



## N<sub>2</sub>O and NH<sub>3</sub> emissions from a bioreactor landfill operated under limited aerobic degradation conditions

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### Abstract

The combination of leachate recirculation and aeration to landfill may be an efficient way for *in-situ* nitrogen removal. However, nitrogenous substances contained in the landfill layer are concomitantly transformed into N<sub>2</sub>O and NH<sub>3</sub>, leading to increased emissions into the atmosphere. In the present study, the emissions of N<sub>2</sub>O and NH<sub>3</sub> were measured under conditions of fresh or partially stabilized refuse with or without leachate recirculation or intermittent aeration. The results showed that the largest N<sub>2</sub>O emission (12.4 mg-N/L of the column) was observed in the aerated column loaded with partially stabilized refuse and recycled with the leachate of low C/N ratio; while less than 0.33 mg-N/L of the column was produced in the other columns. N<sub>2</sub>O production was positively correlated with the prolonged aerobic time and negatively related with the C/N ratio in the recycled leachate. NH<sub>3</sub> volatilization increased with enhanced gas flow and concentration of free ammonia in the leachate, and the highest cumulative volatilization quantity was 1.7 mg-N/L of the column.

**Key words:** municipal solid waste; bioreactor landfill; aeration; N<sub>2</sub>O emission; NH<sub>3</sub> volatilization

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### Introduction

In recent years, the effectiveness of leachate recirculation in bioreactor municipal solid waste (MSW) landfills has been well documented in lab-scale, pilot-scale and full-scale studies (Berge et al., 2005; Reinhart et al., 2002). In addition to decreasing the cost for leachate treatment, leachate recirculation can accelerate waste settlement and gas production and subsequently generate additional landfill capacity. Nonetheless, operating an anaerobic landfill as a bioreactor with leachate recirculation poses many problems, for example, the high ammonia concentration in the effluent leachate (Berge et al., 2006). Ammonia accumulation occurs even when the organic fractions of waste have been stabilized, since ammonia is difficult to be removed by nitrification under low O<sub>2</sub> concentration or be converted to N<sub>2</sub> by the Anammox process due to deficient nitrite (Burton and Watson-Craik, 1998). Furthermore, leachate recycling can increase ammonification, resulting in even higher ammonia concentration than that in the leachate from conventional sanitary landfills.

The addition of air to landfill layers can provide a favorable environment for simultaneous nitrification and denitrification, thereby allowing nitrogen removal and

waste degradation (Berge et al., 2007; Shao et al., 2008). Prantl et al. (2006) reported that aeration caused a rapid and complete reduction of ammonium in well-decomposed refuse. Shao et al. (2008) observed that limited aeration could significantly reduce the nitrogen loading of leachate in a fresh landfill. Other studies in different scales have been conducted (Jun et al., 2007; Onay and Pohland, 1998; Price et al., 2003; Ritzkowski et al., 2006), most of which focused on the efficiency of nitrification or denitrification or both following aeration of landfills filled with refuse at different stages of decomposition.

Leachate recirculation combined with aeration to landfill induces not only nitrogen removal, but also large amounts of N<sub>2</sub>O production, a powerful greenhouse gas with a global-warming potential 296 times higher than that of CO<sub>2</sub> (IPCC, 2001). N<sub>2</sub>O could be produced by *in-situ* denitrification in landfills due to only leachate recirculation. Price et al. (2003) injected KNO<sub>3</sub> solution into the lab-scale reactors loaded with fresh refuse and observed that 1.7%–6.1% of the externally added NO<sub>3</sub><sup>−</sup>-N was converted into N<sub>2</sub>O. Vigneron et al. (2007) added the leachate containing NO<sub>3</sub><sup>−</sup>-N or NO<sub>2</sub><sup>−</sup>-N into MSW with its putrescible fraction replaced by manure compost, and found that the ratio of the produced N<sub>2</sub>O to N<sub>2</sub> was less than 5%, and N<sub>2</sub>O was mainly produced during the

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hydrolysis and acidogenesis in refuse layers.  $N_2O$  could also be generated from the aerated landfills where nitrification and denitrification existed simultaneously. Berge et al. (2006) aerated the simulated landfill layers loaded with compost and recycled ammonia solution, and observed that 5.2%–15.6% of the externally added N was converted into  $N_2O$ , which was attributed to incomplete denitrification originated from high oxygen concentration and low C/N ratio. As for the monitoring in field-scale landfills, Powell et al. (2006) conducted aeration in a closed landfill cell; they inferred that  $N_2O$  production was increasing since the gas flow increased with the  $N_2O$  concentration unchanged. Tsujimoto et al. (1994) tested two landfills and also observed that the  $N_2O$  concentration from gas collection well was higher in the landfill cells with higher oxygen concentration.

The major influence factors include the composition of landfilled waste, the characteristics of recycled leachate and the aeration condition. Nevertheless, although  $N_2O$  production was studied, previous studies paid more attention to different aspects of landfill operations. Owing to different conditions used in these studies, i.e., the diverse waste compositions, different landfills ages, the different types of recycled leachate, with or without aeration, it is difficult to draw conclusions whether the  $N_2O$  production would be promoted or repressed through comparison of existing publications.

In the present study, the effects of major factors on  $N_2O$  emissions from bioreactor landfills, i.e. characteristics of recycled leachate, waste composition and aeration, were studied on the same platform. By using the same benchmark, comparable data would be expected to explain the effects of these factors on  $N_2O$  production. In addition,  $NH_3$  emission was monitored to assess the influence of aeration on  $NH_3$  volatilization.

