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

2

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12

### 13 **Abstract**

14

15 Nitrogen aspects and hydrological processes need to be integrated in order to understand sources

16 and relevant mechanisms. Landfills are the dominant disposal approach to deal with solid waste in

17 urban areas in China. Landfills require adequate land and pose a potential threat to aquifer

18 contamination, particularly in the humid zone, such as Guangzhou. The unlined Likeng landfill in

19 Guangzhou was investigated in three campaigns during the period of 2001–2007: water was

20 sampled and analyzed for major ions, heavy metals, and stable isotopes of <sup>18</sup>O and <sup>2</sup>H in water,

21 and <sup>18</sup>O and <sup>15</sup>N in nitrate. Contamination sources, water components, and groundwater flow were

22 examined with multiple evidence, revealing a mixture of various sources from landfill effluent,

23 septic tank leakage, fertilizer, and manure following complex processes of recharge, mixing, and  
24 denitrification. The effluent from the landfill was rich in  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ , and  $\text{Cl}^-$  ions. The  
25 same process of high  $\text{NH}_4^+$  in effluent resulting in episodic increases in  $\text{NO}_3^-$  due to  $\text{NH}_4^+$   
26 oxidation was found in Likeng landfill compared to the landfills in Denmark and the United States.  
27 Twenty-five percent of the precipitation was lost to evaporation before recharging the aquifer,  
28 indicating a possible maximum recharge rate of 75% and the potential for a large amount of water  
29 penetration to the landfill if not well constructed. Apparent groundwater flow velocity of  $3.7 \times 10^{-7}$   
30 m/s (11.67 m/a) was found for the front of the effluent under the landfill by considering the  
31 vertical and horizontal flow involved. These findings can provide background to delineate the  
32 plume from Likeng landfill and to conceptualize the natural attenuation processes of other toxic  
33 compounds, which are imperative for a remediation strategy.

34

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

## 36 **Introduction**

37 Nitrogen has increased globally in the environment mainly due to human activities in the past  
38 century. Scanlon et al. (2007) attributed degraded water quality, including nutrient balance, to the  
39 conversion from natural to agricultural ecosystems, which is associated with decreased  
40 evapotranspiration and increased recharge and streamflow. The spatial pattern of nitrate in  
41 groundwater in the North China Plain is related to fertilizer overuse, wastewater irrigation, and the  
42 regional groundwater flow system (Chen et al., 2005; 2006). High nitrogen content in all water  
43 bodies (e.g., rivers, groundwater, and lakes) is associated with ecosystem eutrophication  
44 (Smolders et al., 2010; Lunau et al., 2013) and health concerns (e.g., methemoglobinemia) (Sadeq

45 et al., 2008), particularly due to high nitrate in drinking waters. As nitrate is relatively mobile  
46 within aquifer systems, it may contribute to high nutrients in coastal areas via submarine  
47 groundwater discharge and thus result in a change in N/P ratios (Slomp and Van Cappellen, 2004).

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

55 N source identification and relevant processes are two key aspects of N cycle research. N  
56 sources are typically classified as either point or areal (i.e., nonpoint) sources. Fertilizers in  
57 agricultural lands and runoff and drainage from urban areas are two major areal sources of N,  
58 while sewage from factories, treatment plants, and landfill sites are major point sources (Othman  
59 et al., 2012; Carey et al., 2013; Pierobon et al., 2013). The preferential flow that percolates  
60 through waste deposits affects leachate production, aerobic and anaerobic biological processes,  
61 and then N transformation (Bengtsson et al., 1994). While the N source itself does not depend on  
62 water movement, the water cycle does affect its accumulation, distribution, and transformation via  
63 precipitation (fall-out), advection, and dispersion. Vertical and/or horizontal distribution of nitrate  
64 can thus be used to estimate the groundwater flow velocity (Chen et al., 2006). Isotopes of  $^{15}\text{N}$  and  
65  $^{18}\text{O}$  (in nitrate and water, respectively) are widely used to identify N sources and transformation  
66 mechanisms (Kendall and McDonnell, 1998), which include both N and water cycles (e.g.,

67 denitrification and mixing). Actually, a multiple tracer approach with other indicators is necessary,  
68 such as Cl/Br ratio to assess the impact of septic tanks (Katz et al., 2011); multiple isotopes (H, O,  
69 N, S, and Sr) to elucidate pollution sources and relevant causes (Hosono et al., 2011);  
70 chlorofluorocarbons (CFCs) and fecal indicator bacteria, such as *E. coli*, to assess the impact of  
71 landfills (Carlson et al., 2011); and the ratio of  $\text{NO}_3^-$ /acesulfame to differentiate agricultural from  
72 domestic wastewater sources (Robertson et al., 2013). Several models have been developed to  
73 simulate the changes in both N components and hydrological processes (Howard et al., 1996; Brun  
74 et al., 2002), though many mechanisms remain unknown.

75 Landfills are commonly used to dispose of solid waste in both developed and developing  
76 countries. Municipal landfills were found to be a significant threat to groundwater quality (Sanjay  
77 et al., 2010; Bjerg et al., 2011). The volume and chemical characteristics of leachate produced by  
78 landfills are controlled by water balance, vegetation, landfill age, and landfill cover conditions  
79 (Bhavna et al., 2013). Four regimes were proposed to elucidate varied processes and reactions of  
80 leachate plumes (Cozzarelli et al., 2011). Minor leachate production of 30–40 mm/a was estimated  
81 from young landfills in Sweden, with percolation through the waste deposits occurring as a  
82 preferential flow (Bengtsson et al., 1994). A simple dilution model revealed that physical mixing  
83 was the most important attenuation process in the pollution plume within the landfill (Brun et al.,  
84 2002). Ionic balance was calculated for leachate from a landfill in West Malaysia with a high error  
85 of more than 13%, indicating the complexity in chemical composition (Rahim et al., 2010).

86 Solid waste has increased exponentially in China due to rapid urbanization in the past 30  
87 years, and annual domestic waste was estimated to be around  $1.5 \times 10^8$  tons in 2003 (Hai et al.,  
88 2009; Fig. 1), around 90% of which was disposed in landfills (Huang et al., 2006; Wang et al.,

89 2009). Although the total number of landfills has been reported recently in yearly statistical books,  
90 these numbers only represent large landfills and the actual number is not known. There were 935  
91 landfills in 2008, reported in a business press release  
92 ([//www.21cbh.com/HTML/2009-7-3/HTML\\_0M0OX5W0728Y.html](http://www.21cbh.com/HTML/2009-7-3/HTML_0M0OX5W0728Y.html)). Unfortunately, more than  
93 half of these landfills were not constructed and maintained in accordance with national standards  
94 regulating waste disposal in landfills (Wang et al., 2009). Much research has been done to  
95 investigate the leachate from landfills and potential threats to groundwater use, and public health  
96 in China, such as heavy metals (Wang et al., 2009), phthalate esters (Zheng et al., 2007; Liu et al.,  
97 2010), and microbes (Tian et al., 2005). Although high content of ammonium and relevant  
98 processes were present in leachate plumes (Bjerg et al., 2011; Cozzarelli et al., 2011), little  
99 research has reported the pollution of nitrate in aquifers due to high nitrogen content from leachate  
100 of the landfills.

101

102 Fig. 1 Change in the amount of domestic waste in China (1979–2011) and Guangzhou  
103 (2001–2011). Data sources: Annual statistical data for urban construction in China in 2011  
104 ([www.bjinfobank.com](http://www.bjinfobank.com)).

105

106 This study intended to investigate the chemical characteristics of leachate from Likeng  
107 landfill and changes during the period of 2001–2007. The impacts of the landfill, particularly  
108 nitrate produced from the leachate on the local aquifer, were examined by integrating nitrogen  
109 aspects and hydrological processes. Various nitrate sources and relevant processes were identified  
110 with multiple lines of evidence from stable isotopes and chemical patterns. As Likeng landfill is

111 located in the upstream section of Liuxi River, which is used for water supply to Guangzhou,  
112 identification of pollutant sources from leachate can help to protect water resources and  
113 ecosystems in the downstream section.

