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Nitrogen aspects of hydrological processes with a case study in Likeng landfill, Guangzhou, China

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Abstract

Nitrogen aspects and hydrological processes need to be integrated in order to understand sources and relevant mechanisms. Landfills are the dominant disposal approach to deal with solid waste in urban areas in China. Landfills require adequate land and pose a potential threat to aquifer contamination, particularly in the humid zone, such as Guangzhou. The unlined Likeng landfill in Guangzhou was investigated in three campaigns during the period of 2001–2007: water was sampled and analyzed for major ions, heavy metals, and stable isotopes of $^{18}$O and $^2$H in water, and $^{16}$O and $^{15}$N in nitrate. Contamination sources, water components, and groundwater flow were examined with multiple evidence, revealing a mixture of various sources from landfill effluent,
septic tank leakage, fertilizer, and manure following complex processes of recharge, mixing, and
denitrification. The effluent from the landfill was rich in Na\(^+\), Ca\(^{2+}\), K\(^+\), HCO\(_3^-\), and Cl\(^-\) ions. The
same process of high NH\(_4^+\) in effluent resulting in episodic increases in NO\(_3^-\) due to NH\(_4^+\)
oxidation was found in Likeng landfill compared to the landfills in Denmark and the United States.
Twenty-five percent of the precipitation was lost to evaporation before recharging the aquifer,
indicating a possible maximum recharge rate of 75% and the potential for a large amount of water
penetration to the landfill if not well constructed. Apparent groundwater flow velocity of 3.7×10\(^{-7}\)
m/s (11.67 m/a) was found for the front of the effluent under the landfill by considering the
vertical and horizontal flow involved. These findings can provide background to delineate the
plume from Likeng landfill and to conceptualize the natural attenuation processes of other toxic
compounds, which are imperative for a remediation strategy.

**Keywords:** Landfill; groundwater; nitrate; stable isotopes; hydrological processes; Guangzhou

**Introduction**

Nitrogen has increased globally in the environment mainly due to human activities in the past
century. Scanlon et al. (2007) attributed degraded water quality, including nutrient balance, to the
conversion from natural to agricultural ecosystems, which is associated with decreased

\(\text{evapotranspiration} \) and increased recharge and streamflow. The spatial pattern of nitrate in
groundwater in the North China Plain is related to fertilizer overuse, wastewater irrigation, and the
regional groundwater flow system (Chen et al., 2005; 2006). High nitrogen content in all water
bodies (e.g., rivers, groundwater, and lakes) is associated with ecosystem eutrophication

(Smolders et al., 2010; Lunau et al., 2013) and health concerns (e.g., methemoglobinemia) (Sadeq
et al., 2008), particularly due to high nitrate in drinking waters. As nitrate is relatively mobile within aquifer systems, it may contribute to high nutrients in coastal areas via submarine groundwater discharge and thus result in a change in N/P ratios (Slomp and Van Cappellen, 2004).

Nitrogen transformation and cycle are closely related to water movement in the unsaturated and saturated zones, and nitrogen aspects of hydrological processes need to be integrated systematically. Actually, the rate of denitrification, dissimilatory nitrate reduction to ammonium, and other relevant N processes are complicated, involving changes in electron donors and acceptors, organic carbon, dissolved oxygen, and other processes (Korom, 1992), which are inherently related to water movement and cycles via land use changes and possibly climate change.

N source identification and relevant processes are two key aspects of N cycle research. N sources are typically classified as either point or areal (i.e., nonpoint) sources. Fertilizers in agricultural lands and runoff and drainage from urban areas are two major areal sources of N, while sewage from factories, treatment plants, and landfill sites are major point sources (Othman et al., 2012; Carey et al., 2013; Pierobon et al., 2013). The preferential flow that percolates through waste deposits affects leachate production, aerobic and anaerobic biological processes, and then N transformation (Bengtsson et al., 1994). While the N source itself does not depend on water movement, the water cycle does affect its accumulation, distribution, and transformation via precipitation (fall-out), advection, and dispersion. Vertical and/or horizontal distribution of nitrate can thus be used to estimate the groundwater flow velocity (Chen et al., 2006). Isotopes of $^{15}$N and $^{18}$O (in nitrate and water, respectively) are widely used to identify N sources and transformation mechanisms (Kendall and McDonnell, 1998), which include both N and water cycles (e.g.,
Denitrification and mixing. Actually, a multiple tracer approach with other indicators is necessary, such as Cl/Br ratio to assess the impact of septic tanks (Katz et al., 2011); multiple isotopes (H, O, N, S, and Sr) to elucidate pollution sources and relevant causes (Hosono et al., 2011); chlorofluorocarbons (CFCs) and fecal indicator bacteria, such as *E. coli*, to assess the impact of landfills (Carlson et al., 2011); and the ratio of NO\(_3^-\)/acesulfame to differentiate agricultural from domestic wastewater sources (Robertson et al., 2013). Several models have been developed to simulate the changes in both N components and hydrological processes (Howard et al., 1996; Brun et al., 2002), though many mechanisms remain unknown.

