -0.204 |
| Ca ²⁺ | 0.302 | 0.032 | 0.319 |
| Mg ²⁺ | 0.025 | 0.002 | -0.029 |
| NH ₄ ⁺ | 0.004 | 0.019 | -0.036 |
| Total Fe | 0.001 | -0.002 | -0.006 |
| Mn | 0.001 | 0.003 | -0.009 |
| Al | 0.001 | -0.0002 | -0.002 |

cross-products matrix of variances and or correlations (or covariances) among every pair of the standardized variables was calculated. Thirdly, the eigenvalues and eigenvectors of the correlation matrix were calculated. Finally, the matrix of PC scores was calculated based on the eigenvectors matrix, which was constructed in terms of several eigenvalues sorted by size, and several PCs were selected to represent the original data.

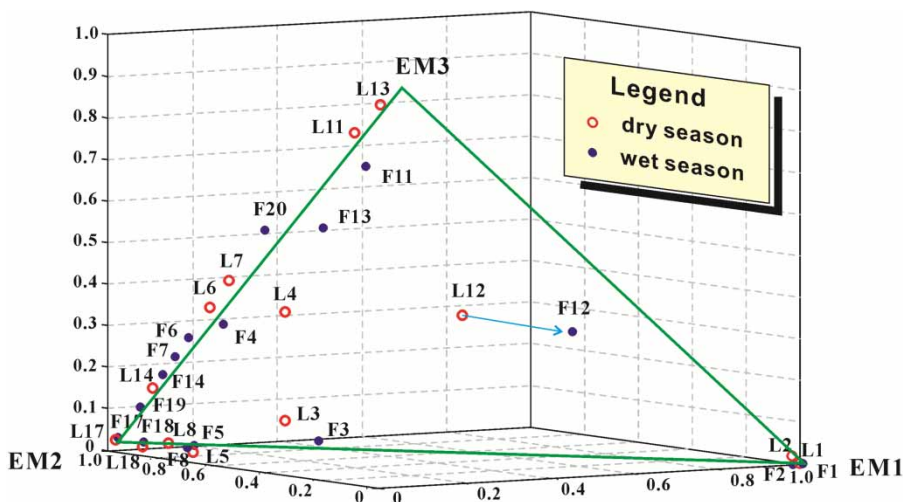
PCA scores are a new variable value based on the samples' component loading and the standardized value of the original variables. The 2D and 3D PCA score plots of all samples except leachate are illustrated in Figure 4. All the PCA scores

in Figure 4 were clustered more clearly into three classifications than the original samples. The first three PCs were selected, which explain 98% of the total variance (Figure 5). The variance contributions of the first three PCs were 81.8%, 12.5% and 3.7%, which suggest most of the information from the 13 variables was included. In Table 3, PC1 is strongly and positively related to HCO₃⁻, Cl⁻, Ca²⁺, Na⁺ and NO₃⁻. PC2 is mainly driven by Cl⁻ and negatively with HCO₃⁻. PC3 is positively associated with NO₃⁻, SO₄²⁻ and Ca²⁺.

End-member mixing analysis

EMMA is commonly used in hyper-spectral remote sensing image analysis, rock end member extraction analysis, etc. Since the 1990s, EMMA has been used to study the mixing of major ions in surface waters, rivers, etc. (Brown et al. 1999; Burns et al. 2001; Frans et al. 2009). In this study, the determination of end members in groundwater samples was by analysis using the ALS method in Pirouette[®] software. Before EMMA was performed, the variants were pre-processed by dividing their maximum values (range scaling). No. 9 sample was collected at the present waste treatment plant, which is not in the landfill leachate zone. Sample 9 was therefore not included in statistical analysis.

Three end-members were determined on the basis of PCA. The EMMA results are shown in Figure 6, Samples 1 and 17 representing two end-members. The concentration of Na⁺ and Cl⁻ in Sample 1 is very high (EM1), which can be directly related to the leachate. The high concentration of HCO₃⁻ in Sample 17 may be related to the background water and rainfall (EM2). End-member 3 (EM3) is close to L13, and is composed

**Figure 6** | EMMA in the dry season and wet season.

of the ions NO_3^- and Na^+ , which could be associated with the anthropogenic and agricultural pollution. The EMMA results show a more concrete mixing detail. Some samples, such as Samples 5, 14, 18 and 19, demonstrate characteristics near those of the background water (Sample 17). Samples 3 and 12 are affected by the leachate (Sample 1 and Sample 2), particularly in the wet season. The other samples (4, 6, 7, 11, 13 and 20) are related to the anthropogenic and agricultural pollution. When the wet season comes they are diluted with the rain water, demonstrating the typical characteristics mixed with the background water.

Sources and pathways of groundwater pollution

There are two pollution sources of groundwater around the landfill. One is from the anthropogenic and agricultural pollution; the other is derived from the landfill leachate.