114

#### 115 **Background for the study area**

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

129 The hydrogeological conditions are relatively complex with bedrock of granite in the south  
130 part of the landfill, and a mixture of carbonate and sandstone interfingering with shale in the north  
131 part. The landfill is at risk of deep percolation and contamination to the underlying aquifers due to  
132 probable fractures in the granite and high porosity in the carbonate and sandstone.

133 Annual average rainfall was calculated to be 1741.9 mm in Guangzhou during the period of  
134 1951–2008. Average monthly distribution is given in Fig. 2, with rainfall in the wet season from  
135 April–September accounting for approximate 80% of annual rainfall. As the pan evaporation  
136 measured by E601 was 1100 mm in the Pearl River delta (Zeng et al., 2010), close to actual  
137 evapotranspiration in this humid region, runoff from the landfill site was calculated to be  $1.62 \times 10^5$   
138  $\text{m}^3$ , which has to be collected and drained to avoid percolation to the landfill and thus reduce the  
139 leachate.

140

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

142

### 143 **Material and methods**

144 Three field campaigns were implemented on March 5, 2001; March 15, 2005; and March  
145 24–25, 2007 with 17, 15, and 17 water samples collected from domestic wells/leachate,  
146 respectively (Fig. 3, Table 4). These wells ranged from 1.5–50 m in depth. The screen was usually  
147 installed for the bottom layers as informed by the local residents, while specific screen depths  
148 were unknown. The wells were purged at least 5 minutes before sampling. After filtration with a  
149  $0.45 \mu\text{m}$  membrane filter, samples were collected in pre-cleaned plastic bottles, brought back to  
150 the laboratory, and stored at the temperature below  $4^\circ\text{C}$  until analysis for major ions and hydrogen  
151 and oxygen stable isotopes. Electrical conductivity (EC), dissolved oxygen (DO),  
152 oxidation–reduction potential, temperature, and pH were measured in situ. Major ions of  $\text{Cl}^-$ ,  
153  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{NH}_4^+$  were measured by ion chromatography (Shimazu  
154 CTO-10A), while  $\text{HCO}_3^-$  was obtained by titration ( $0.01 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ ). Stable isotopes ( $^{18}\text{O}$  and



155  $^2\text{H}$  or D) were undertaken by mass spectrometry (Finnigan MAT Delta S). All analyses were done  
156 at Chiba University, Japan. Heavy metals were analyzed for the samples collected in 2005 by  
157 various methods, including graphite furnace atomic absorption spectrometry for Pb and Cd,  
158 atomic fluorescence spectrophotometry for Hg and As, flame atomic absorption spectrometry for  
159 Fe and Mn, and indirect flame atomic absorption spectrometry for Al. The  $\text{Cr}^{+6}$  was measured by  
160 the spectrophotometric method. Detection limitations for relevant heavy metals are given in Table  
161 1.

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

172

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

176 **Results and Discussions**

177 *Chemical characteristics of landfill effluent*

178       The amount and characteristics of landfill effluent are related to climatic and hydrological  
179 conditions (Cozzarelli et al., 2011; Bhavna et al., 2013). It is thus reasonably anticipated that high  
180 leachate could be produced from the humid area, such as in Guangzhou, China. Municipal solid  
181 waste in Guangzhou has three features: 1) high organic matter composition that easily decomposes;  
182 2) high water content of more than 50%; and 3) mixture of various sources, such as domestic,  
183 industrial, commercial, and medical waste. The effluent, i.e. direct discharge from the landfill, was  
184 collected in March 2005 from a small ditch indicated as “+” in Fig. 3, and major ions and basic  
185 effluent data are given in Table 2. Low DO indicated the reduction condition in the landfill, while  
186 low temperature compared to well 2 (21.5°C, depth of 10 m, next to the effluent treatment site)  
187 indicated a low energy level during the production of effluent, probably due to high water content.  
188 According to the data in Table 2, the effluent could be classified as Na–K–HCO<sub>3</sub> type with a high  
189 content of ammonium, which was converted from organic-N waste via ammonification. Potassium  
190 in the effluent was 687.3 mg/L in Likeng landfill by Luo et al. (2009) during a campaign within  
191 the period from August 2006 to August 2007, while the chloride was 2025 mg/L, similar to the  
192 value given in Table 2. Similar chloride content of 2047 mg/L was found in a landfill in Malaysia  
193 (Rahim et al., 2010). High content of potassium with a median value of 414 mg/L was reported in  
194 Norman Landfill (Cozzarelli et al., 2011). As annual precipitation in Guangzhou is twice that in  
195 Norman Landfill (around 960 mm/a), half the potassium concentration would have been expected  
196 due to the dilution effect. In contrast, potassium content four times as high was found in Likeng  
197 landfill. It could be concluded here that high potassium content is typical in landfill leachate,  
198 particularly in the humid area. Relatively high contents of Na<sup>+</sup>, Ca<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and Cl<sup>-</sup> were found

199 in the effluent from Risby landfill in Denmark (Milosevic et al., 2012), and could be classified as  
200 Na–Ca–HCO<sub>3</sub>–Cl type, although absolute concentrations were much lower than those in Likeng.

201 High temperature can accelerate the ammonification process within the landfill, and it is  
202 reasonable to have higher NH<sub>4</sub><sup>+</sup> in the effluent in the summer than that in the winter. NH<sub>4</sub><sup>+</sup>–N was  
203 525 mg/L in July, almost twice as that in January (272 mg/L) (Table 3; Yang et al., 2010) in one  
204 landfill in northern Jiangsu Province of China. Actually, ammonification and production of NH<sub>4</sub><sup>+</sup>  
205 in landfills are complex processes, associated with precipitation, temperature, composition of  
206 waste, age of operation, and other factors; it is hard to find a simple correlation between the  
207 amount of NH<sub>4</sub><sup>+</sup> and any one independent parameter. Main chemical characteristics of effluents  
208 reported in China are summarized in Table 3, and relevant characteristics in Denmark and the  
209 United States are given as well for the comparison. Ammonification is the dominant process  
210 during the production of effluent with no or low contents of NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> detected, which may  
211 then increase later to a relatively high level due to nitrification, as shown in Likeng (Table 3).  
212 Same process of high NH<sub>4</sub><sup>+</sup> resulting in episodic increases in NO<sub>3</sub><sup>-</sup> due to NH<sub>4</sub><sup>+</sup> oxidation was  
213 documented by Cozzarelli et al. (2011). Highly variable NH<sub>4</sub><sup>+</sup>–N was also found in several  
214 landfills in Ontario, Canada, ranging from 7.6–1820 mg/L (Howard et al., 1996). High levels of  
215 chloride and ammonium in Likeng were consistent with the ranges given by Mikac et al. (1998).  
216 Heavy metals were measured in 2005 in the effluent and groundwater at well 1, which is located  
217 next to the drainage channel of treated effluent.

218

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

220 Seven wells were sampled during three campaigns in March 2001, 2005, and 2007, enabling

221 comparison of the change in groundwater quality within 6 years. Concentrations of all major ions  
222 except  $\text{Mg}^{2+}$  showed an obvious increase (Fig. 4), indicating the possible impacts of the effluent  
223 from the landfill. The average concentration of  $\text{NO}_3^-$  in 2007 was approximately twice that in  
224 2001; in particular it increased from 3.9 mg/L in 2001 to 53.3 mg/L in 2007 at well 1 (Table 4).  
225 Nitrate pollution to a depth of 50 m poses a serious threat of the landfill to the deep aquifer in the  
226 study area. Ranges of nitrate concentration in 2001, 2005 and 2007 were 3.9-288.8, 3.4-226.1 and  
227 0.47-322 mg/L respectively, with relevant standard deviations of 111.8, 101.3, and 143.3,  
228 showing a highest level in 2007. Although much higher contents of nitrate were detected in the  
229 other wells in the vegetable field (e.g., wells 8 and 9), they remained relatively stable within 6  
230 years. The reasons for low nitrate at well 10 in 2001 (but high level in 2007) remain unknown.