Landfills are commonly used to dispose of solid waste in both developed and developing countries. Municipal landfills were found to be a significant threat to groundwater quality (Sanjay et al., 2010; Bjerg et al., 2011). The volume and chemical characteristics of leachate produced by landfills are controlled by water balance, vegetation, landfill age, and landfill cover conditions (Bhavna et al., 2013). Four regimes were proposed to elucidate varied processes and reactions of leachate plumes (Cozzarelli et al., 2011). Minor leachate production of 30–40 mm/a was estimated from young landfills in Sweden, with percolation through the waste deposits occurring as a preferential flow (Bengtsson et al., 1994). A simple dilution model revealed that physical mixing was the most important attenuation process in the pollution plume within the landfill (Brun et al., 2002). Ionic balance was calculated for leachate from a landfill in West Malaysia with a high error of more than 13%, indicating the complexity in chemical composition (Rahim et al., 2010).

Solid waste has increased exponentially in China due to rapid urbanization in the past 30 years, and annual domestic waste was estimated to be around 1.5×10\(^8\) tons in 2003 (Hai et al., 2009; Fig. 1), around 90% of which was disposed in landfills (Huang et al., 2006; Wang et al., 2006;...
Although the total number of landfills has been reported recently in yearly statistical books, these numbers only represent large landfills and the actual number is not known. There were 935 landfills in 2008, reported in a business press release (//www.21cbh.com/HTML/2009-7-3/HTML_0M0OX5W0728Y.html). Unfortunately, more than half of these landfills were not constructed and maintained in accordance with national standards regulating waste disposal in landfills (Wang et al., 2009). Much research has been done to investigate the leachate from landfills and potential threats to groundwater use, and public health in China, such as heavy metals (Wang et al., 2009), phthalate esters (Zheng et al., 2007; Liu et al., 2010), and microbes (Tian et al., 2005). Although high content of ammonium and relevant processes were present in leachate plumes (Bjerg et al., 2011; Cozzarelli et al., 2011), little research has reported the pollution of nitrate in aquifers due to high nitrogen content from leachate of the landfills.

Fig. 1 Change in the amount of domestic waste in China (1979–2011) and Guangzhou (2001–2011). Data sources: Annual statistical data for urban construction in China in 2011 (www.bjinfobank.com).

This study intended to investigate the chemical characteristics of leachate from Likeng landfill and changes during the period of 2001–2007. The impacts of the landfill, particularly nitrate produced from the leachate on the local aquifer, were examined by integrating nitrogen aspects and hydrological processes. Various nitrate sources and relevant processes were identified with multiple lines of evidence from stable isotopes and chemical patterns. As Likeng landfill is
located in the upstream section of Liuxi River, which is used for water supply to Guangzhou, identification of pollutant sources from leachate can help to protect water resources and ecosystems in the downstream section.

**Background for the study area**

Likeng landfill site was originally a small reservoir with an area of about $2.52 \times 10^5$ m$^2$ enclosed by mountains except one outlet to the west. Located 25 km north of the city center, it was converted to a landfill in 1990, the third in Guangzhou. The storage capacity was enlarged from an original volume of $2.87 \times 10^6$ m$^3$ to that of $5.5 \times 10^6$ m$^3$ with a top at 135 m above sea level and a depth of 80 m. The landfill was lined with a clay layer to prevent percolation of leachate at the bottom, and a pond was built in the lower reach to collect and treat leachate from the landfill. It was operated during the period of 1992–2004, during which time it collected total domestic waste of around $9.0 \times 10^6$ tons, primarily from four districts of Guangzhou: Baiyun, Fangcun, Yuexiu, and Liwan. Part of the waste was burned in an annex facility next to Likeng landfill. The amount of annual domestic waste from the 10 districts of Guangzhou during the period of 2001–2011 is given in Fig. 1. The amount of annual domestic waste in Guangzhou before 2001 is not given due to an administrative boundary change in 2000, when Guangzhou increased from 8 districts to 10 districts.

The hydrogeological conditions are relatively complex with bedrock of granite in the south part of the landfill, and a mixture of carbonate and sandstone interfingering with shale in the north part. The landfill is at risk of deep percolation and contamination to the underlying aquifers due to probable fractures in the granite and high porosity in the carbonate and sandstone.
Annual average rainfall was calculated to be 1741.9 mm in Guangzhou during the period of 1951–2008. Average monthly distribution is given in Fig. 2, with rainfall in the wet season from April–September accounting for approximate 80% of annual rainfall. As the pan evaporation measured by E601 was 1100 mm in the Pearl River delta (Zeng et al., 2010), close to actual evapotranspiration in this humid region, runoff from the landfill site was calculated to be $1.62 \times 10^5$ m$^3$, which has to be collected and drained to avoid percolation to the landfill and thus reduce the leachate.

Fig. 2 Monthly average rainfall in Guangzhou during the period of 1951–2008.

Material and methods

Three field campaigns were implemented on March 5, 2001; March 15, 2005; and March 24–25, 2007 with 17, 15, and 17 water samples collected from domestic wells/leachate, respectively (Fig. 3, Table 4). These wells ranged from 1.5–50 m in depth. The screen was usually installed for the bottom layers as informed by the local residents, while specific screen depths were unknown. The wells were purged at least 5 minutes before sampling. After filtration with a 0.45 µm membrane filter, samples were collected in pre-cleaned plastic bottles, brought back to the laboratory, and stored at the temperature below 4°C until analysis for major ions and hydrogen and oxygen stable isotopes. Electrical conductivity (EC), dissolved oxygen (DO), oxidation–reduction potential, temperature, and pH were measured in situ. Major ions of Cl$^-$, SO$_4^{2-}$, NO$_3^-$, K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, and NH$_4^+$ were measured by ion chromatography (Shimazu CTO-10A), while HCO$_3^-$ was obtained by titration (0.01 mol L$^{-1}$ H$_2$SO$_4$). Stable isotopes ($^{18}$O and


$^{2}$H or D) were undertaken by mass spectrometry (Finnigan MAT Delta S). All analyses were done at Chiba University, Japan. Heavy metals were analyzed for the samples collected in 2005 by various methods, including graphite furnace atomic absorption spectrometry for Pb and Cd, atomic fluorescence spectrophotometry for Hg and As, flame atomic absorption spectrometry for Fe and Mn, and indirect flame atomic absorption spectrometry for Al. The Cr$^{+6}$ was measured by the spectrophotometric method. Detection limitations for relevant heavy metals are given in Table 1.

