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Short tests to couple N_2O emission mitigation and nitrogen removal strategies for landfill leachate recirculation

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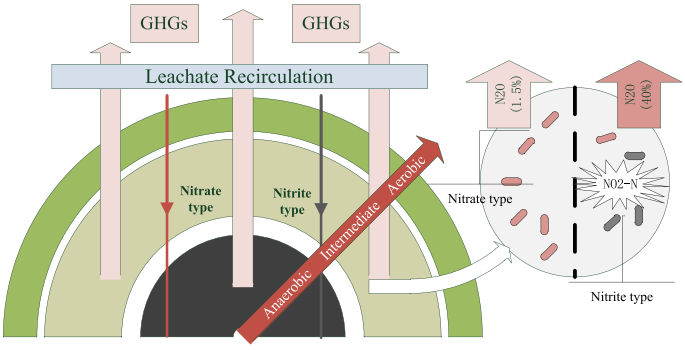
HIGHLIGHTS

- N_2O emission from landfill leachate was affected by nitrogen speciation.
- Increased nitrite in recirculated leachate led to higher N_2O emission.
- Nitrate type leachate is optimal for coupled N_2O control and nitrogen removal.
- Carbon source availability alters the relative contributions of N_2O pathways.

GRAPHICAL ABSTRACT



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ABSTRACT

Landfills implemented with onsite leachate recirculation can efficiently remove pollutants, but currently they are reckoned as N_2O emission hot spots. In this project, we evaluated the relationship between N_2O emission and nitrogen (N) removal efficiency with different types of leachate recirculated. Nitrate supplemented leachate showed low N_2O emission rates with the highest N removal efficiency (~70%), which was equivalent to ~1% nitrogen emitted as N_2O. Although in nitrite containing leachates' N removal efficiencies also reached to ~60%, their emitted N_2O comprised ~40% of total removed nitrogen. Increasing nitrogen load promoted N_2O emission and N removal efficiency, except in ammonia type leachate. When the ratio of BOD to total nitrogen increased from 0.2 to 0.4, the N_2O emission flux from nitrate supplemented leachate decreased from ~25 to <0.5 μg N/kg-soil · h. We argue prior to leachate in situ recirculation, sufficient pre-aeration is critical to mitigate N_2O surges and simultaneously enhance nitrogen removal efficiency.

1. Introduction

Landfill leachate contains a cocktail of highly concentrated organics, nutrients and heavy metals, which imposes potential risks on the environment and human health. Leachate is notorious for its great variation in quality and quantity, which may frustrate conventional treatment

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technologies and adversely affect effluent quality. Leachate in situ recirculation, where landfill is considered as a huge bio-filter treating leachate through a series of physical, chemical and biological processes, not only improves leachate treatment but also accelerates waste stabilization (Abdallah et al., 2014). However, this accelerated process greatly promotes emission of greenhouse gases (GHGs), such as nitrous oxide. N_2O ranks among the persistent trace gases (144 years life-span) in the earth's atmosphere: its 100 year global warming potential (GWP) is estimated to be 298 times greater than that of carbon dioxide. Present-day N_2O content averages around 322.5 ppb, of which 40% is attributed to anthropogenic sources (WMO, 2010).

As described in Fig. 1, nitrous oxide can be produced via four distinct pathways, namely, heterotrophic and autotrophic denitrification, ammonia oxidation and dissimilatory nitrate reduction to ammonia (Giles et al., 2012; Wrage et al., 2001). The operational conditions in landfill leachate recirculation potentially include all of them. Specifically, N_2O could be emitted through nitrification in topsoil, or aeration layers. In these zones, intermediates like hydroxylamine are usually considered potential substrates for denitrification where N_2O emerges from incomplete NH_2OH oxidation. Moreover, in the anoxic or anaerobic (intermediate and bottom layers) zones, stepwise denitrification also contributes to nitrous oxide emission if reactions proceed under low pH and C/N ratio conditions (Wrage et al., 2001), where N_2O reductase inhibition stops heterotrophic denitrification at the N_2O stage. Apart from the coupled process in multiple landfill layers, autotrophic denitrification (attributed to ammonia oxidizers mainly) can also reduce nitrite via NO to N_2O, a pathway facilitated by low dissolved oxygen (DO) content and low retention time (Yang et al., 2009).