231

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

233

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

241 High variation of chemical features was found in 2001, and the highest ratio of  $\text{HCO}_3^-$  type  
242 was detected compared to water samples collected in 2005 and 2007. Most water samples in 2007

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

252

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

255

256 *Identification of contamination sources*

257

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

259

260 As chloride is relatively conservative compared to nitrogen transport processes of both  
261 convection and dispersion, the ratio of nitrate to chloride was used as an indicator to differentiate  
262 sources and possibly inherent processes (Chen et al., 2006). Two groups of nitrate sources can be  
263 identified by the relationships of dual isotopes and the ratio. Based on the two boxes in Fig. 6, the  
264 field survey, and communication with local farmers, the group with higher  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values

265 of nitrate was associated with the source from the landfill, while that with lower values was  
266 located in the vegetable field and probably associated with the mixture of fertilizer and manure.  
267 Volatilization usually results in highly enriched  $\delta^{15}\text{N-NH}_4^+$  in the leachate, while the nitrification  
268 may produce depleted nitrate due to fractionation as reported by North et al. (2004), such as  $23.31$   
269  $\pm 3.76\text{‰}$  for  $\delta^{15}\text{N-NH}_4^+$  and  $-4.54 \pm 2.05\text{‰}$  for  $\delta^{15}\text{N-NO}_3^-$ . If ammonium was fully transferred to  
270 nitrate via nitrification when the effluent penetrated the aquifer, highly enriched  $\delta^{15}\text{N-NO}_3^-$  would  
271 then be generated. Relatively high nitrate concentrations of 14.3 mg/L and 39.2 mg/L were  
272 detected in 2005 and 2007, respectively, at monitoring well 2 next to the landfill and effluent  
273 treatment site (physical-chemical-biological treatment level), but low ammonium concentrations  
274 of 0.9 mg/L and 0 mg/L were detected, respectively, indicating a fully converted nitrification  
275 process.

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

286 *Impact of evaporation on isotopic features*

287

288 Fig. 7 Relationship between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in water and local meteoric water line.

289

290 Stable isotopes of  $^{18}\text{O}$  and D were measured in 2005 and 2007, revealing different  
 291 intersection angles with the local meteoric water line (LMWL) (Fig. 7) and the general trend of  
 292 the observed points. A large angle or small slope in 2005 reflected a strong impact of evaporation  
 293 on water before recharging to the aquifer. High pan (E601) evaporation rates were gauged during  
 294 the period of 2003–2005, while they were relatively low in 2006 (Fig. 8). It is interesting to note  
 295 that low pan evaporation rate was also found in 2006 in Norman landfill (Mendoza-Sanchez et al.,  
 296 2013). As isotopic signals of groundwater reflected the accumulated features of recharged water  
 297 prior to sampling in March 2007, low evaporation in 2006 weakened the fractionation and thus  
 298 reduced the isotopic values. Water temperature ranged from 20–25°C during the field campaign,  
 299 thus the equilibrium fractionation factor,  $10^3 \ln \alpha^{18}\text{O}_{\text{l-v}}$  (close to enrichment factor,  $\epsilon^{18}\text{O}_{\text{l-v}}$ ), for such  
 300 water temperature range was found to be 9.7 (20°C) and 9.3 (25°C) (Clark and Fritz, 1997). The  
 301 dynamic fractionation can be calculated using average humidity ( $h$ ) of around 70% according to  
 302 the Gonfiantini (1986) relationship given as:

$$303 \quad \Delta \epsilon^{18}\text{O}_{\text{bl-v}} = 14.2 * (1-h) = 14.2 * 0.3 = 4.26\%$$

304 Total enrichment was calculated as:

$$305 \quad \epsilon^{18}\text{O}_{\text{total}} = \epsilon^{18}\text{O}_{\text{v-l}} + \Delta \epsilon^{18}\text{O}_{\text{v-bl}} = -5.44 \text{ (20°C)} \text{ or } -5.04 \text{ (25°C)}$$

306 Fig. 7 shows a total enrichment of approximately 1.5‰, which was used to calculate the ratio  
 307 remainder  $f$  according to the formula given in Clark and Fritz (1997), yielding an evaporation rate  
 308  $(1-f)$  of 24% (20°C) and 26% (25°C) of total precipitation.

309

310 Fig. 8 Monthly pan evaporation during the period of 2001–2008 in Guangzhou.

311

312 The runoff coefficient in the humid climate zone can be as high as 0.5–0.6, indicating that  
313 40–50% of the precipitation was lost to evapotranspiration. A rough estimation of about 25%  
314 water loss to evaporation before aquifer recharge was reasonable in such a humid area, with the  
315 gap probably due to transpiration, depression storage, interception, or other unknown factors.  
316 Nevertheless, a maximum recharge rate to the saturated zone was estimated to be 75% in Likeng  
317 landfill site, though the actual rate would be much less. In comparison, average recharge at  
318 Norman landfill site over a 10-year period was found to be 36% of rainfall (Mendoza-Sanchez et  
319 al., 2013), ranging from 16–64% of rainfall (Scholl et al., 2005). As rainfall in Guangzhou is twice  
320 as high as that at Norman landfill (a climate of between humid subtropical and semi-arid with  
321 annual average precipitation of 880 mm), a recharge rate higher than 36% of rainfall would be  
322 expected.

323

324 *N processes: mixing and denitrification from the relationship of  $\delta^{15}\text{N}-\text{NO}_3^-$  and residual  $\text{NO}_3^-$*

325

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

328

329 A negative linear relationship was obtained between  $\delta^{15}\text{N}$  and  $\ln(\text{NO}_3^-)$  for denitrification  
330 following the classical equation of Rayleigh fractionation, while a reverse relationship,  $\delta^{15}\text{N} =$



331  $A \cdot 1/\ln(\text{NO}_3) + B$  (A and B are two constant parameters relevant to the concentration and isotopic  
332 value of various end members), was derived for the mixing or dilution process (Mariotti et al.,  
333 1988). Several sources of nitrate were identified in the previous section, but none of them  
334 followed the relationship of mixing or denitrification given by Mariotti et al. (1988), as indicated  
335 by a positive relationship for the same source in Fig. 9. Two probable causes for such deviation  
336 were: 1) mixing of several sources may not follow the simple scenario of two end members; and 2)  
337 the simultaneous occurrence of mixing and denitrification, and nitrification and volatilization  
338 complicate these two processes. Thus, multiple tracers are necessary to identify sources and  
339 relevant processes.

340

#### 341 *Integration of N sources and groundwater movement with multiple tracers*

342 Well 3 is located in an isolated house and far from the vegetable field with a low nitrate  
343 concentration. As it is located in the lower part of a natural slope land of forest, potential  
344 anthropogenic N sources were eliminated from the field survey and ground truth, and nitrate was  
345 assumed to come from natural soil background levels, with  $\delta^{15}\text{N}$  of 12.5‰ before the landfill was  
346 built. As  $\delta^{15}\text{N}$  was found in the range of 10–22‰ for the source of manure/urine and 2–9‰ for  
347 natural soil organic-N (Heaton, 1986; Clark and Fritz, 1997), the background value here with a  
348 lowest  $\delta^{15}\text{N}$  for the cluster in upper left in Fig. 10 indicated that the natural soil organic-N had  
349 small impacts from the leakage of septic tanks. Nitrate in precipitation, usually having a high  
350  $\delta^{18}\text{O}-\text{NO}_3$  (Chen et al., 2009), could contribute as well to the high  $\delta^{18}\text{O}-\text{NO}_3$  at well 3 (Fig.11).  
351 Although well 2 and 3 are not connected hydrogeologically, they do naturally have a common or  
352 similar recharge source (Fig. 3) in terms of the groundwater flow system. A lowest value in

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

364

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

367

368 The relationship between  $\delta^{15}\text{N}$  and chloride clearly revealed three source groups: one at wells  
369 8, 9, and 10 (filled circle) with a high linear coefficient ( $R^2 = 0.978$ ), one source group at well 1  
370 (unfilled circle), in addition to a cluster including wells 2 and 3 (unfilled circle) (Fig. 10). A  
371 simple relationship between Cl and nitrate could be used as well to differentiate the sources at  
372 wells 1 and 4 (filled triangle) from the others (unfilled triangle), which fell on the linear line ( $R^2 =$   
373 0.959) (Fig. 10) and could be classified into two clusters with a threshold of chloride content at  
374 100 mg/L.