The nitrates in the filtered water samples were concentrated in situ on the anion exchange column (DOWEX 1 9 8, 200–400 mesh, chloride form), and then converted to solid AgNO$_3$ in the laboratory according to the method introduced by Silva et al. (2000). The AgNO$_3$ was then analyzed for $\delta^{15}$N using a DELTA plus XL mass spectrometer connected with a CE EA1112 C/N/S analyzer in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Analysis of $^{18}$O was done using a MAT 253 mass spectrometer connected with a high-temperature conversion elemental analyzer. Dissolved organic matter and oxygen-bearing ions other than NO$_3^-$ were carefully removed during the preparation of AgNO$_3$ for $^{18}$O analysis. The $^{18}$O, $^2$H, and $^{15}$N for water samples were expressed as per mill difference of the isotopic ratios of a sample (sp) and a standard, referred to as standard mean ocean water for $^{18}$O and D, and as AIR for $^{15}$N.

Fig. 3 Schematic location and map of sampling sites at Likeng landfill site. Potentiometric surface with contour interval of 3 m was given for the data measured in 2007, indicating a general groundwater flow to the north in this area.

Results and Discussions
Chemical characteristics of landfill effluent

The amount and characteristics of landfill effluent are related to climatic and hydrological conditions (Cozzarelli et al., 2011; Bhavna et al., 2013). It is thus reasonably anticipated that high leachate could be produced from the humid area, such as in Guangzhou, China. Municipal solid waste in Guangzhou has three features: 1) high organic matter composition that easily decomposes; 2) high water content of more than 50%; and 3) mixture of various sources, such as domestic, industrial, commercial, and medical waste. The effluent, i.e. direct discharge from the landfill, was collected in March 2005 from a small ditch indicated as “+” in Fig. 3, and major ions and basic effluent data are given in Table 2. Low DO indicated the reduction condition in the landfill, while low temperature compared to well 2 (21.5°C, depth of 10 m, next to the effluent treatment site) indicated a low energy level during the production of effluent, probably due to high water content.

According to the data in Table 2, the effluent could be classified as Na–K–HCO$_3$ type with a high content of ammonium, which was converted from organic-N waste via ammonification. Potassium in the effluent was 687.3 mg/L in Likeng landfill by Luo et al. (2009) during a campaign within the period from August 2006 to August 2007, while the chloride was 2025 mg/L, similar to the value given in Table 2. Similar chloride content of 2047 mg/L was found in a landfill in Malaysia (Rahim et al., 2010). High content of potassium with a median value of 414 mg/L was reported in Norman Landfill (Cozzarelli et al., 2011). As annual precipitation in Guangzhou is twice that in Norman Landfill (around 960 mm/a), half the potassium concentration would have been expected due to the dilution effect. In contrast, potassium content four times as high was found in Likeng landfill. It could be concluded here that high potassium content is typical in landfill leachate, particularly in the humid area. Relatively high contents of Na$^+$, Ca$^{2+}$, HCO$_3^-$, and Cl$^-$ were found.
in the effluent from Risby landfill in Denmark (Milosevic et al., 2012), and could be classified as Na–Ca–HCO$_3$–Cl type, although absolute concentrations were much lower than those in Likeng.

High temperature can accelerate the ammonification process within the landfill, and it is reasonable to have higher NH$_4^+$ in the effluent in the summer than that in the winter. NH$_4^+$–N was 525 mg/L in July, almost twice as that in January (272 mg/L) (Table 3; Yang et al., 2010) in one landfill in northern Jiangsu Province of China. Actually, ammonification and production of NH$_4^+$ in landfills are complex processes, associated with precipitation, temperature, composition of waste, age of operation, and other factors; it is hard to find a simple correlation between the amount of NH$_4^+$ and any one independent parameter. Main chemical characteristics of effluents reported in China are summarized in Table 3, and relevant characteristics in Denmark and the United States are given as well for the comparison. Ammonification is the dominant process during the production of effluent with no or low contents of NO$_3^-$ and NO$_2^-$ detected, which may then increase later to a relatively high level due to nitrification, as shown in Likeng (Table 3).

Same process of high NH$_4^+$ resulting in episodic increases in NO$_3^-$ due to NH$_4^+$ oxidation was documented by Cozzarelli et al. (2011). Highly variable NH$_4^+$–N was also found in several landfills in Ontario, Canada, ranging from 7.6–1820 mg/L (Howard et al., 1996). High levels of chloride and ammonium in Likeng were consistent with the ranges given by Mikac et al. (1998).

Heavy metals were measured in 2005 in the effluent and groundwater at well 1, which is located next to the drainage channel of treated effluent.