## 1 Materials and methods

### 1.1 Materials

The fresh refuse loaded into the simulated landfill columns was prepared according to the actual MSW composition in Shanghai (He, 2002). The refuse components were collected from a residential area in downtown Shanghai, with a cellulose/lignin ratio of 2.81. The partially stabilized refuse was excavated from a bioreactor landfill cell with leachate recirculation in Tianziling MSW landfill

site located in Hangzhou City, China. The partially stabilized refuse, which had been landfilled for 18 months, had a cellulose/lignin ratio of about 0.9. The physicochemical characteristics of the fresh refuse and partially stabilized refuse are shown in Table 1.

Refuse from both sources was coarsely shredded into particles  $< 1 \times 1$  cm to improve homogeneity and then mixed by hand. The fresh refuse was inoculated with 10% aerobic activated sludge (the characteristics are shown in Table 1) in wet weight base on initiate decomposition. For all the analysis in the experiment, the characteristics of inoculum sludge, such as C and N content and weight, were included in the refuse. Deionized water was added to the columns to ensure the loaded refuse was completely saturated, and the quantities of added water and the moisture contents of saturated refuse were recorded.

### 1.2 Experimental design and operation

Five simulated landfill columns under different operations were established to compare the emissions of  $N_2O$  and  $NH_3$ . The characteristics of the five simulated landfill columns are listed in Table 2. Briefly, column 1 simulated a traditional sanitary landfill and served as the control. Column 2 was set-up to study the *in-situ* denitrification capacity of a young anaerobic landfill in which leachate was recycled after *ex-situ* nitrification treatment. Column 3 with intermittent aeration was to simulate the *in-situ* simultaneous nitrification and denitrification in a young aerated bioreactor landfill, where leachate generated by itself was recycled. Columns 4 and 5 were to simulate the *in-situ* simultaneous nitrification and denitrification of an old aerated bioreactor landfill for treating fresh and old leachate, respectively.

The columns, made of PPR plastic (100-mm diameter, 300-mm height), were designed to allow effective drainage and recirculation of the leachate, as well as air addition and gas sampling (Fig. 1). To promote the even distribution of the leachate and to prevent clogging during leachate drainage, two 25-mm-thick layers of pottery were placed at the top and bottom of the reactor. Both the anaerobic and aerated columns were capped and well-sealed with flanges and rubber bands to prevent gas leakage. All experiments were carried out in a thermostatically controlled reactor in which the temperature was kept at  $(35 \pm 5)^\circ\text{C}$ .

All the columns with intermittent aeration (columns 3, 4 and 5) were aerated twice a day. Each time, to ensure all the

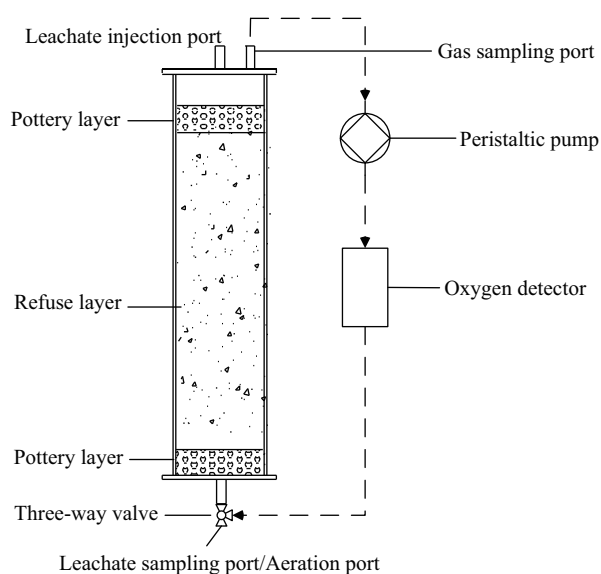
**Table 1** Physical compositions of the refuse and chemical compositions of the refuse and inoculum sludge

Physical fractions	Composition (% in dry weight) <sup>a</sup>						
	Food waste	Plastics	Paper	Rubber and leather	Textile	Glass and metal	Others
Fresh refuse	61.6	15.0	7.1	5.0	4.7	2.3	4.3
Partially stabilized refuse	— <sup>b</sup>	12.6	4.7	3.7 <sup>c</sup>	3.8	0.5	74.5 <sup>d</sup>
Elements	C	H	N	S	O	Ash	
Fresh refuse	36.5	2.4	3.1	0.12	28.7	29.2	
Partially stabilized refuse	18.4	1.4	1.8	0.4	8.4	69.6	
Inoculum sludge	20.4	3.4	3.9	1.1	40.2	30.8	

<sup>a</sup> The moisture contents of the fresh, partially stabilized refuse and inoculum sludge were 58.8%, 42.1% and 88.2%, respectively; <sup>b</sup> food waste could not be picked out from the residue; <sup>c</sup> stone; <sup>d</sup> the residue was indiscernible.

**Table 2** Operation parameters of the simulated landfill columns

Operation features	Column 1	Column 2	Column 3	Column 4	Column 5
Landfilled refuse	Fresh refuse	Fresh refuse	Fresh refuse	Partially stabilized refuse	Partially stabilized refuse
Refuse quantity (g)	765.0	765.0	765.0	940.9	952.6
Inoculum sludge (g)	84.9	85.2	85.1	0	0
Added water quantity (g)	278	301	330	500	500
Moisture content (% W/W)	71.2	71.8	72.4	62.2	62.0
Density (g/L)	550	550	550	610	610
Leachate recirculation	No	Yes	Yes	Yes	Yes
Quality of recycled leachate	—	Old with nitrate added	Produced by itself	Fresh	Old
Recycling loading	—	50 mL per 5 days	Twice per day as produced	50 mL per 12 hr	50 mL per 12 hr
Aeration	No	No	Yes	Yes	Yes
Aeration quantity (L/(kg refuse-day))	—	—	4.23	3.83	3.78

**Fig. 1** Experimental simulating column.

gas in the free air space of the column was replaced, 1.8 L of air was injected into each column from the aeration port at bottom. Just prior to aeration, the leachates in columns 3, 4 and 5 were drained out and the recycled leachates were injected into the columns. Columns 4 and 5 were loaded with 50 mL of recycled leachate per 12 hours, whereas the volume injected into column 3 was roughly equal to the leachate volume drained out. In column 2, 50 mL of old leachate was recycled every five days, although problems with drainage of the column were encountered.