375

376 Fig. 11 Relationship between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\text{Cl}^-$ . The cluster of wells 8, 9, and 10 can be clearly  
377 identified.

378

379 Similar results were achieved using the relationship between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\text{Cl}^-$ , as indicated  
380 in Fig. 11. The  $\delta^{18}\text{O}-\text{NO}_3^-$  of source X was estimated at 4.8‰ following the same approach to  
381 calculate  $\delta^{15}\text{N}$ . As chloride is relatively conservative, its concentration at the front of the effluent  
382 can be calculated using the following equation (Ogata, 1970):

$$383 \quad C = \frac{C_0}{2} \left[ \operatorname{erfc}\left(\frac{L - v_x t}{2\sqrt{D_L t}}\right) + \exp\left(\frac{v_x L}{D_L}\right) \operatorname{erfc}\left(\frac{L + v_x t}{2\sqrt{D_L t}}\right) \right]$$

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

388 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  
389 wastewater irrigation area (Chen et al., 2006); the horizontal rate was estimated to be 126 m/a in a  
390 small catchment in Zhuhai using CFC data (Zhao, 2008). A conservative value of  $V_x = 3.7 \times 10^{-7}$   
391 m/s was chosen by considering both horizontal and vertical flows from Likeng landfill.  $D_L =$   
392  $2.5 \times 10^{-7} \text{ m}^2/\text{s}$  was used by assuming a longitudinal dispersivity of  $\alpha_L = 0.676 \text{ m}$  and ignoring  
393 molecular diffusion. This dispersivity was within the range of 0.3–4.5 m by Bjerg et al. (2011).

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

396

397 *Nitrate dynamics from multiple tracers*

398

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

401

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

$$405 \quad \delta^{18}\text{O}_{\text{nitrate}} = 2/3 * (\delta^{18}\text{O}_{\text{water}} + \epsilon_{\text{water}}) + 1/3 * (\delta^{18}\text{O}_{\text{O}_2} + \epsilon_{\text{O}_2}) \text{ (Mayer et al., 2001)}$$

406 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  
407 second term of the right component in the above equation,  $1/3 * (\delta^{18}\text{O}_{\text{O}_2} + \epsilon_{\text{O}_2})$ , was estimated to be  
408 9.061‰ if isotopic fractionations of  $\epsilon_{\text{water}}$  and  $\epsilon_{\text{O}_2}$  were ignored. Actually,  $\delta^{18}\text{O}_{\text{O}_2}$  was measured to  
409 be 23.5‰ (Mayer et al., 2001);  $1/3 * 23.5 = 7.83\%$  was close to the estimation here. A straight line  
410 passing well 9 and following the rule of 2:1 is given in Fig. 12. The dots at wells 8 and 10 with a  
411 similar source to well 9 fell approximately within this line, while the dots from other sources were  
412 located above the line with higher  $\delta^{18}\text{O}\text{-NO}_3^-$  and did not keep the rule of 2:1, probably due to  
413 respiratory isotope fractionation, evaporative effects (Kendall and McDonnell, 1998; Burns and  
414 Kendall, 2002), or other effects during nitrification and denitrification of effluent seepage and  
415 treatment at Likeng landfill site.

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

418 The  $\delta^{18}\text{O}_{\text{water}}$  for source X was then estimated to be -2.31‰.

419 With the rule of 2:1 and local monthly (amount-weighted average) range of precipitation  
420  $\delta^{18}\text{O}$  of  $-9.14$  to  $0.34\text{‰}$  from nearby International Atomic Energy Agency (IAEA) station of  
421 Guangzhou (IAEA, 2003; Chen et al., 2009), the range of  $\delta^{18}\text{O}-\text{NO}_3^-$  of  $1.7-7.9\text{‰}$  can be  
422 estimated for the reduced N sources of  $\text{NO}_3^-$  as indicated by two horizontal dashed lines in Fig. 13.  
423 Three wells in the vegetable field, one well (17) in the residential area, and sources X were found  
424 within the estimated range, while the other dots were higher than the upper range of  $7.9\text{‰}$ , likely  
425 showing different sources or processes. Three boxes are given in Fig. 13, indicating various nitrate  
426 sources from fertilizer, soil organic-N, and manure/sewage. All samples collected in the study area  
427 were located within the box from the manure and sewage source.

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

438

439 Fig. 13 Relationship between  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  and its application in N source identification  
440 by using three boxes for various nitrate sources adopted from Silva et al. (2002).

441

442 **Conclusions**

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

- 451 1) Effluent rich in  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ , and  $\text{Cl}^-$  with relatively low temperature was produced  
452 under warm and wet climatic conditions, which may promote the nitrification of ammonium  
453 to nitrate in the aquifer. Nitrate concentration in the groundwater approximately doubled  
454 during the period of 2001–2007, indicative of the impact of the landfill on the local aquifer.
- 455 2) Moderate evaporation of around 25% of the precipitation was estimated before recharge to the  
456 aquifer. As actual evaporation accounts for roughly 50% of the precipitation in Guangzhou,  
457 the other 25% of precipitation is probably lost to transpiration in the dry season, such as in  
458 March.
- 459 3) Multiple tracers were used to differentiate the various sources of nitrogen and depict the  
460 effluent movement underground. The conservative ion of chloride and the ratio of  $\text{NO}_3^-/\text{Cl}^-$   
461 could serve as good indices to simply identify the different nitrate sources. For example,  $\text{Cl}^-$   
462 of more than 100 mg/L is usually associated with the source from fertilizer and manure

463 application.

464 4) The relationships between nitrate concentration and  $\delta^{15}\text{N}/\delta^{18}\text{O}$  did not follow the normal rules  
465 for denitrification and mixing, likely indicating a mixture of multiple (more than two) end  
466 members and the simultaneous occurrence of several processes.

467 These findings can provide strong bases to delineate the plume from Likeng landfill and to  
468 conceptualize natural attenuation processes of other toxic compounds, such as xenobiotic organic  
469 compounds or heavy metals in landfill leachate. Secondly, some findings may be used as in situ  
470 indicators to support further research on conceptual and/or numerical models of this landfill, and  
471 monitored natural attenuation, which was regarded a possible remediation strategy in landfills  
472 (Bjerg et al., 2011).

#### 473 **Acknowledgments**

474 This research was supported financially by the following projects: the National Natural Sciences  
475 Foundation of China (no. 41371055), the Innovation and Application Research Fund of the Water  
476 Sciences Department of Guangdong Province (2009–2011, 2014-2016), and the Fundamental  
477 Research Funds for the Central Universities (13lgjc08, Sun Yatsen University). The authors thank  
478 Dr Fajin Chen for his help in analyzing  $^{15}\text{N}$  and  $^{18}\text{O}\text{-NO}_3^-$ , and Kate Bentsen (Chinese Research  
479 Academy of Environmental Science) for editing the manuscript for grammar. The authors also  
480 thank two anonymous reviewers for helpful comments.