The area of the anthropogenic and agricultural pollution is mainly distributed in the northwestern depression, where the sewage, farmland watering and runoff converge, then go to the north. The groundwater there showed the characteristics of non-point source pollution with a relatively high concentration of NO_3^- , Na^+ and a little NH_4^+ , such as

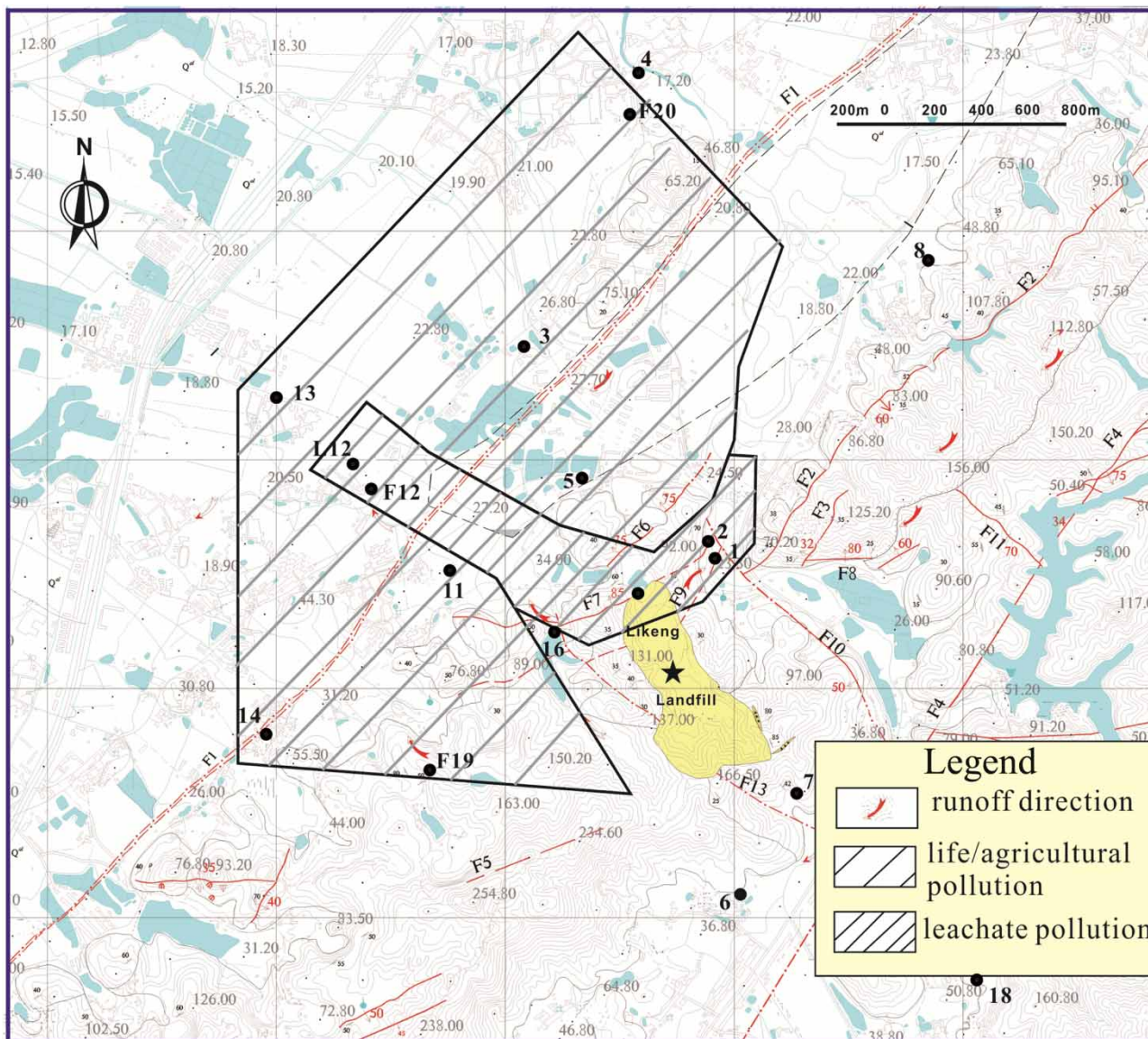


Figure 7 | Types and distribution of groundwater pollution around the Likeng landfill.

Samples 4 and 13. When the wet season came, the contaminant is diluted by rainfall, moving into the background water (Figure 6). This pollution presented the ion-exchange in the Durov diagram (Figure 3). The leachate pollution is characterized by a point source, as in Samples 2 and 12, for instance. The pathways of groundwater pollution are presented in Figure 7:

- (1) The leachate migrated along the faults (F7 and F9) below the landfill and caused the groundwater near the faults to be heavily polluted. This is a little affected by rainfall during the wet season, as shown in Samples 1 and 2.
- (2) The leachate leaked into the ground. A site on the north margin of the landfill was reserved to provide leachate sampling for monitoring. Although the site has been closed and buried since 2009, our results indicate that leachate continues to leak from the site.

The leachate is likely carried by a stream or migrates along Fault F7, spilling at the western low-lying areas. In the dry season, the pollution is not very considerable. However, during the wet season the rainfall carried the spilled leachate, making the shallow underground pollution heavier, as Sample 12 showed (Figures 6 and 7). The leachate pollution demonstrated the reverse ion-exchange or mixing in the Durov diagram (Figure 3).

CONCLUSIONS

A comprehensive study of the groundwater around the Likeng landfill was carried out in the study. The groundwater chemical types were found to be from $\text{HCO}_3\text{-Ca}$ to $\text{Cl}\cdot\text{HCO}_3\text{-Na}\cdot\text{K}$. The hydro-geochemical processes exhibit ion exchange, linear mixing and reverse ion-exchange, depending on the contamination types and pathways.

The EMMA results suggest there are two contamination sources. One is leachate pollution caused by the leachate leaking along faults, which exhibits point-source pollution characteristics of high Cl^- , Na^+ and reverse ion-exchange in the wet season. The other is the non-point source of the anthropogenic and agricultural pollution, which distributes within the depression exhibiting a relatively high concentration of NO_3^- , Na^+ and NH_4^+ , characterized by ion-exchange during the wet season. Our results indicate that the leachate is still leaking along the faults, particularly in the wet season. It is very necessary to take measures to prevent the expansion of the contamination.

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