**Temporal change of groundwater quality from 2001–2007**

Seven wells were sampled during three campaigns in March 2001, 2005, and 2007, enabling
comparison of the change in groundwater quality within 6 years. Concentrations of all major ions except Mg\(^{2+}\) showed an obvious increase (Fig. 4), indicating the possible impacts of the effluent from the landfill. The average concentration of NO\(_3^-\) in 2007 was approximately twice that in 2001; in particular it increased from 3.9 mg/L in 2001 to 53.3 mg/L in 2007 at well 1 (Table 4).

Nitrate pollution to a depth of 50 m poses a serious threat of the landfill to the deep aquifer in the study area. Ranges of nitrate concentration in 2001, 2005 and 2007 were 3.9-288.8, 3.4-226.1 and 0.47-322 mg/L respectively, with relevant standard deviations of 111.8, 101.3, and 143.3, showing a highest level in 2007. Although much higher contents of nitrate were detected in the other wells in the vegetable field (e.g., wells 8 and 9), they remained relatively stable within 6 years. The reasons for low nitrate at well 10 in 2001 (but high level in 2007) remain unknown.

Fig. 4 Average concentrations (mg/L) of major ions in seven wells during the three campaigns.

All water samples, including the effluent, during the three campaigns were plotted in the piper diagram (Fig. 5). The dot close to the effluent was a water sample from the drainage channel, and showed similar chemical facies as that of the effluent; high concentrations of NH\(_4^+\) and K\(^+\) were detected at 127.6 mg/L and 100.9 mg/L, respectively, while no nitrate was detected, indicating a dominant ammonification process. Nitrification took place in the interaction of surface water in the drainage channel and the adjacent aquifer, and high nitrate content was produced, as was the case at well 1.

High variation of chemical features was found in 2001, and the highest ratio of HCO\(_3^-\) type was detected compared to water samples collected in 2005 and 2007. Most water samples in 2007
were classified as SO$_4$–Cl type, which accounted for 50–60% of the total anions (Fig. 5). The evolution of chemical facies from HCO$_3$– type to SO$_4$–Cl type during the period of 2001–2007 was shown by the arrow in Fig. 5. Vegetable production is the main land use except in the mountain area, residential area, and landfill, as shown in Fig. 3, and three wells of 8, 9, and 10 are located in the vegetable field. As chemical features of water samples in the vegetable fields with high fertilizer inputs and high production remained relatively stable, the shift of the chemical types revealed the impacts of the landfill and its effluent on surface water and groundwater. The local groundwater flow indicated in Fig. 3 and relevant mass transport could also affect this shift, in addition to possible various N sources from different areas as mentioned.

Fig. 5 Piper diagram for all water samples collected during the three campaigns. Evolution of chemical facies is indicated by the arrow.

Identification of contamination sources

Fig. 6 Use of dual isotopes to identify various sources of nitrate.

As chloride is relatively conservative compared to nitrogen transport processes of both convection and dispersion, the ratio of nitrate to chloride was used as an indicator to differentiate sources and possibly inherent processes (Chen et al., 2006). Two groups of nitrate sources can be identified by the relationships of dual isotopes and the ratio. Based on the two boxes in Fig. 6, the field survey, and communication with local farmers, the group with higher $\delta^{15}$N and $\delta^{18}$O values
of nitrate was associated with the source from the landfill, while that with lower values was located in the vegetable field and probably associated with the mixture of fertilizer and manure. Volatilization usually results in highly enriched $\delta^{15}\text{N}\text{–NH}_4^+$ in the leachate, while the nitrification may produce depleted nitrate due to fractionation as reported by North et al. (2004), such as $23.31 \pm 3.76\%_\text{o}$ for $\delta^{15}\text{N}\text{–NH}_4^+$ and $-4.54 \pm 2.05\%_\text{o}$ for $\delta^{15}\text{N}\text{–NO}_3^-$. If ammonium was fully transferred to nitrate via nitrification when the effluent penetrated the aquifer, highly enriched $\delta^{15}\text{N}\text{–NO}_3^-$ would then be generated. Relatively high nitrate concentrations of 14.3 mg/L and 39.2 mg/L were detected in 2005 and 2007, respectively, at monitoring well 2 next to the landfill and effluent treatment site (physical-chemical-biological treatment level), but low ammonium concentrations of 0.9 mg/L and 0 mg/L were detected, respectively, indicating a fully converted nitrification process.

Sources of three groundwater samples (wells 8, 9, and 10) from the shallow aquifer in the vegetable field were identified easily with $\delta^{15}\text{N}\text{–NO}_3^-$ ranging from 10–15%, $\delta^{18}\text{O}\text{–NO}_3^-$ at around 6%, and the ratio of $\text{NO}_3^-/\text{Cl}^-$ close to 1.0. The other three wells (12, 15, and 17) had ratios of more than 1.0 (high content of nitrate), and were located in the residential area, where the leakage of septic tanks was usually noticeable (Lu et al., 2008). Well 1, affected by the treated leachate, showed the highest $\delta^{15}\text{N}\text{–NO}_3^-$ of approximately 30%. The leachate from the landfill was treated through a series of regular physical, chemical, and biological processes to reduce chemical oxygen demand (COD) and ammonium components before discharging to the channel, which thusly produced enriched $\delta^{15}\text{N}\text{–NO}_3^-$ as volatilization and denitrification were involved in the treatment.

Impact of evaporation on isotopic features
Fig. 7 Relationship between $\delta^{18}$O and $\delta^D$ in water and local meteoric water line.