481

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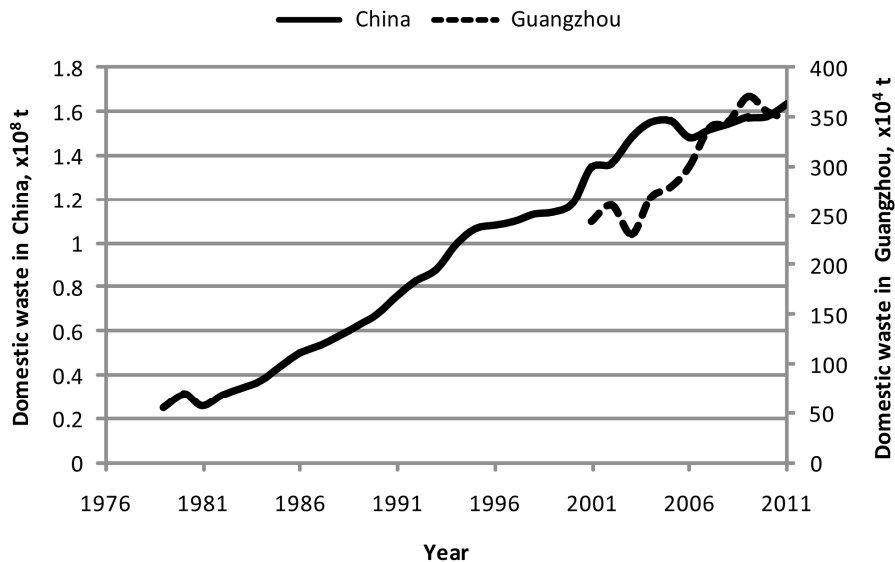
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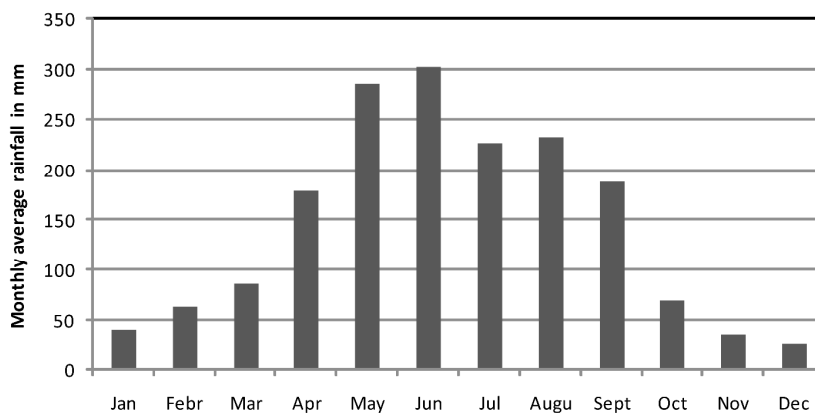
635

636 Fig. 1 Change in the amount of domestic waste in China (1979–2011) and Guangzhou

637 (2001–2011). Data sources: Annual statistical data for urban construction in China in 2011

638 (www.bjinfobank.com).

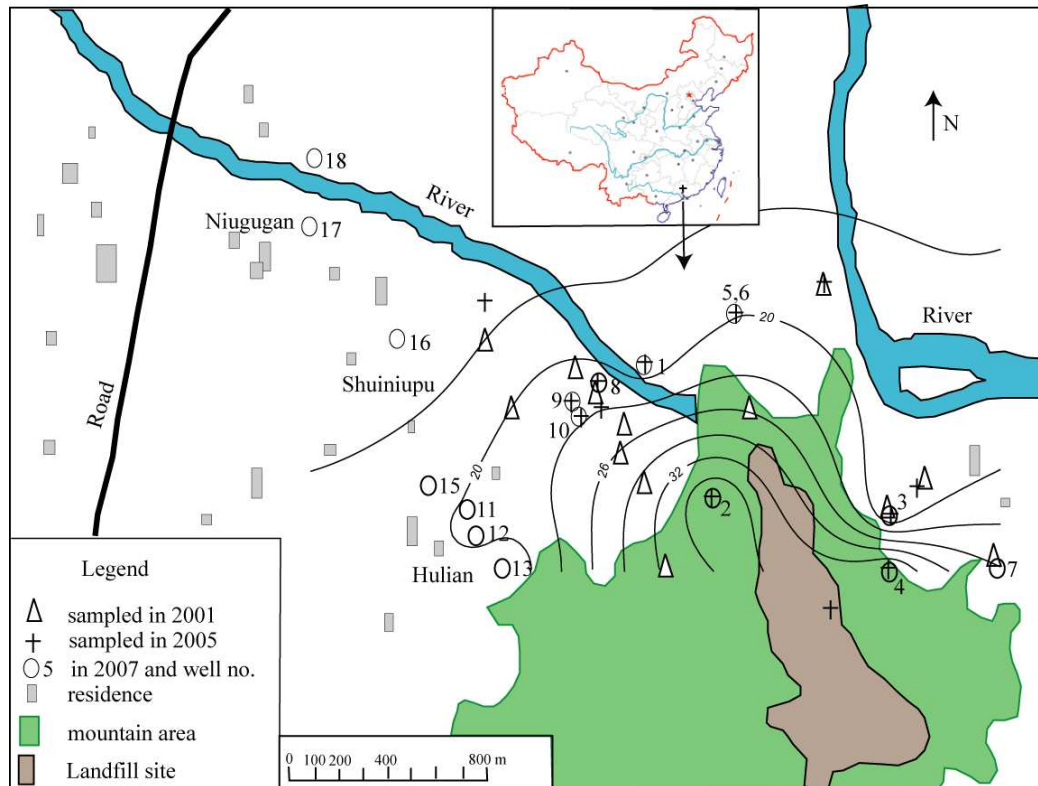
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640

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

642

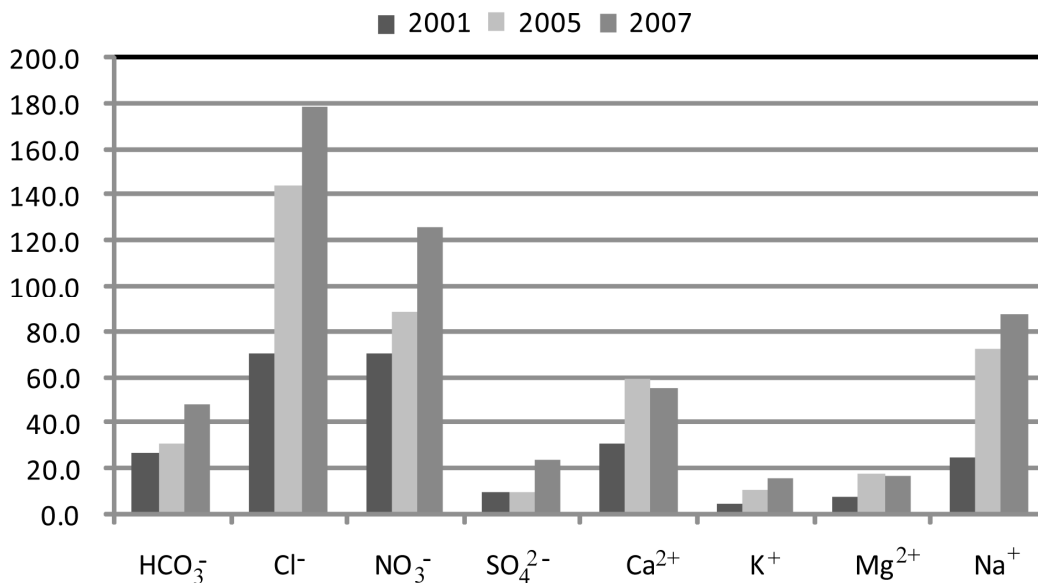


643

644 Fig. 3 Schematic location and map of sampling sites at Likeng landfill site. Potentiometric surface

645 with contour interval of 3 m was given for the data measured in 2007, indicating a general

646 groundwater flow to the north in this area.