The fresh leachate recycled into column 4 was from an active MSW landfill in Shanghai that has been in operation for three years. The old leachates recycled into columns 2 and 5 were from the Tianziling landfill in Hangzhou, which had been closed one year before this study. In addition, the leachate recycled into column 2 was treated with KNO<sub>3</sub> to achieve a nitrate concentration of about 500 mg/L, which

simulated the leachate after nitrification treatment. The characteristics of the recycled leachates in columns 2, 4 and 5 are shown in Table 3. As for column 3, self-generated leachate was recycled and its characteristics changed with time.

### 1.3 Sampling method and frequency

For the aerated columns (columns 3, 4 and 5), every time before aeration, gas sample was withdrawn from the sealed gas sampling port and the pressure in the columns was monitored by connecting the port to a U-tube manometer. The volume of generated gas was calculated from the pressure in the columns. While the gas sampling and pressure measurement of anaerobic columns (columns 1 and 2) were conducted before leachate sampling. Leachate in the columns was collected from the bottom sampling port before aeration if there was, and the collection frequency was once every two days during the initial 20 days and then once every three days from then on.

### 1.4 Analytical methods

The concentrations of CO<sub>2</sub> and CH<sub>4</sub> were measured with a gas chromatograph (GC) (GC102M, Shanghai Precision & Scientific Instrument Co., Ltd., China) equipped with a thermal conductivity detector (TCD) and a 2-m stainless steel column packed with Porapak Q (60/80 mesh). The temperature of the injector, oven and detector were set at 50, 50 and 130°C, respectively. The carrier gas was N<sub>2</sub> at a flow rate of 50 mL/min. The concentration of N<sub>2</sub>O was measured with a GC (GC122, Shanghai Precision & Scientific Instrument Co., Ltd., China) equipped with an electron-capture detector (ECD) and a 3-m stainless steel column packed with Porapak Q (80/100 mesh). The temperature of the oven and detector were set at 55 and 330°C, respectively. The carrier gas was N<sub>2</sub> at a flow rate of 60 mL/min. NH<sub>3</sub> in the gas was absorbed with boric acid solution and then colorimetrically determined

**Table 3** Characteristics of the recycled leachates in columns 2, 4 and 5

	pH	COD (mg/L)	NH <sub>4</sub> <sup>+</sup> -N (mg/L)	Kjedahl nitrogen (mg/L)	Sum of NO <sub>2</sub> <sup>-</sup> -N and NO <sub>3</sub> <sup>-</sup> -N (mg/L)
Column 2	7.6–7.8	2040–3320	931–995	1070–1130	484–627
Column 4	5.8–6.5	78,000–96,000	1550–2690	1840–3010	43–73
Column 5	7.6–7.8	2040–3320	931–995	1070–1130	46–62

at 420 nm (APHA et al., 1998). The measurement for  $O_2$  concentration was realized by two sampling ports along the columns. As shown in Fig. 1, the top gas sampling port was sequentially connected to a peristaltic pump, an oxygen detector and the bottom sampling port by pipes. When the pump was switched on, the gas in the column was driven into the oxygen detector (CYS-1, Xuelian Co., China) for analysis of  $O_2$  concentration.

The characteristics of input leachate and output leachate from the columns was monitored for pH, Kjeldahl nitrogen,  $NH_4^+$ -N, sum of  $NO_2^-$ -N and  $NO_3^-$ -N, and chemical oxygen demand (COD). The pH was measured with a digital pH meter (PHS-25, Shanghai Precision & Scientific Instrument Co., Ltd., China). Kjeldahl nitrogen and  $NH_4^+$ -N were measured using a distillation method. The sum of  $NO_2^-$ -N and  $NO_3^-$ -N was determined by reduction and distillation. COD was measured following the potassium dichromate-ferrous ammonium sulfate method (State Environmental Protection Administration of China, 2002).

The moisture content of the refuse was measured by drying at 70°C for 48 hr. Volatile solid (VS) was determined by drying at 550°C to constant weight. The carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) contents of the refuse were measured using an elemental analyzer (CHNS-932, LECO Instruments Ltd., UK). The concentration of celluloses and lignins were determined based on the measurement of acid detergent fiber and ash contents of the refuse samples (Faithfull, 2002).