Stable isotopes of $^{18}$O and D were measured in 2005 and 2007, revealing different intersection angles with the local meteoric water line (LMWL) (Fig. 7) and the general trend of the observed points. A large angle or small slope in 2005 reflected a strong impact of evaporation on water before recharging to the aquifer. High pan (E601) evaporation rates were gauged during the period of 2003–2005, while they were relatively low in 2006 (Fig. 8). It is interesting to note that low pan evaporation rate was also found in 2006 in Norman landfill (Mendoza-Sanchez et al., 2013). As isotopic signals of groundwater reflected the accumulated features of recharged water prior to sampling in March 2007, low evaporation in 2006 weakened the fractionation and thus reduced the isotopic values. Water temperature ranged from 20–25°C during the field campaign, thus the equilibrium fractionation factor, $10^3 \ln \alpha^{18}$O$_{l-v}$ (close to enrichment factor, $\varepsilon^{18}$O$_{v-l}$), for such water temperature range was found to be 9.7 (20°C) and 9.3 (25°C) (Clark and Fritz, 1997). The dynamic fractionation can be calculated using average humidity ($h$) of around 70% according to the Gonfiantini (1986) relationship given as:

$$\Delta \varepsilon^{18}$O$_{bl-v} = 14.2 * (1-h) = 14.2 * 0.3 = 4.26 \text{‰}$$

Total enrichment was calculated as:

$$\varepsilon^{18}$O$_{total} = \varepsilon^{18}$O$_{v-l} + \Delta \varepsilon^{18}$O$_{v-bl} = -5.44 \text{ (20°C)} \text{ or } -5.04 \text{ (25°C)}$$

Fig. 7 shows a total enrichment of approximately 1.5‰, which was used to calculate the ratio remainder $f$ according to the formula given in Clark and Fritz (1997), yielding an evaporation rate $(1-f)$ of 24% (20°C) and 26% (25°C) of total precipitation.
Fig. 8 Monthly pan evaporation during the period of 2001–2008 in Guangzhou.

The runoff coefficient in the humid climate zone can be as high as 0.5–0.6, indicating that 40–50% of the precipitation was lost to evapotranspiration. A rough estimation of about 25% water loss to evaporation before aquifer recharge was reasonable in such a humid area, with the gap probably due to transpiration, depression storage, interception, or other unknown factors. Nevertheless, a maximum recharge rate to the saturated zone was estimated to be 75% in Likeng landfill site, though the actual rate would be much less. In comparison, average recharge at Norman landfill site over a 10-year period was found to be 36% of rainfall (Mendoza-Sanchez et al., 2013), ranging from 16–64% of rainfall (Scholl et al., 2005). As rainfall in Guangzhou is twice as high as that at Norman landfill (a climate of between humid subtropical and semi-arid with annual average precipitation of 880 mm), a recharge rate higher than 36% of rainfall would be expected.

Fig. 9 Relationship between $\delta^{15}$N–NO$_3^-$ and residual NO$_3^-$ in Likeng landfill. Solid dots indicate three sampling sites in the vegetable field with the same N source.

A negative linear relationship was obtained between $\delta^{15}$N and ln(NO$_3^-$) for denitrification following the classical equation of Rayleigh fractionation, while a reverse relationship, $\delta^{15}$N =
A*1/ln(NO₃) + B (A and B are two constant parameters relevant to the concentration and isotopic value of various end members), was derived for the mixing or dilution process (Mariotti et al., 1988). Several sources of nitrate were identified in the previous section, but none of them followed the relationship of mixing or denitrification given by Mariotti et al. (1988), as indicated by a positive relationship for the same source in Fig. 9. Two probable causes for such deviation were: 1) mixing of several sources may not follow the simple scenario of two end members; and 2) the simultaneous occurrence of mixing and denitrification, and nitrification and volatilization complicate these two processes. Thus, multiple tracers are necessary to identify sources and relevant processes.

Integration of N sources and groundwater movement with multiple tracers

Well 3 is located in an isolated house and far from the vegetable field with a low nitrate concentration. As it is located in the lower part of a natural slope land of forest, potential anthropogenic N sources were eliminated from the field survey and ground truth, and nitrate was assumed to come from natural soil background levels, with δ¹⁵N of 12.5‰ before the landfill was built. As δ¹⁵N was found in the range of 10–22‰ for the source of manure/urine and 2–9‰ for natural soil organic-N (Heaton, 1986; Clark and Fritz, 1997), the background value here with a lowest δ¹⁵N for the cluster in upper left in Fig. 10 indicated that the natural soil organic-N had small impacts from the leakage of septic tanks. Nitrate in precipitation, usually having a high δ¹⁸O–NO₃ (Chen et al., 2009), could contribute as well to the high δ¹⁸O–NO₃ at well 3 (Fig. 11).

Although well 2 and 3 are not connected hydrogeologically, they do naturally have a common or similar recharge source (Fig. 3) in terms of the groundwater flow system. A lowest value in
$\delta^{18}O$-H$_2$O at well 3 in Fig. 12 indicated a recharge source from an upper land or mountain area of higher altitude. The monitoring well 2 is located around 200 m from the landfill and next to the effluent treatment site. As the effluent pond and relevant treatment facilities were well built with concrete and no leakage was reported, nitrate content at well 2 was supposed to come from the front of the effluent that seeped from the landfill. Based on a simple mixture scenario 1:1 (background and front of the effluent, source X in Fig. 10), $\delta^{15}N$ and Cl$^-$ of source X were calculated as 24.5‰ and 96.6 mg/L, respectively. The other mixture scenarios would affect the location of source X in Figs.10-13, but would not affect the general trend of linear mixture, chloride content of source X was much less than that of the effluent at Likeng, due mainly to the decline process associated with convection and diffusion. A high value of $\delta^{15}N$ is viable if highly enriched ammonium is fully nitrified to nitrate in the aquifer as discussed previously.