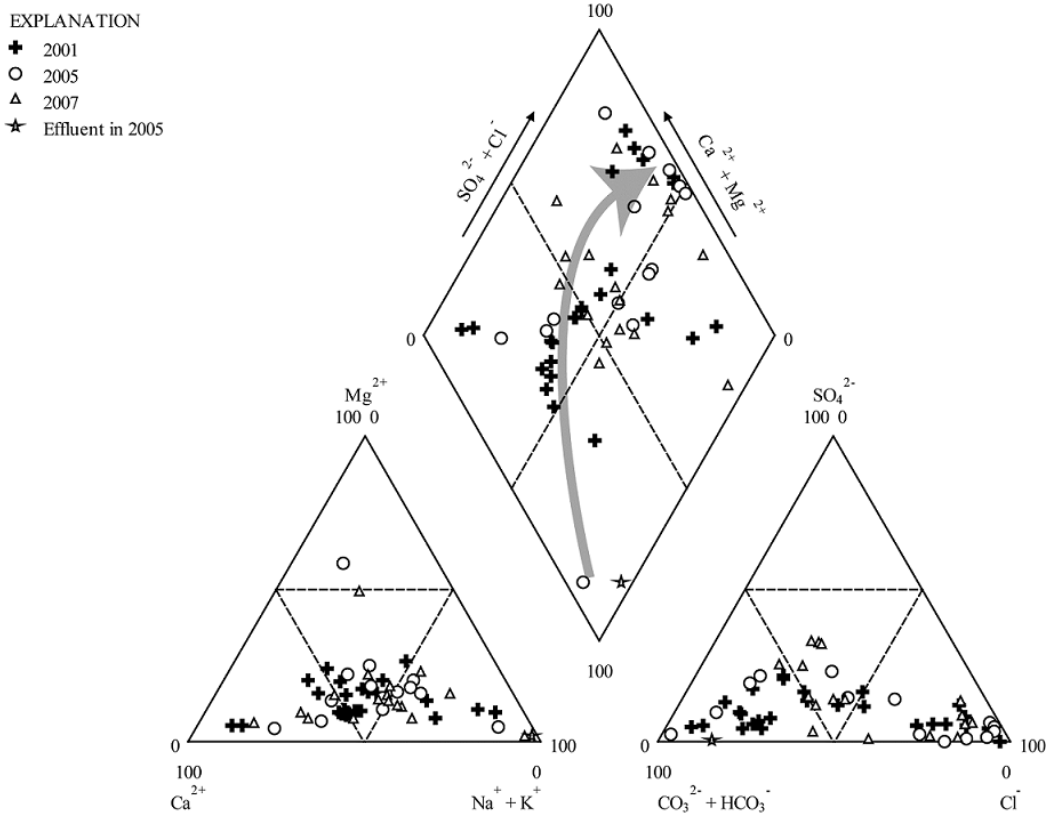


647

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



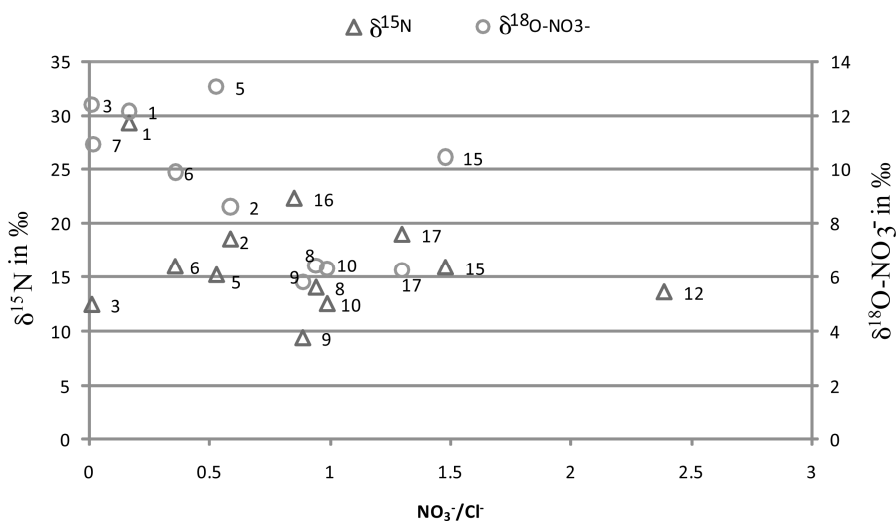
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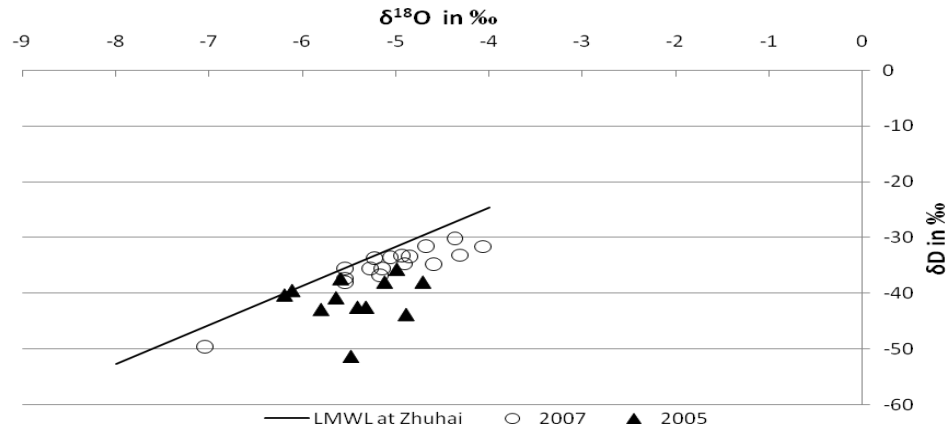
651 Fig. 5 Piper diagram for all water samples collected during the three campaigns. Evolution of

652 chemical facies is indicated by the arrow.