## 2 Results

### 2.1 Leachate characterization

#### 2.1.1 Organic compounds

The COD concentrations in the output leachates were related to the compositions of the landfilled refuse, the characteristics of recycled leachate, and the aeration levels. As shown in Fig. 2, a high COD concentration was maintained in columns 1 and 2, filled with fresh refuse, and in

column 4, recycled with high organic loading of leachate. Comparatively, the COD concentration in the leachate of column 5, loaded with partially stabilized refuse and recycled with old leachate, fluctuated between 1200 and 5400 mg/L, much less than other four columns ( $> 20,000$  mg/L). The difference between the COD concentrations in columns 2 and 3 indicated that aeration accelerated the decomposition of fresh refuse. This was in agreement with the study of Prantl et al. (2006), who found that aeration into the stimulated landfill columns loaded with old refuse posed quickly decrease in COD concentration in the output leachate compared with anaerobic columns. The addition of  $KNO_3$  at 500 mg-N/L (as a loading of 0.0098 mg-N/(g-refuse-day)) to column 2 posed similar COD concentration to that in column 1 with no leachate recirculation. However, when considering the output and recycled amounts of leachate, the accumulated COD mass transferred into leachate during the tested period in column 2 was 22.0 g, nearly three times larger than that in column 1 (7.15 g). Similarly, Price et al. (2003) found that the addition of nitrate into refuse, by leachate recirculation to a simulated landfill in active methane productive phase, induced inhibition of methane production as well as COD increase in the effluent leachate. They suggested that the increased COD may be due to the fermentation of refuse and rich in organic acid, which was consistent with the decrease in pH.

#### 2.1.2 Nitrogen compounds

The concentrations of nitrogen compounds in the output leachates from the columns are summarized in Fig. 3. The  $NH_4^+$ -N and COD concentrations in the output leachate depended on the respective concentrations in the recycled leachate. In column 4, the  $NH_4^+$ -N and COD concentrations in the recycled leachate were 2040–3320 and 78,000–96,000 mg/L (Table 3), respectively. Correspondingly, the highest concentrations in the output leachates were close to those in the recycled leachates after saturated adsorption during the initial 20 days. In column 5, the  $NH_4^+$ -N and COD concentrations in the recycled leachate were 931–995 and 1550–2690 mg/L, respectively, and the concentrations in the output leachate decreased to no more than 650 mg/L after 70 days. Furthermore, aeration also played an important role on the decomposition of  $NH_4^+$ -N in the columns. In column 3, filled with fresh refuse and aerated, the  $NH_4^+$ -N concentration in the output leachate decreased to less than 500 mg/L after 30 days, while it remained at about 1000 mg/L in the anaerobic columns (columns 1 and 2).

The sum of  $NO_2^-$ -N and  $NO_3^-$ -N in the output leachate (Fig. 3c) was mainly affected by the aeration level and the nitrate content of the recycled leachate. In columns that were aerated or treated with nitrate (columns 2, 3, 4 and 5), the sum of  $NO_2^-$ -N and  $NO_3^-$ -N in the output leachates remained at about 50 mg/L, relatively high over the course of the experiment. As to the control column (column 1) with no aeration or nitrate addition, the sum of  $NO_2^-$ -N and  $NO_3^-$ -N in the output leachate was less than 20 mg/L after 40 days.

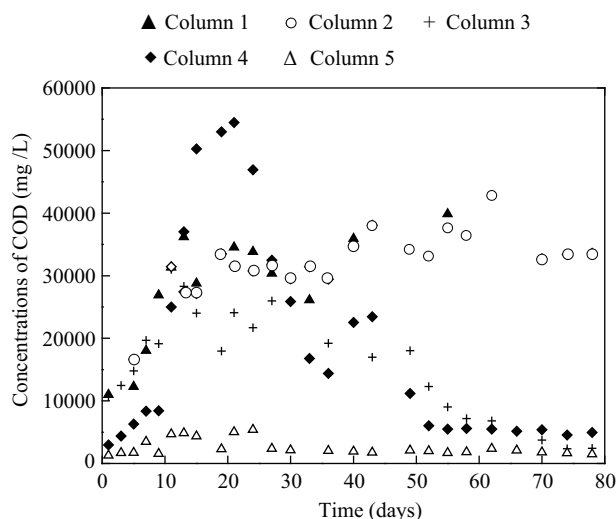
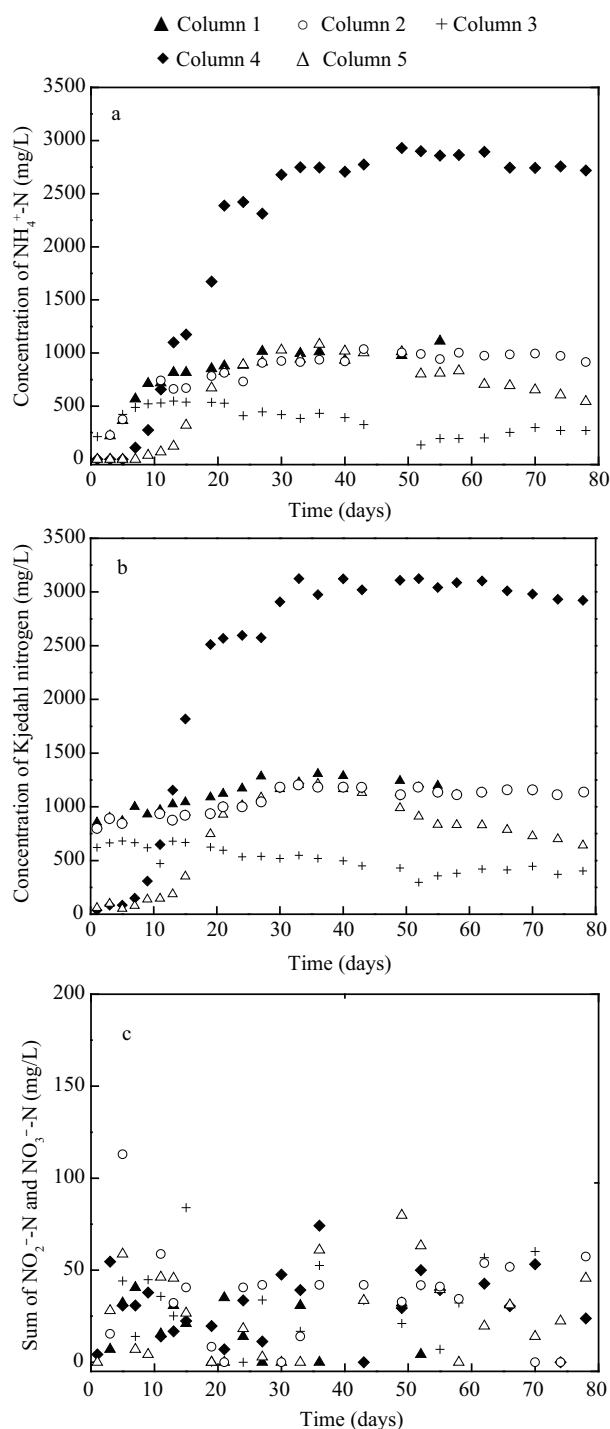