Fig. 10 Relationships of $\delta^{15}N$ (left) and NO$_3^-$ (right) with Cl$^-$, and their implication in identifying N sources (dashed line to identify source X).

The relationship between $\delta^{15}N$ and chloride clearly revealed three source groups: one at wells 8, 9, and 10 (filled circle) with a high linear coefficient ($R^2 = 0.978$), one source group at well 1 (unfilled circle), in addition to a cluster including wells 2 and 3 (unfilled circle) (Fig. 10). A simple relationship between Cl and nitrate could be used as well to differentiate the sources at wells 1 and 4 (filled triangle) from the others (unfilled triangle), which fell on the linear line ($R^2 = 0.959$) (Fig. 10) and could be classified into two clusters with a threshold of chloride content at 100 mg/L.
Fig. 11 Relationship between δ\[^{18}\text{O} \]–NO\[^{-3}\] and Cl\(^{-}\). The cluster of wells 8, 9, and 10 can be clearly identified.

Similar results were achieved using the relationship between δ\[^{18}\text{O} \]–NO\[^{-3}\] and Cl\(^{-}\), as indicated in Fig. 11. The δ\[^{18}\text{O} \]–NO\[^{-3}\] of source X was estimated at 4.8‰ following the same approach to calculate δ\[^{15}\text{N} \]. As chloride is relatively conservative, its concentration at the front of the effluent can be calculated using the following equation (Ogata, 1970):

\[
C = \frac{C_0}{2} \left[ \text{erfc}\left(\frac{L - \nu t}{2\sqrt{D_L t}}\right) + \exp\left(\frac{\nu L}{D_L}\right) \text{erfc}\left(\frac{L + \nu t}{2\sqrt{D_L t}}\right) \right]
\]

where \(C\) is the concentration of chloride at some distance, \(L\), from the continuous source of the landfill with an initial Cl\(^{-}\) concentration of the effluent, \(C_0\), at time \(t\); \(\text{erfc}\) is the complementary error function, \(D_L\) is the longitudinal coefficient of the hydrodynamic dispersion, and \(\nu_L\) is the average linear groundwater velocity.

Groundwater flowed at a horizontal rate of 1.8–62.5 m/a and a vertical rate of 2–2.5 m/a in a wastewater irrigation area (Chen et al., 2006); the horizontal rate was estimated to be 126 m/a in a small catchment in Zhuhai using CFC data (Zhao, 2008). A conservative value of \(\nu_L = 3.7 \times 10^{-7}\) m/s was chosen by considering both horizontal and vertical flows from Likeng landfill. \(D_L = 2.5 \times 10^{-7}\) m\(^2\)/s was used by assuming a longitudinal dispersivity of \(\alpha_L = 0.676\) m and ignoring molecular diffusion. This dispersivity was within the range of 0.3–4.5 m by Bjerg et al. (2011).

Given \(L = 200\) m, \(t = 15\) years, \(D_L = 2.5 \times 10^{-7}\) m\(^2\)/s, and \(C_0 = 2333.7\) mg/L, then \(C = 121.8\) mg/L was obtained, which was very close to the result of 1:1 scenario (96.6 mg/L, source X).
Nitrate dynamics from multiple tracers

Fig. 12 Use of the relationship between $\delta^{18}$O–NO$_3^-$ and $\delta^{18}$O–H$_2$O to identify N sources and relevant processes.

Well 9, with water depth of 1.5 m, acted as a pond that caught rain water for use in irrigation of vegetables; the component of nitrate here should follow the rule of 2:1 for the relative contribution of ambient O from surrounding water and atmospheric O$_2$ given as:

$$\delta^{18}\text{O}_{\text{nitrate}} = \frac{2}{3}(\delta^{18}\text{O}_{\text{water}} + \varepsilon_{\text{water}}) + \frac{1}{3}(\delta^{18}\text{O}_{\text{O}_2} + \varepsilon_{\text{O}_2})$$  (Mayer et al., 2001)

As $\delta^{18}\text{O}_{\text{nitrate}}$ and $\delta^{18}\text{O}_{\text{water}}$ were measured as 5.821‰ and −4.86‰, respectively, at well 9, the second term of the right component in the above equation, $\frac{1}{3}(\delta^{18}\text{O}_{\text{O}_2} + \varepsilon_{\text{O}_2})$, was estimated to be 9.061‰ if isotopic fractionations of $\varepsilon_{\text{water}}$ and $\varepsilon_{\text{O}_2}$ were ignored. Actually, $\delta^{18}\text{O}_{\text{O}_2}$ was measured to be 23.5‰ (Mayer et al., 2001); $\frac{1}{3} \times 23.5 = 7.83$‰ was close to the estimation here. A straight line passing well 9 and following the rule of 2:1 is given in Fig. 12. The dots at wells 8 and 10 with a similar source to well 9 fell approximately within this line, while the dots from other sources were located above the line with higher $\delta^{18}$O–NO$_3^-$ and did not keep the rule of 2:1, probably due to respiratory isotope fractionation, evaporative effects (Kendall and McDonnell, 1998; Burns and Kendall, 2002), or other effects during nitrification and denitrification of effluent seepage and treatment at Likeng landfill site.