N_2O emission from landfill is estimated to be minor importance for the total N_2O emission, considering the small area of landfill as compared to other land-use classes, but it has been identified as an emerging anthropogenic N_2O emission source with fluxes one to three of magnitude higher than from fertilized soil (Rinne et al., 2005). N_2O–N emission from leachate treatment systems has been estimated at ~7.99 g capita/yr (Wang et al., 2014), and N_2O emissions from the biological treatment of sewage, manure, landfill leachate and industrial effluent contribute up to 10% of the total anthropogenic emission (Desloover et al., 2012). However, in terms of N_2O control and nitrogen removal during recirculation, operators usually consider them separately. Partial nitrification of ammonia to nitrite rather than nitrate via techniques, like air addition or semi-aeration, is advocated from the perspective of energy conservation and high nitrogen removal efficiency currently (Aziz et al., 2010). However, the added molecular oxygen and induced nitrite acclimatization can both constrain N_2O reductase activity (Noda et al., 2003; Otte et al., 1996). Research shows that major emission could stem from aerobic denitrification rather than anaerobic (Robertson et al., 1995). Therefore these techniques are not recommended from a greenhouse gas control perspective. Apart from that, emission surges fluctuate as a function of loading rates, soil properties (e.g. moisture content, pH value and texture) and leachate quality, particularly with respect to nitrogen speciation (Silva et al., 2008; Xie et al., 2013). In summary, the heterogeneity of waste composition and conflicting technical implications compound landfill management. Thus research focusing on coupled nitrogen removal and nitrous oxide mitigation by in-situ recirculation, as one of the most viable and economical methods, is urgently needed especially in the context of emission and pollutant reduction.

In this project, static chamber–gas chromatography technique was employed to simulate leachate in-situ recirculation in anaerobic condition where three aspects were investigated: (1) simulated leachate with different nitrogen composition (NH_3–N, equal molar of NH_3–N and NO_2–N, NO_2–N and NO_3–N); (2) different total nitrogen loads (90, 180 and 360 mg N/kg soil); (3) different biodegradable organics to nitrogen ratio (BOD/TN 0.2, 0.3 and 0.4). Meanwhile N_2O emission and relevant nitrogen removal efficiency were analyzed. This research evaluated the effects of these three variables in laboratory scale bioreactors and further elucidated mechanisms of simultaneous N_2O mitigation and nitrogen removal enhancement for in situ leachate recirculation.

2. Materials and methods

2.1. Raw and simulated leachate

Leachate samples were collected both from the equalization basin of the Shanghai Laogang (LG) landfill site and from a waste transfer station at Xupu (XP), Shanghai. Their relevant characteristics are listed in Table 1. The liquid samples draining from LG are typical aged leachate while the ones from XP are fresh. The Magnesium–Ammonium–Phosphate (MAP) method was employed to remove ammonia in the raw leachate, precipitated as struvite, where at least 90% ammonia can be stripped (Barnes et al., 2007). The specific process, operational parameters and test results of the MAP procedure are provided in the Supporting Information (SI). After that, leachate was prepared into different batches, as shown in Table 2. In Parts 1 and 2, only aged leachate samples were used, sodium nitrate/nitrite was added into the treated samples as anions–N source, and four types of simulated leachate