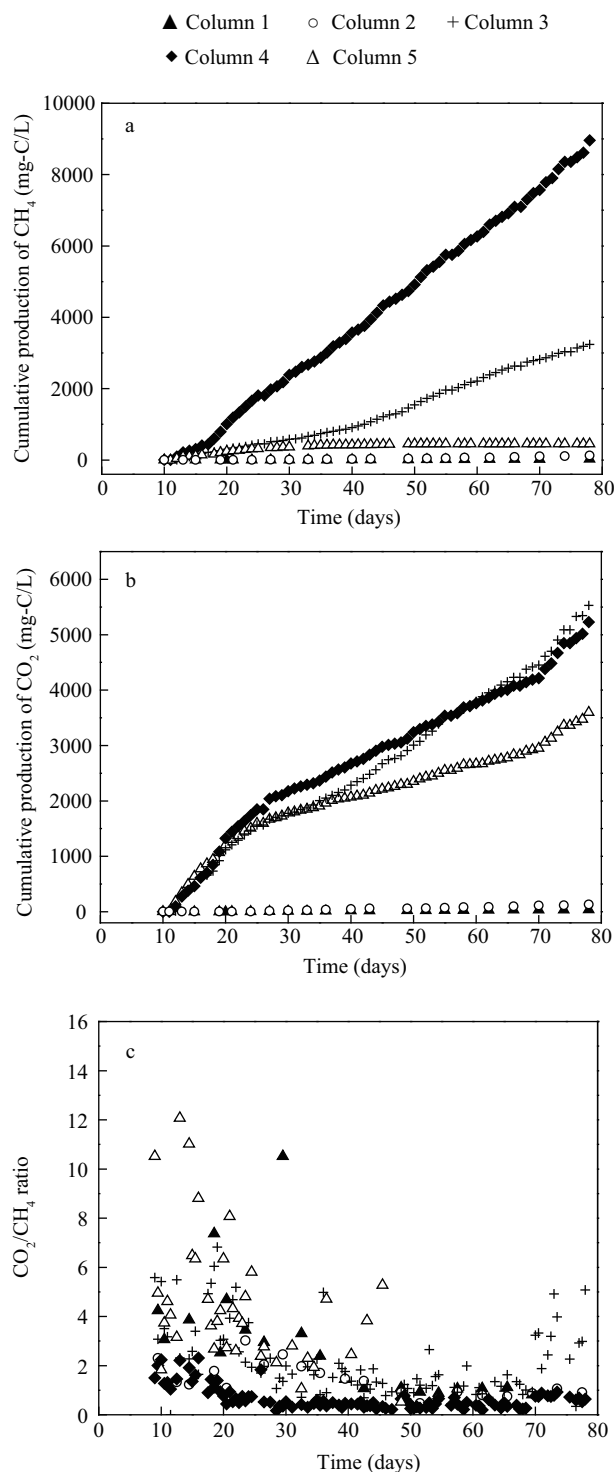
Fig. 2 Temporal evolution of COD in the output leachate from different columns.



**Fig. 3** Temporal evolution of nitrogen compounds in the output leachate from different columns. (a) ammonia nitrogen; (b) Kjeldahl nitrogen; (c) sum of nitrite and nitrate nitrogen.

## 2.2 Production of CH<sub>4</sub> and CO<sub>2</sub>

The cumulative productions of CH<sub>4</sub> and CO<sub>2</sub> from the five simulated landfill columns and temporal molar ratios of CO<sub>2</sub>/CH<sub>4</sub> are shown in Fig. 4. Compared with the columns with the aerated columns (columns 3, 4 and 5), only small amount of biogas (CH<sub>4</sub> and CO<sub>2</sub>) was produced in the anaerobic ones (columns 1 and 2). The gas quantities and CO<sub>2</sub>/CH<sub>4</sub> molar ratios in aerated columns were related to the organic loading of the refuse and recycled leachate. In column 3, filled with fresh refuse, and column 4,



**Fig. 4** Cumulative productions of CH<sub>4</sub> (a) and CO<sub>2</sub> (b) and temporal molar ratios of CO<sub>2</sub>/CH<sub>4</sub> (c) from different columns.

recycled with leachate of high COD concentration, the cumulated productions of biogas were the highest with CH<sub>4</sub> production of 8840 and 3230 mg-C/L of the column as a reactor and CO<sub>2</sub> production of 5150 and 5480 mg-C/L, respectively. While for column 5 loaded with partially stabilized refuse and leachate of low COD concentration, the cumulated productions of CH<sub>4</sub> and CO<sub>2</sub> were 455 and 3600 mg-C/L respectively, clearly lower than the other two aerated columns.