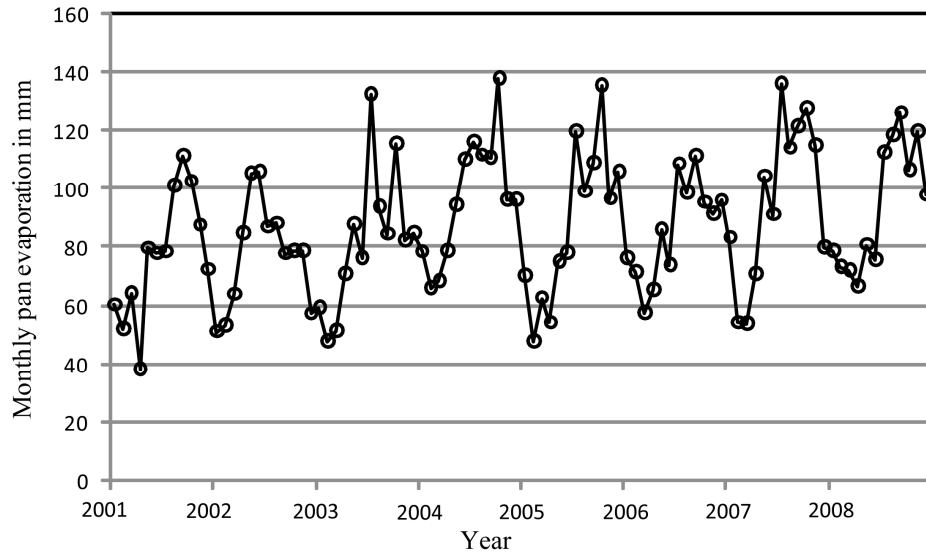


653

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

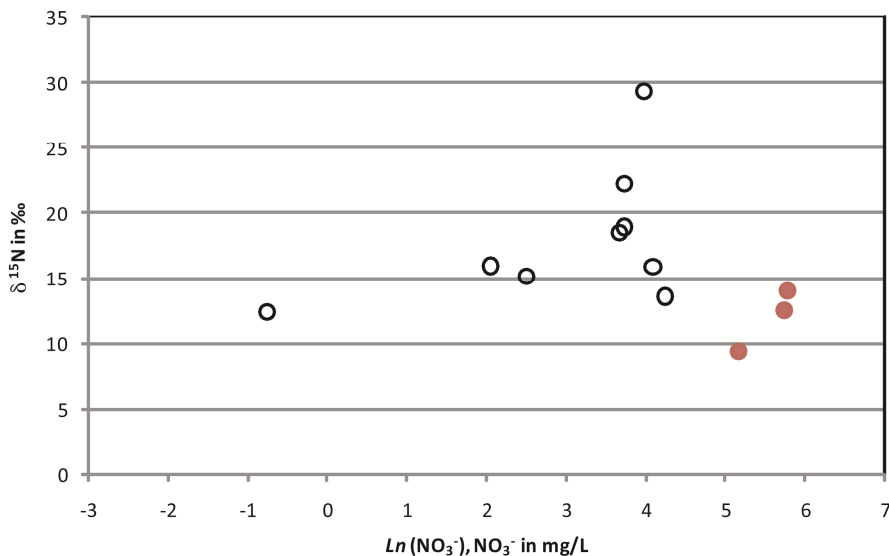


655

656 Fig. 7 Relationship between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in water and local meteoric water line.

657

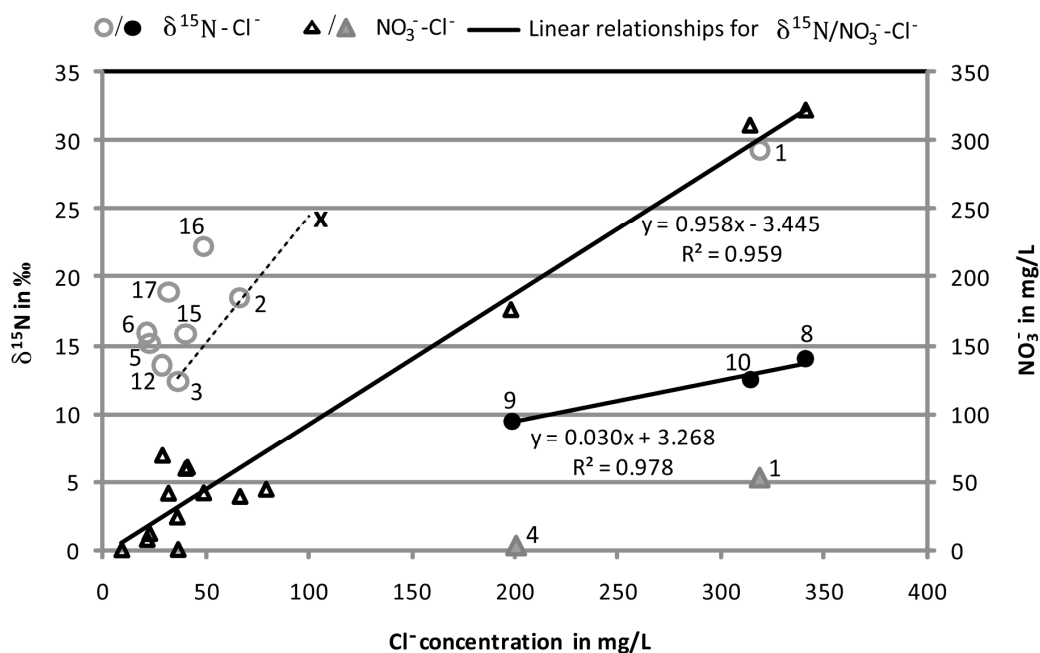
658 Fig. 8 Monthly pan evaporation during the period of 2001–2008 in Guangzhou.



659

660 Fig. 9 Relationship between  $\delta^{15}\text{N}-\text{NO}_3^-$  and residual  $\text{NO}_3^-$  in Likeng landfill. Solid dots

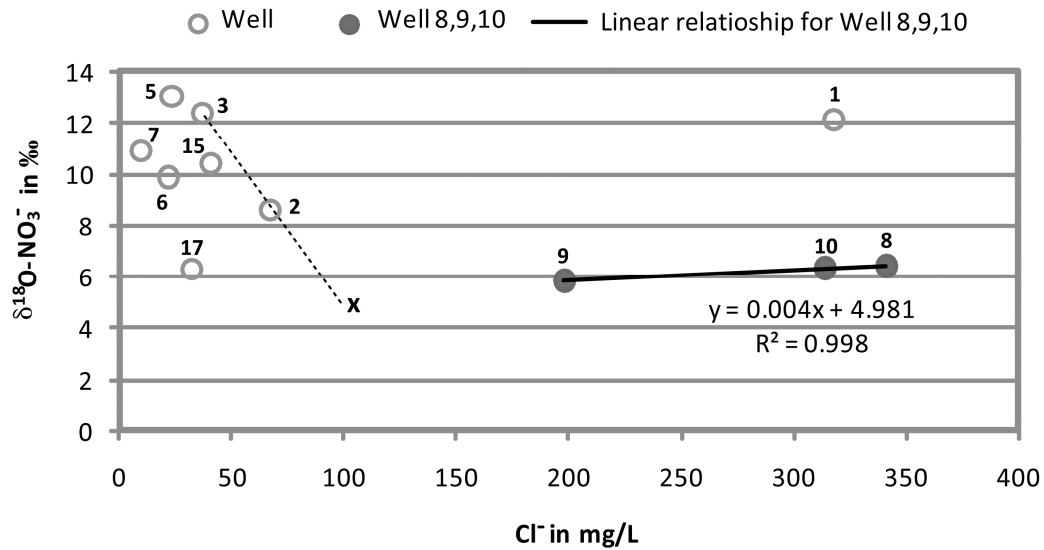
661 indicate three sampling sites in the vegetable field with the same N source.



662

663 Fig. 10 Relationships of  $\delta^{15}\text{N}$  (left) and  $\text{NO}_3^-$  (right) with  $\text{Cl}^-$ , and their implication in identifying

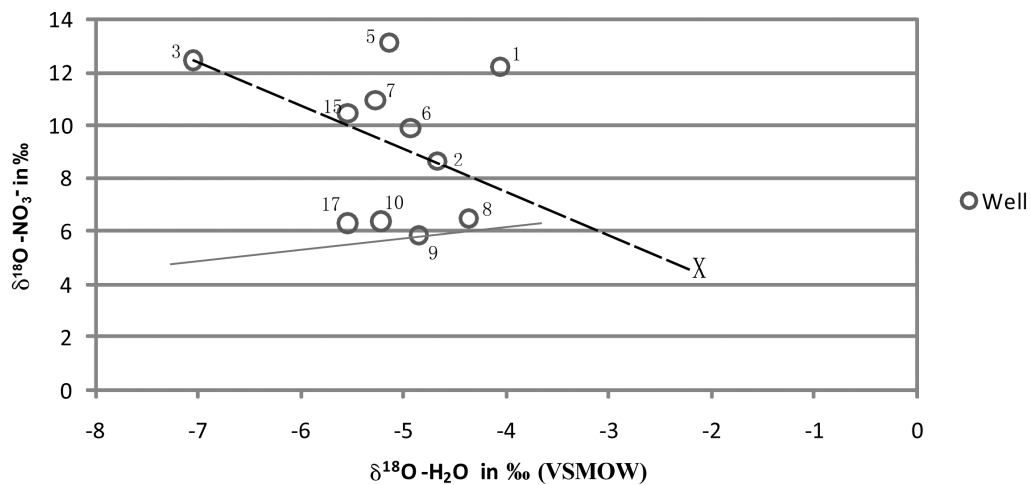
664 N sources (dashed line to identify source X).