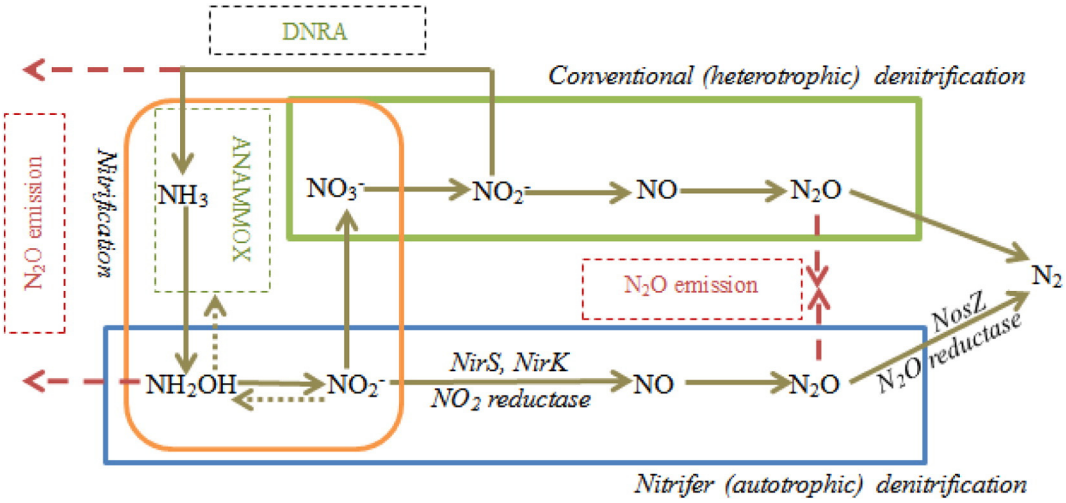

Fig. 1. Schematic diagram of the N_2O pathway involved in conventional nitrification and denitrification processes, where the transformation from ammonia to nitrogen gas was carried out by symbiosis/coexistence of different groups of microorganisms; the DNRA stands for dissimilatory nitrate reduction to ammonia, which in most cases is carried out in top soil layers and could generate nitrous oxide; the *NirS*, *NirK* and *NosZ* are nitrite and nitrous oxide reduction enzyme respectively.

Table 1
Characteristics of leachate from two sampling sites, LG and XP.

Leachate	COD mg/L	BOD5 mg/L	TN mg/L[a]	NH_3–N mg/L	pH	ORP mV
LG (aged)	2000–2600	340–520	1100–1350	850–1100	7.8–8.3	−375 to −235
XP (fresh)	40,000–65,000	20,000–35,000	950–1700	450–850	5.5–6.5	n.a.

[a] Nitrate and nitrite concentration in both of the raw leachate was <1.0 mg/L.

consisting of NH3–N, NO_2–N, NO_3–N and NH_3–N/NO_3–N with equal N-mol ratio were prepared in total. Besides, in Part 3, the fresh and aged leachates were both treated (by the MAP method) and mixed thereby producing simulated samples with 0.2, 0.3 and 0.4 BOD/TN ratios. Sodium nitrate was then added in the mixed samples to meet the required loading rate (Table 2).

2.2. Refuse solid samples

Solid samples (aged refuse soil) were taken from the 20 cm depth in Shanghai Laogang landfill site. Their general physical property is 1.6–1.75 g/cm^3 of density, 34%–36% of moisture content and 15%–20% of the VSS. Subsequent to removing plastic material, gravel and plants debris, the residuals were sifted out through sieves with 2 mm mesh. The recirculated leachate in practical operation scenario usually experiences three, aerobic–anoxic–anaerobic, treatment stages. In our research, we constructed bench scale reactors, simulating the last treatment phase (anaerobic), to analyze the nitrous oxide production rates and corresponding nitrogen removal efficiencies.

2.3. Incubation and sampling procedures

Table 2 lists three parts involved in this experiment. Different simulated leachates were employed as influent being added into aged refuse reactors, in order to investigate the total nitrogen removal efficiency and N_2O production rates at different ions–nitrogen forms and loading rates. 250 mL rubber sealed serum bottles were used to simulate anaerobic treatment phase in the incubation experiment where 25 g sifted aged refuse and 3 mL leachate was added precisely into each bottle, and then the in-bottle moisture content was adjusted to 52%. The leachate to soil (aged refuse) ratio was set according to the loading rates of the conventional leachate treatment units (Xie et al., 2012). Distilled water was adopted in the control group to provide emission flux benchmarks (Table S1). To create anaerobic operational conditions, original air in bottles was stripped by flushing with nitrogen gas for 5 min. All bottles were placed in a biochemical incubator (Jinghong SHP-150, China) at 25 °C.