### 2.3 N<sub>2</sub>O emission

The cumulative emissions of N<sub>2</sub>O from the different landfill columns are shown in Fig. 5. There was little difference in N<sub>2</sub>O emissions in the five columns during the initial ten days. After then, the N<sub>2</sub>O emission rate in column 3 increased rapidly during the next ten days, and slowed down in the last period of the experiment. From day 20, the N<sub>2</sub>O emission in column 5 (partially stabilized refuse with low organic loading of the recycled leachate) started to increase and the increase rate was accelerated after day 38. While relatively neglectable emissions of N<sub>2</sub>O were maintained in the other three columns. At the end of the experiment, cumulative N<sub>2</sub>O emissions in columns 1–5 were 0.001, 0.053, 0.328, 0.090, and 12.4 mg-N/L of the column as a reactor, respectively.

With regard to the global warming potential, the CO<sub>2</sub> equivalents for cumulated N<sub>2</sub>O emission in columns 1–5 were 0.001, 0.04, 0.23, 0.07 and 8.8 g CO<sub>2</sub>-eq, while those for CH<sub>4</sub> were 1.5, 7.5, 190, 540, 27 g CO<sub>2</sub>-eq, respectively. Compared with CH<sub>4</sub>, N<sub>2</sub>O was not a significant green house contributor in columns 1, 2, 3 and 4. Whereas, the green house contribution derived from N<sub>2</sub>O was comparable to CH<sub>4</sub> in column 5.

### 2.4 NH<sub>3</sub> volatilization

Due to the lack of stable methanogenesis in column 1, there was not enough gas to analyze the NH<sub>3</sub> concentration. The cumulative volatilizations of NH<sub>3</sub> from the other four simulated landfill columns are presented in Fig. 6. During the initial 20 days, there was no obvious difference in NH<sub>3</sub> volatilization, and the accumulated amount was less than 0.2 mg-N/L. After then, NH<sub>3</sub> volatilization in the

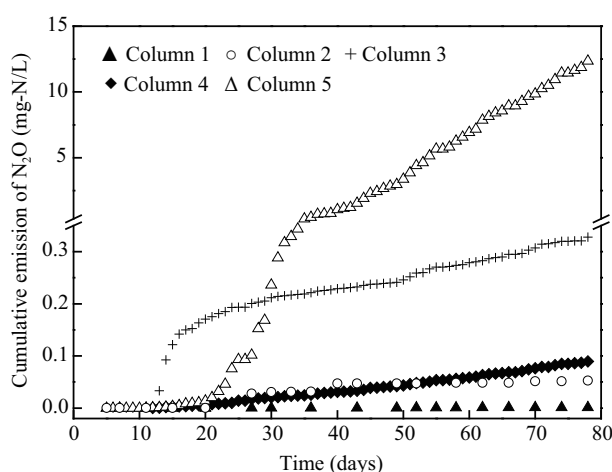


Fig. 5 Cumulative emissions of N<sub>2</sub>O from different columns.

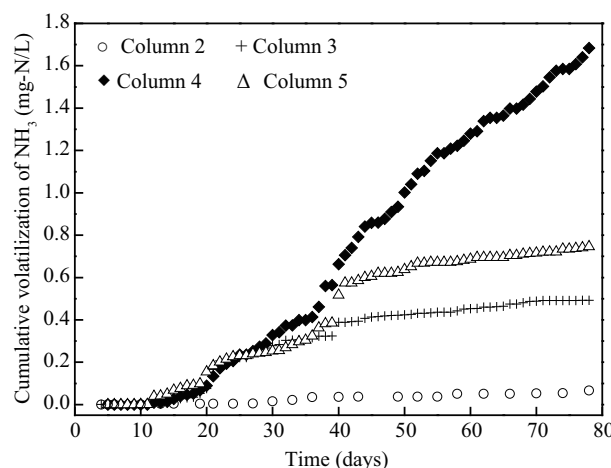


Fig. 6 Cumulative volatilizations of NH<sub>3</sub> from different columns.

aerated columns increased at different rates. The volatilization rate in column 4 was high and the final cumulative quantity of volatile NH<sub>3</sub> reached approximately 1.7 mg-N/L over the entire tested period. In contrast, the rate of NH<sub>3</sub> volatilization in columns 3 and 5 were slower, and the final cumulative volatilization quantities were about 0.49 and 0.75 mg-N/L, respectively. At the same time, the volatilization rate in column 2 (recycled with nitrate-supplemented old leachate) remained low and the accumulated amount at the end of the tested period was only about 0.066 mg-N/L.

### 2.5 Nitrogen conversion

The conversions of nitrogen compounds in the different columns are presented in Table 4. The decomposition of nitrogen compounds in the refuse was high in those columns with leachate recirculation and intermittent aeration. In columns 3, 4 and 5, the decrease proportion of nitrogen mass in the refuse demonstrated that 82.4%, 66.5% and 74.3% of the initial nitrogen in the refuse underwent decomposition, respectively. To discuss the nitrogen migration via leachate pathway, the ratio of the nitrogen difference between “output in leachate” and “input in leachate” (Table 4) to the nitrogen in “initial refuse” Table 4 were 21.0%, –35.8% and –20.4% for columns 3, 4 and 5, respectively. This illustrated that only 21% of the initial nitrogen transferred from the refuse to leachate in column 3, while in columns 4 and 5, instead of nitrogen emission from refuse, some nitrogen in the recycled leachate was sequestered in the refuse. N<sub>2</sub>O and NH<sub>3</sub> emissions were very small compared with the sum of the nitrogen in the input materials (the initial refuse and recycled leachate). Only 0.000030%, 0.0026%, 0.020%,

Table 4 Nitrogen conversion in the simulated landfill columns

		Column 1	Column 2	Column 3	Column 4	Column 5
N in refuse	Initial (g N)	10.1	10.1	10.1	9.80	9.90
	End (g N)	–	6.79	1.77	3.29	2.55
N in leachate	Input (g N)	0	1.14	0	16.5	6.30
	Output (g N)	0.29	0.85	2.12	12.9	4.27
N in gas	N <sub>2</sub> O (mg N)	0.003	0.13	0.79	0.22	29.6
	NH <sub>3</sub> (mg N)	ND	0.16	1.18	4.04	1.79

–: Chemical characteristics of the end refuse in column 1 were not investigated; ND: not detected.