665

666 Fig. 11 Relationship between  $\delta^{18}\text{O}-\text{NO}_3^-$  and  $\text{Cl}^-$ . The cluster of wells 8, 9, and 10 can be clearly

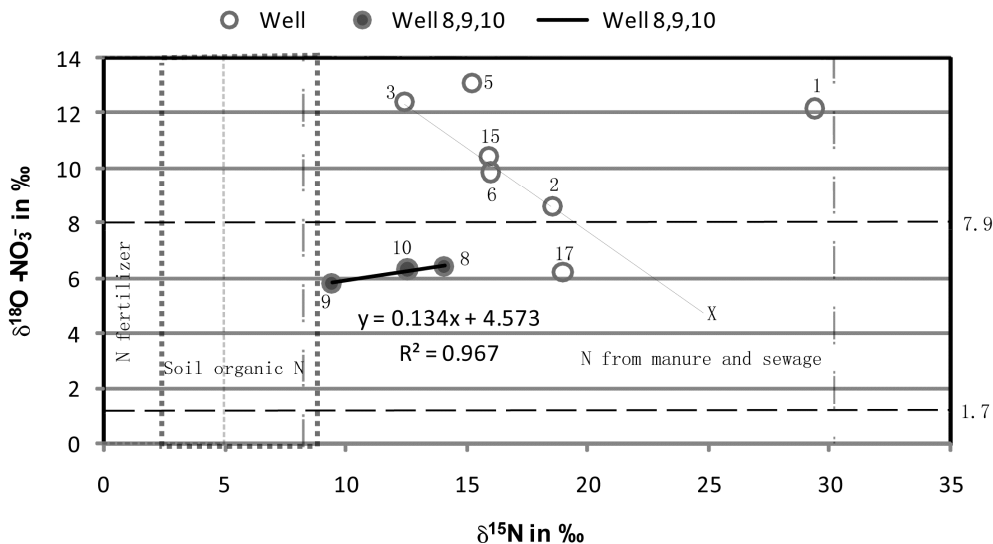
667 identified.



668

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

670 relevant processes.



671

672 Fig. 13 Relationship between  $\delta^{18}\text{O}$  and  $\delta^{15}\text{N}$  of  $\text{NO}_3^-$  and its application in N source identification

673 by using three boxes for various nitrate sources adopted from Silva et al. (2002).

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

Items	Pb ( $\mu\text{g/L}$ )	Cd ( $\mu\text{g/L}$ )	Hg ( $\mu\text{g/L}$ )	As ( $\mu\text{g/L}$ )	Fe (mg/L)	Mn (mg/L)	Al (mg/L)	Cr <sup>+6</sup> (mg/L)
Effluent	60.65	4.9	6.6	63	15.15	3.3	ND	0.06
Well 1	ND	ND	ND	1.85	0.15	0.19	0.21	0.012
Detection limit	0.01	0.001	0.06	0.06	0.03	0.01	0.1	0.004

679

680 Table 2 Basic information and major ions in the effluent from Likeng landfill in 2005

Basic data measured in situ					Major ions (mg/L)								
T (°C)	pH	EC (ms/m)	ORP (mv)	DO (mg/L)	$\text{NO}_3^-$	$\text{Cl}^-$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+-\text{N}$	$\text{K}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$
13	8.56	3290	25	1.45	0	2333.7	22576.3	144.5	1879.7	1103	2025.5	1.7	39.5

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685 Table 3 Summary of characteristics for the effluents reported in China, Denmark, and the United  
 686 States

Landfill	NO <sub>3</sub> -N	NH <sub>4</sub> <sup>+</sup> -N	COD	pH
	mg/L			
Five landfills in southern Jiangsu Province (Yang et al., 2008)		4–860	226–4426	6.7–8.4
Shanghai (Zheng et al., 2007)		600–860	2800–5380	7.6
Hangzhou (Zheng et al., 2007)		1390–1760	4690–8100	6.9–8.1
Six landfills in Beijing (Li et al., 2008)		1100–2930	1690–8640	6.83–7.91
Likeng in Guangzhou (Lin et al., 2007: first line; Luo et al., 2009: second line)*	68.4	1046	1280	7.6
	72.2	950	759.6	7.23
Jinan (Zhu et al., 2005)		1012–1381	3775–6110	
Landfill in northern Jiangsu Province (Yang et al., 2010)	26.3–70.3	272–525	9357–17864	7.44–8.46
Norman landfill in USA (Cozzarelli et al., 2011)	<0.05–2.7	209–650		6.6–7.0
106 old landfills in Denmark (Kjeldsen and Christophersen, 2001)		110	320	7.0

687 \*Effluent was collected from a pond, which was used to store wastewater after  
 688 physical-chemical-biological treatment.

689  
 690

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)

Well no	Longitude	Latitude	Well depth (m)	2007													
				Water depth (m)	pH	EC (ms/m)	T (°C)	ORP (mv)	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	NO <sub>2</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SiO <sub>2</sub>
1	113°20'15.9"	23°16'20.6"	50	5.12	6.63	164.5	23.4	-19	318	53.3	52.4	2.08	44.2	22.7	158	47.8	4.0
3	113°20'46.7"	23°16'06.2"	31.25	6.97	8.29	26.3	23.1	-166	36.6	0.47	42.4	ND	27.2	1.2	4.8	2.8	NO
5	113°20'27.4"	23°16'25.4"	7.4	5.2	6.83	18.35	22.5	187	22.8	12.1	39.5	ND	11.4	2.3	20.05	2.2	5.7
6	113°20'27.4"	23°16'25.4"	21.58	5.13	7.1	20.8	22.5	136	21.6	7.75	46.6	ND	11.7	2.3	19.4	2.3	5.2
8	113°20'07.7"	23°16'18.6"	6.45	2.52	5.8	195	18.8	203	341	322	52.5	ND	111	35.2	158	38.4	4.2
9	113°19'56.3"	23°16'22.8"	1.48	1.47	6.22	114.7	20.9	162	198	176	39.0	ND	73.8	25.1	83.4	9.7	5.5
10	113°19'59.6"	23°16'15.7"	4.25	1.2	5.31	178.7	19.9	174	314	311	67.2	ND	112	27.9	168	13.4	4.9

Well no	2001												2005											
	pH	EC (ms/m)	T (°C)	ORP (mv)	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	SiO <sub>2</sub>	pH	EC (ms/m)	T (°C)	ORP (mv)	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>
1	6.03	9.08	24.8	85	9.4	3.9	23.2	6.7	1.7	5.8	2.8	10.5	5.9	28.2	22.4	230	31.4	16.9	23.2	10.7	4.1	20.0	6.3	1.3
3	4.97	50.3	23.3	76	150.0	11.3	7.9	29.4	10.4	41.4	4.1	6.3	5.89	119.1	21.8	83	244.3	6.0	98.8	62.5	25.9	73.0	5.9	2.7
5	6.17	21.1	21.6	254	25.1	7.4	29.3	13.8	1.8	12.8	2.4	4.3	5.56	11.95	20.7	NO	13.3	3.4	18.9	4.9	1.8	11.7	1.3	0.4
6	6.09	9.64	24.2	51	9.5	6.2	37.2	8.9	1.8	7.2	1.4	9.6	5.88	17.75	20.6	281	17.7	8.2	31.7	12.2	1.9	16.5	1.9	0.4
8	6.01	116.6	19.8	-95	193.7	288.8	37.2	97.4	24.8	72.1	12.6	5.0	5.28	170.3	19	255	251.0	226.1	11.0	96.5	28.9	151.6	37.1	4.8
9	5.91	61.3	21.3	-102	94.8	160.3	41.5	54.4	16.2	31.0	6.9	5.3	5.05	208	17	291	241.0	187.0	12.2	124.7	34.7	148.5	13.7	3.8
10	5.63	9.35	21.1	-114	9.6	14.3	15.9	6.4	1.5	6.0	3.0	7.9	5.51	133.5	17	270	209.3	173.7	23.8	107.3	33.0	89.7	10.5	2.7

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  $^{18}\text{O}$ , D and  $^{15}\text{N}$ .