The sampling was conducted on days 1, 2, 3 and 5 when 20 mL gas was drawn out by syringe. 24 h prior to each sampling, nitrogen gas was used to replace the headspace in bottles. When the incubation experiment was terminated, 10 g soil samples were taken from every bottle. The samples were mixed with KCl solution (2 M) and placed in a constant temperature oscillator (Jinghong TSQ-280, China) for 1 h at 120 r/min rate. The slurry was filtered (cellulose ester, 0.45 μm) through a vacuum pump and the nitrogen compounds of soil extracts and their corresponding concentration in filtrate were analyzed.

Table 2
Experimental focus in different parts.

Parts	Main focus and independent variables	Remarks[a]
Part 1	Effects of N-forms in influent leachate: NH_3–N, NH_3–N/NO_2–N = 1, NO_2–N and NO_3–N	All four types of leachate used
Part 2	Effects of N-loading rates: 360, 180 and 90	All four types of leachates used
Part 3	Effects of BOD/TN ratios: 0.2, 0.3 and 0.4; N-loading rate: 180	NO_3–N type leachate used

[a] N-loading rate unit in mg N/kg (soil).

2.4. Chemical analyses

Nitrous oxide gas concentration was measured by gas chromatography (GC, Agilent 7890A, USA) fitted with an electron capture detector (ECD) for N_2O detection, and using pure nitrogen gas as carrier gas at a flow rate of 35 cm^3/min. Working temperature of the separation and back flushing columns (Porapak-Q) and ECD were 55 °C and 330 °C respectively. The measurement of landfill leachate and soil extract parameters, COD, BOD_5, ammonia (NH_3–N), and total nitrogen (TN), and nitrate (NO_3–N) and nitrite (NO_2–N) was in accordance with the Standard Methods (APHA, 1998).

2.5. Data analysis

Mass concentrations (MC) of nitrous oxide obtained by gas chromatography in nM were converted to emission flux whose unit was μg N/kg-soil · h. The equation is listed below where V stands for the volume of bottles, 250 mL;M for the molar mass of N_2O, 44 g/mol;m for the dry weight of the soil samples, 25 g.

$$f(N_2O) = \frac{MC(N_2O) * V * M(N_2O) * \frac{28}{44}}{m * 24h}.$$

Considering that the organic nitrogen in mature leachate (injected for incubation) can be hardly degraded (Xie et al., 2012), nitrogen content is defined as the sum of NH_3–N, (NO_3–N) and NO_2–N in the soil extract. Nitrogen removal efficiency (R) calculation was based on the discrepancy between nitrogen content in original soil extract plus injected leachate (sum of nitrate, nitrite and ammonia) and nitrogen content in soil extract after incubation.

All treatments were done in triplicate and data for the variations are given as mean ± standard deviation (SD). All statistical analyses of the data were performed using SPSS 18.0 software (SPSS, Inc., Chicago, IL, USA), and $p < 0.05$ was considered statistically significant. No data was transformed prior to testing to enhance normality unless otherwise noted.

3. Results

3.1. Effects of nitrogen speciation on N_2O emission

Fig. 2 shows the nitrous oxide emission flux over five days. For the ammonia and nitrate groups (solid lines), the net emission flux was less than 1 μg N/kg-soil · h. In the first three days, net emission flux was essentially constant at 0.1 μg N/kg-soil · h, and then slightly increased to 0.6 and 0.3 μg N/kg-soil · h respectively in day 5. The nitrite and mixed (ammonia/nitrite with equal ratio) group (dashed lines) was in a sharp contrast. Their peak emission fluxes were detected in the first day for mixed leachate influent and the second day for nitrite type leachate, and both were around 650 μg N/kg-soil · h. However, the subsequent analysis from day 2 to day 5 showed parallel decline to 230 (NH_3–N/NO_2–N) and 400 μg N/kg-soil · h (NO_2–N) on day 5.