The front of the effluent, source X, could be easily identified by extending the connection line of wells 3 and 2 to the same distance between them as in the scenario when 1:1 was assumed.

The $\delta^{18}\text{O}_{\text{water}}$ for source X was then estimated to be −2.31‰.
With the rule of 2:1 and local monthly (amount-weighted average) range of precipitation $\delta^{18}O$ of $-9.14$ to $0.34\%$ from nearby International Atomic Energy Agency (IAEA) station of Guangzhou (IAEA, 2003; Chen et al., 2009), the range of $\delta^{18}O$–$NO_3^-$ of 1.7–7.9$\%$ can be estimated for the reduced N sources of $NO_3^-$ as indicated by two horizontal dashed lines in Fig. 13.

Three wells in the vegetable field, one well (17) in the residential area, and sources X were found within the estimated range, while the other dots were higher than the upper range of 7.9$\%$, likely showing different sources or processes. Three boxes are given in Fig. 13, indicating various nitrate sources from fertilizer, soil organic-N, and manure/sewage. All samples collected in the study area were located within the box from the manure and sewage source.

Three wells of 8, 9 and 10 are located in the vegetable field within a distance of less than 200 m (Fig. 3), and the same source of N was identified from isotopic features previously. A good positive linear relationship existed for wells 8, 9, and 10, probably indicating denitrification. The simultaneous occurrence of denitrification and mixing of varied sources, e.g., chemical fertilizer, manure and organic N, could account for the low correlation factor of 0.134 in the regression equation, lower than the expected value of 0.5 between $\delta^{18}O$ and $\delta^{15}N$ for the dominant denitrification process (Chen et al., 2009). The mixing process of background levels (well 3) with the front of the effluent and likely leakage from skeptic tanks could explain the other points except well 1. The complex treatment process for the effluent may result in exceptional isotopic values at well 1 as given in Fig. 13.

Fig. 13 Relationship between $\delta^{18}O$ and $\delta^{15}N$ of $NO_3^-$ and its application in N source identification by using three boxes for various nitrate sources adopted from Silva et al. (2002).
Conclusions

Various sources of nitrogen and their association with hydrological processes complicate the nitrogen aspects of hydrological processes, which have to be considered in order to deal with groundwater contamination of either areal or point sources. The case study at Likeng landfill presented three obvious nitrogen sources: fertilizer/manure in the vegetable field, septic tank leakage in the residential area, and effluent from the landfill. Water cycle process, water movement, mixing, and denitrification were deemed the main processes affecting the spatial and temporal distribution of nitrogen levels in the study area. Major conclusions from this case study were given as:

1) Effluent rich in Na$^+$, Ca$^{2+}$, K$^+$, HCO$_3^-$, and Cl$^-$ with relatively low temperature was produced under warm and wet climatic conditions, which may promote the nitrification of ammonium to nitrate in the aquifer. Nitrate concentration in the groundwater approximately doubled during the period of 2001–2007, indicative of the impact of the landfill on the local aquifer.

2) Moderate evaporation of around 25% of the precipitation was estimated before recharge to the aquifer. As actual evaporation accounts for roughly 50% of the precipitation in Guangzhou, the other 25% of precipitation is probably lost to transpiration in the dry season, such as in March.

3) Multiple tracers were used to differentiate the various sources of nitrogen and depict the effluent movement underground. The conservative ion of chloride and the ratio of NO$_3^-$/Cl$^-$ could serve as good indices to simply identify the different nitrate sources. For example, Cl$^-$ of more than 100 mg/L is usually associated with the source from fertilizer and manure.
The relationships between nitrate concentration and $\delta^{15}$N/$\delta^{18}$O did not follow the normal rules for denitrification and mixing, likely indicating a mixture of multiple (more than two) end members and the simultaneous occurrence of several processes. These findings can provide strong bases to delineate the plume from Likeng landfill and to conceptualize natural attenuation processes of other toxic compounds, such as xenobiotic organic compounds or heavy metals in landfill leachate. Secondly, some findings may be used as in situ indicators to support further research on conceptual and/or numerical models of this landfill, and monitored natural attenuation, which was regarded a possible remediation strategy in landfills (Bjerg et al., 2011).

Acknowledgments

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References


5. Burns DA, Kendall C, 2002. Analysis of $\delta^{15}N$ and $\delta^{18}O$ to differentiate NO$_3^-$ sources in runoff at two watersheds in the Catskill Mountains of New York. Water Resources Research 38: 9.1–9.11


10. Chen JY, Tang CY, Yu JJ, 2006. Use of $^{18}O$, $^2$H and $^{15}$N to identify nitrate contamination of...
groundwater in a wastewater irrigated field near the city of Shijiazhuang, China. Journal of Hydrology 326: 367–378


Vegetated and Unvegetated Drainage Ditches Impacted by Diffuse and nitrogen point sources of pollution. Clean-Soil Air Water 41(1):24-31


applications of nitrogen and oxygen isotopes in tracing nitrate sources in urban environments.

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Fig. 1 Change in the amount of domestic waste in China (1979–2011) and Guangzhou (2001–2011). Data sources: Annual statistical data for urban construction in China in 2011 (www.bjinfobank.com).

Fig. 2 Monthly average rainfall in Guangzhou during the period of 1951–2008.
Fig. 3 Schematic location and map of sampling sites at Likeng landfill site. Potentiometric surface with contour interval of 3 m was given for the data measured in 2007, indicating a general groundwater flow to the north in this area.