0.016% and 0.19% of the total nitrogen added to columns 1–5 was emitted as N<sub>2</sub>O and NH<sub>3</sub>, respectively. Although the environment in column 5 seemed to be favorable for the conversion of nitrogen to N<sub>2</sub>O, the proportion of the nitrogen emitted as N<sub>2</sub>O (0.18%) was nonetheless much lower than the total nitrogen added to the column. The significant reduction of nitrogen mass (Table 4) in the aerated columns (61.4%, 38.2% and 60.0% of the total nitrogen added for columns 3, 4 and 5, respectively) may be due to the production of N<sub>2</sub>, which was not measured in this experiment. For the explanation of the nitrogen loss as N<sub>2</sub>, it was suggested that nitrification and denitrification occurred simultaneously in the aerated columns.

### 3 Discussion

#### 3.1 Metabolism in the columns

As shown in Fig. 7, pH in column 1 was around 5–6, much lower than the optimum pH (6.5–7.6) (Rittmann and McCarty, 2001) for methanogenesis. The lower pH in column 1 illustrated that methanogenesis was inhibited by intermediate organic acids produced from the hydrolysis and acidogenesis of easily biodegradable organic waste, which was consisted with that few organics were gasified and the organic carbon and nitrogen compounds in the output leachate remained stable. The quality of the output leachate in column 2 was similar to that in column 1. Considering the high concentration of NO<sub>3</sub><sup>−</sup>-N in the recycled leachate (> 500 mg/L) added into the refuse, the sum of NO<sub>2</sub><sup>−</sup>-N and NO<sub>3</sub><sup>−</sup>-N in the output leachate from column 2 (about 50 mg/L) was only about 10% of the input leachate. Accordingly, the metabolism in column 2 predominantly occurred at the stage of hydrolysis and acidogenesis, although denitrification may occur due to the decreased concentration of NO<sub>2</sub><sup>−</sup>-N and NO<sub>3</sub><sup>−</sup>-N. In column 3, except for the initial 10 days, the loading of COD and nitrogen in the leachate decreased continually, the biogas (CH<sub>4</sub> and CO<sub>2</sub>) production was 8770 mg-C/L, and the conversion of nitrogen clearly demonstrated nitrogen loss as N<sub>2</sub> (Table 4). Therefore, aerobic metabolism, methano-

genesis, nitrification, and denitrification were carried out simultaneously in column 3. The apparent metabolism in column 4 was similar to that in column 3, but relatively lower ratio of CO<sub>2</sub>/CH<sub>4</sub> (Fig. 4c) demonstrated lower proportion of aerobic metabolism in column 4. In column 5, metabolism showed the features of a mixed state, but nearly no CH<sub>4</sub> was identified after day 50, indicating the predominance of aerobic metabolism.

#### 3.2 Factors affecting N<sub>2</sub>O emission

N<sub>2</sub>O is generated during the biological processes of nitrification and denitrification (Price et al., 2003; Wrage et al., 2001), and its emission is related to the nitrification and denitrification capacity of an ecosystem (Carter, 2007). If the ratio of nitrogen loss in the columns were used to define (Table 4) the nitrification-denitrification capacity, the expected order for the capacity was column 3 > column 5 > column 4 > column 2; however, this was not the case. As for the actually N<sub>2</sub>O emission results, the highest N<sub>2</sub>O emission amount, nearly 12.4 mg-N/L, was observed in column 5, while less than 0.33 mg-N/L of N<sub>2</sub>O were produced in the other columns. This was to say that the N<sub>2</sub>O emission was not positively correlated with the nitrification-denitrification capacity and other environmental factors must have influenced the N<sub>2</sub>O production. Previous researches about N<sub>2</sub>O emission from landfills and other ecosystems (Berge et al., 2005; Chiu and Chung, 2003; Huang et al., 2004; Hwang and Hanaki, 2000; Kanerva et al., 2007; Mathieu et al., 2006) showed that pH, O<sub>2</sub> and the C/N ratio had great effects on N<sub>2</sub>O production.

In this study, the pH values of the output leachates from columns 4 and 5 evolved quite similarly (Fig. 7), while the N<sub>2</sub>O quantity differed significantly, indicating that pH was not the dominant factor in the two columns. For the aerated columns (columns 3, 4 and 5), the time spent before O<sub>2</sub> content in the columns declined down to 3% after aeration was monitored and defined as prolonged aerobic time in this study (Table 5). The prolonged aerobic time in column 5 maintained larger than those of the other two columns, which was consistent with the lowest CH<sub>4</sub> production in column 5 (Fig. 4c). It seems that aerobic niche posed strong production of N<sub>2</sub>O. The bio-available C/N ratio in the columns also affects N<sub>2</sub>O production. From the C/N ratios of the recycled leachate in the aerated columns, i.e., 16–30, 16–20 and 1.5–3.0 in columns 3, 4 and 5, respectively, it was observed that a high ratio of C/N corresponded to less N<sub>2</sub>O production.