3.2. Effects of nitrogen loading rates on N_2O emission

As shown in Fig. 3, simulated leachate with three different nitrogen loadings, 90, 180 and 360 mg N/kg-soil, all increased the nitrous oxide

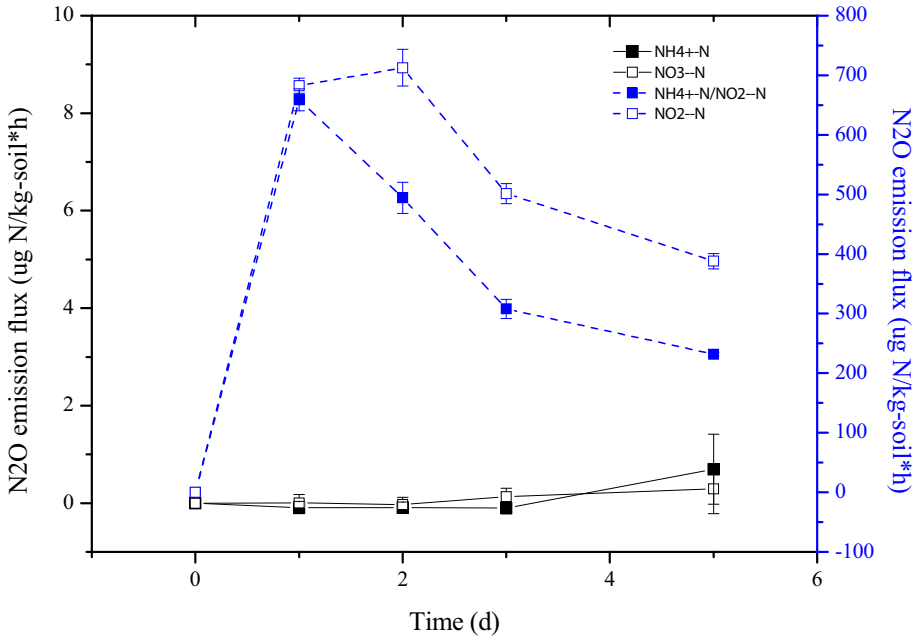

Fig. 2. Nitrous oxide emission flux in Part 1; dashed lines: nitrite and ammonia/nitrite (equal ratio) containing leachate; solid lines: ammonia and nitrate containing leachate. Error bars represent the standard deviation of replicate experiments (n = 3).

emission. Similar to the results in Part 1, addition of ammonia type leachate emitted least N_2O, where the highest flux (~0.3 μg N/kg-soil · h, 360 mg N/kg-soil loading) took place in day 5 while the flux under another two loading rates were both below 0.1 μg N/kg-soil · h. Likewise, nitrate type leachate did not prompt an emission surge immediately after injection; the peak value occurred in day 5 with a rate of ~12 μg N/kg-soil · h at a load of 360 mg N/kg-soil. The highest flux of the mixed type leachate appeared in the first three days, day 1 (90 mg N/kg-soil), 2 (180 mg N/kg-soil) and 3 (360 mg N/kg-soil), whose fluxes were 190, 490 and 585 μg N/kg-soil · h respectively. However, they all decreased to <100 μg N/kg-soil · h in the day 5. The nitrite type leachate on the other hand brought about steady daily increment in flux during the 5 days. The fluxes all gradually increased to 450–550 μg N/kg-soil · h in the initial three days. After that, bottles loaded with 360 and