Fig. 4 Average concentrations (mg/L) of major ions in seven wells during the three campaigns.
Fig. 5 Piper diagram for all water samples collected during the three campaigns. Evolution of chemical facies is indicated by the arrow.

Fig. 6 Use of dual isotopes to identify various sources of nitrate.
Fig. 7 Relationship between δ\(^{18}\)O and δD in water and local meteoric water line.

Fig. 8 Monthly pan evaporation during the period of 2001–2008 in Guangzhou.
Fig. 9 Relationship between $\delta^{15}$N–NO$_3^-$ and residual NO$_3^-$ in Likeng landfill. Solid dots indicate three sampling sites in the vegetable field with the same N source.

Fig. 10 Relationships of $\delta^{15}$N (left) and NO$_3^-$ (right) with Cl$^-$, and their implication in identifying N sources (dashed line to identify source X).
Fig. 11 Relationship between δ¹⁸O–NO₃⁻ and Cl⁻. The cluster of wells 8, 9, and 10 can be clearly identified.

Fig. 12 Use of the relationship between δ¹⁸O–NO₃⁻ and δ¹⁸O–H₂O to identify N sources and relevant processes.
Fig. 13 Relationship between δ^{18}O and δ^{15}N of NO$_3^-$ and its application in N source identification by using three boxes for various nitrate sources adopted from Silva et al. (2002).

### Table 1 Heavy metals in the effluent and groundwater at well 1 in Likeng landfill in 2005

<table>
<thead>
<tr>
<th>Items</th>
<th>Pb (µg/L)</th>
<th>Cd (µg/L)</th>
<th>Hg (µg/L)</th>
<th>As (µg/L)</th>
<th>Fe (mg/L)</th>
<th>Mn (mg/L)</th>
<th>Al (mg/L)</th>
<th>Cr^{+6} (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effluent</td>
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<td>4.9</td>
<td>6.6</td>
<td>63</td>
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<td>0.19</td>
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<td>0.03</td>
<td>0.01</td>
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### Table 2 Basic information and major ions in the effluent from Likeng landfill in 2005

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<th>Major ions (mg/L)</th>
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<td>DO (mg/L)</td>
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<td>Cl$^-$</td>
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<td>Na$^+$</td>
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<td>NH$_4^-$N</td>
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<td>K$^+$</td>
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<td>Mg$^{2+}$</td>
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<td>Ca$^{2+}$</td>
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Table 3 Summary of characteristics for the effluents reported in China, Denmark, and the United States

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<th>NH$_4^+$N</th>
<th>COD</th>
<th>pH</th>
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<tr>
<td>Five landfills in southern Jiangsu Province (Yang et al., 2008)</td>
<td>4–860</td>
<td>226–4426</td>
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</tr>
<tr>
<td>Shanghai (Zheng et al., 2007)</td>
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<td>2800–5380</td>
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<td></td>
</tr>
<tr>
<td>Hangzhou (Zheng et al., 2007)</td>
<td>1390–1760</td>
<td>4690–8100</td>
<td>6.9–8.1</td>
<td></td>
</tr>
<tr>
<td>Six landfills in Beijing (Li et al., 2008)</td>
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<td>1690–8640</td>
<td>6.83–7.91</td>
<td></td>
</tr>
<tr>
<td>Likeng in Guangzhou (Lin et al., 2007: first line; Luo et al., 2009: second line)*</td>
<td>68.4</td>
<td>1046</td>
<td>1280</td>
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<tr>
<td></td>
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<td>7.23</td>
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<tr>
<td>Jinan (Zhu et al., 2005)</td>
<td></td>
<td></td>
<td>1012–1381</td>
<td>3775–6110</td>
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<tr>
<td>Landfill in northern Jiangsu Province (Yang et al., 2010)</td>
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<td>9357–17864</td>
<td>7.44–8.46</td>
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<tr>
<td>Norman landfill in USA (Cozzarelli et al., 2011)</td>
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<td>209–650</td>
<td></td>
<td>6.6–7.0</td>
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<tr>
<td>106 old landfills in Denmark (Kjeldsen and Christophersen, 2001)</td>
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<td>110</td>
<td>320</td>
<td>7.0</td>
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*Effluent was collected from a pond, which was used to store wastewater after physical-chemical-biological treatment.
Table 4 Information and change of chemical contents of seven wells collected in three campaigns during the period of 2001–2007 (ions in mg/L)

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<th>Well no</th>
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<th>Latitude</th>
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<th>pH</th>
<th>EC (ms/m)</th>
<th>Water depth (m)</th>
<th>T (°C)</th>
<th>ORP (mv)</th>
<th>Cl−</th>
<th>NO3−</th>
<th>HCO3−</th>
<th>NO2−</th>
<th>Ca2+</th>
<th>Mg2+</th>
<th>Na+</th>
<th>K+</th>
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<table>
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<tr>
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<th>EC (ms/m)</th>
<th>Water depth (m)</th>
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<th>ORP (mv)</th>
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ND: not detected (<0.1 mg/L); NO: data not available
Environmental Impact Statement

Landfill and its relevant groundwater pollution is becoming a hotspot in China due to the rapid urbanization in the past 30 years. Nitrate pollution in groundwater associated with Likeng landfill of Guangzhou was investigated in three campaigns during a period of six years. Nitrogen sources, transformation and pertinent hydrological processes were integrated by using multiple evidences, e.g., stable isotopes of 18O, D and 15N.