Focusing on columns 4 and 5, the only different operation between them was the characteristics of recycled leachate, which may be the reason for the different prolonged aerobic time and correspondingly the N<sub>2</sub>O

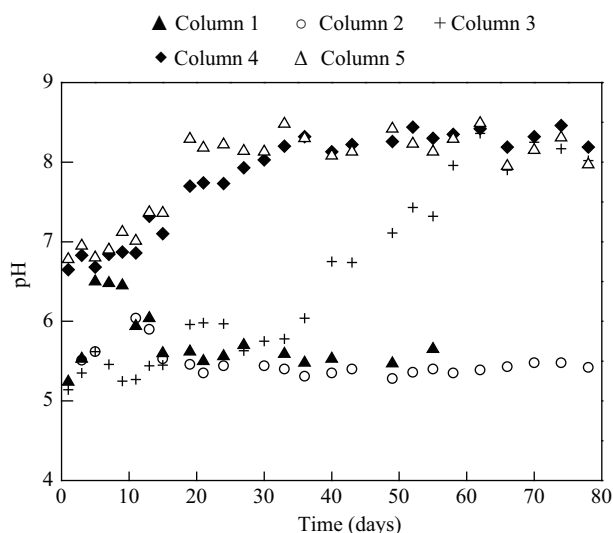


Fig. 7 Temporal evolution of pH in the leachate from different columns.

Table 5 Prolonged aerobic time in the aerated columns

Time (day)	1	10	30	50	70
Column 3 (hr)	8	5	3	1	2
Column 4 (hr)	6	4	2	1	1
Column 5 (hr)	6	5	4	2	3

emissions. In column 4, lot of oxygen was consumed for the decomposition of higher organic compounds in the recycled leachate, and nitrification may be inhibited by the lack of oxygen and denitrification could be well completed with little  $\text{N}_2\text{O}$  emission. While for column 5, little  $\text{CH}_4$  emission confirmed that aeration increased the aerobic extent, which may correspondingly stimulate the nitrification and inhibit the denitrification (Hwang and Hanaki, 2000). As the by-product of nitrification and intermediate of denitrification (Wrage et al., 2001),  $\text{N}_2\text{O}$  emission in columns 4 and 5 could be explained by the different abovementioned metabolisms. In addition, sufficient carbon source posed by high C/N ratio in column 4 may be another benefit for the complete denitrification and subsequently less emission of  $\text{N}_2\text{O}$ .

### 3.3 Factors affecting $\text{NH}_3$ volatilization

The gas retention time in a landfill is sufficiently long to allow  $\text{NH}_3$  volatilization to reach equilibrium. Furthermore,  $\text{NH}_3$  volatilization in a landfill should be positively related to the gas flow passing through the columns (injected air plus the gas generated by metabolism) and to the concentration of  $\text{NH}_4^+\text{-N}$  in the leachate (Berge et al., 2005; Chadwick, 2005). Herein, the pH and the amount of  $\text{NH}_4^+\text{-N}$  in the output leachate were used to calculate the concentration of free ammonia with respect to a reference value (Berge et al., 2005). As depicted in Fig. 8, the free ammonia concentrations in the output leachate followed the decreasing sequence of column 4 > column 5 > column 3 > column 2, consistent with the changes in relative  $\text{NH}_3$  volatilization (Fig. 6). However, the proportion of  $\text{NH}_3$  volatilization in column 4 to that in column 5 was higher than the proportion of the free ammonia concentration, while the opposite was true for the proportion of columns 5 to 3, due to the higher gas flow in columns 3 and 4 than in column 5.

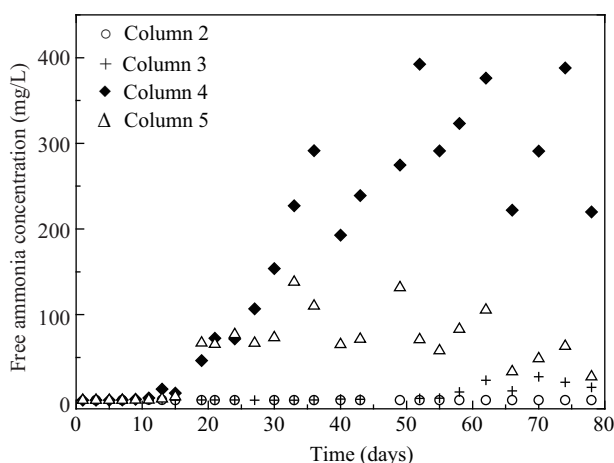


Fig. 8 Temporal evolution of free ammonia in the leachate in different columns.

## 4 Conclusions

Organic waste degradation increased with intermittent aeration and recirculated leachate due to the mixture of

aerobic and anaerobic metabolism in the landfills, as simulated in these column experiments. In columns with intermittent aeration, nitrogen compounds in the refuse were removed to a large extent, but little in form of  $\text{N}_2\text{O}$  and  $\text{NH}_3$ , accounting for no more than 0.19% of the total nitrogen added to the columns. Compared with the neglectable amount of  $\text{N}_2\text{O}$  emitted from the other four columns, the highest  $\text{N}_2\text{O}$  emission quantity (nearly 12.4 mg-N/L) was measured in column 5, loaded with partially stabilized refuse and operated with recirculation of leachate with low organic carbon content and intermittent aeration.  $\text{N}_2\text{O}$  emission was positively correlated with the prolonged aerobic time in the aerated columns and negatively related with the C/N ratio in the recycled leachate, which were correspondingly due to the low carbon content in the recycled leachate.

The highest volatilization of  $\text{NH}_3$ , 1.7 mg-N/L, was observed in column 4 filled with partially stabilized refuse and recycled with leachate of high C/N ratio.  $\text{NH}_3$  volatilization in the landfill was affected by gas flow (injected air plus the gas generated by metabolism) through the landfill and the concentrations of free ammonia in the leachate.

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