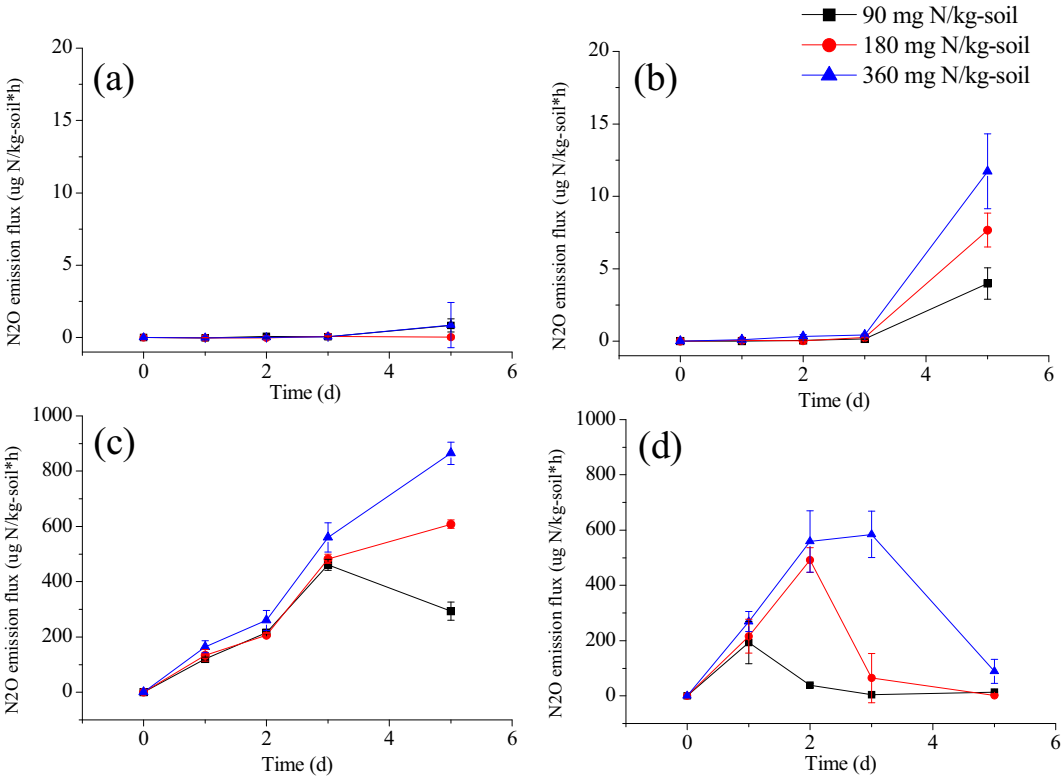

Fig. 3. Influence of total nitrogen loading rates on N_2O emission flux; the triangle, circle and square lines indicate 360, 180 and 90 mg N/kg-soil loading rates respectively; (a), (b), (c) and (d) represent flux of NH_3–N, NO_3–N, NO_2–N and mixed (NH_3–N/NO_2–N = 1) type leachate respectively.

180 mg N/kg-soil leachate still kept 860 and 600 μg N/kg-soil · h emission rate respectively at last, but the flux under 90 mg N/kg-soil loading rate experienced a decline to 294 μg N/kg soil · h. The halved flux may imply the depletion of available nitrogen compounds for N_2O production in influent.

3.3. Effects of BOD/TN ratios on N_2O emission

Fig. 4 shows the nitrous oxide flux during Part 3 where different biodegradable-carbon/nitrogen ratios were investigated as independent variables. Overall, the lower BOD/TN ratio leachate appeared to perform quicker N_2O surges. Bottles injected with 0.2 BOD/TN ratio leachate emitted ~10 μg N/kg-soil hourly on day 3, the peak fluxes were all detected on day 5 irrespective of BOD/TN ratios. The maximum fluxes of three BOD/TN ratio leachates were 2 (0.4), 15 (0.3) and 22 μg N/kg-soil · h (0.2), but all decreased to the nearly none on day 10. Notably, when the BOD/TN ratio shifted from 0.2 to 0.4, the peak flux decreased around 10 times, with statistically significant difference ($p < 0.05$). This implies that the nitrous oxide emission rate is inversely proportional to the degradable carbon content.

3.4. Nitrogen removal in different experimental parts

Table 3 shows nitrogen removal efficiencies of the four types of simulated leachate. Nitrate type leachate had the highest removal efficiency (67%) and the lowest ammonia type leachate, 22% only. Bottles injected with mixed (NH_3–N/NO_2–N) and nitrite type leachate showed removal efficiencies of 48% and 64% respectively. In Part 2, bottles injected with NH_3–N type leachate removed 41% and 45% total nitrogen under 90 and 180 mg N/kg-soil loads respectively, while the 360 mg N/kg-soil loading rate decreased the efficiency to 30%. By contrast, the same loading rate of mixed leachate slightly raised removal efficiency to 58%, and meanwhile the efficiencies in 90 mg N/kg-soil and 180 mg N/kg-soil conditions remained around 50%.

It is interesting to note that doubling the loading rate led to increased nitrogen removal efficiency, though slightly. This stepwise increase pattern of nitrogen removal, more pronounced, was observed from bottles injected with nitrite and nitrate type leachates, and the efficiencies increased from 40% to 56% (for nitrite type) and 52% to 73% (for nitrate) correspondingly. In Part 3, the BOD/TN ratio was proportional to its corresponding nitrogen removal efficiency. Around 75% nitrogen was removed from the leachate (0.4 BOD/TN ratio) and the removal efficiencies of leachate with 0.3 and 0.2 BOD/TN ratio were 70% and 62% respectively. It appeared that higher biodegradable content enhanced nitrogen removal efficiencies and lowered emission rates simultaneously.

4. Discussion

4.1. Evaluation of N_2O emission of different simulated leachates

In this project, nitrite containing leachate gave rise to nitrous oxide emissions that were hundredfold higher than from non-nitrite containing leachate. This difference increased with increasing nitrogen loads (Fig. 3). From the perspective of the nitrogen circle, nitrite was considered an intermediate in both heterotrophic (conventional) and autotrophic (nitrifying bacteria) denitrification process (Fig. 1). In sequencing batch reactors N_2O was reportedly emitted when the nitrite concentration was maintained at the 5 mg/L, which was ascribed to enzyme inhibition (Lemaire et al., 2006); the influent nitrite content applied in our research was at least 225 mg/L (90 N/kg-soil) which would magnify this inhibition. As shown in Fig. 3(c), when the nitrogen loading rate increased from 90 mg N/kg-soil to 360 mg N/kg-soil, max emission flux was doubled (860 μg N/kg-soil · h vs. 450 μg N/kg-soil · h). Also, the leachate whose N_2O flux was higher than the others had correspondingly higher nitrite residuals after incubation (Figs. S2, SI), which may imply that nitrite is the substance inducing N_2O surges. Also, the high N_2O concentrations accompanying these high fluxes can impair rather than merely inhibit nitrite reductase (enzyme *Nir*) due to the high affinity of enzyme's synthetic metal ions for N_2O (Felgate et al., 2012; Schulthess et al., 1995). Similar bench scale tests also revealed nitrite induced nitrous oxide surges (Gong et al., 2012), and when nitrite increased from 10 mg/L to 40 mg/L, N2O, emission flux increased twofold 0.27 mg N_2O–N/(kg-sludge · h) to 0.6 mg N_2O–N/(kg-sludge · h). Moreover, the pronounced flux difference between the mixed and nitrite type leachate also suggested that a high nitrite concentration brings about a pronounced inhibition (Fig. 2). Insufficient aeration in leachate reservoirs and air addition (semi-aerobic) in landfill both resulted in partial nitrification, which were followed by significant N_2O flux surges as well (Lin et al., 2008). Additionally, the aged leachate draining from Laogang landfill could only provide 0.1–0.2 BOD/TN ratio (Table 1), presumably constraining denitrification and resulting in the emission of N_2O. This implies that limited or partial nitrification particularly in aged leachate can lead to greater N_2O emission.

When the influent changed to nitrate type leachate, it did not cause drastic N_2O emission in the initial days (Fig. 2), which is similar to

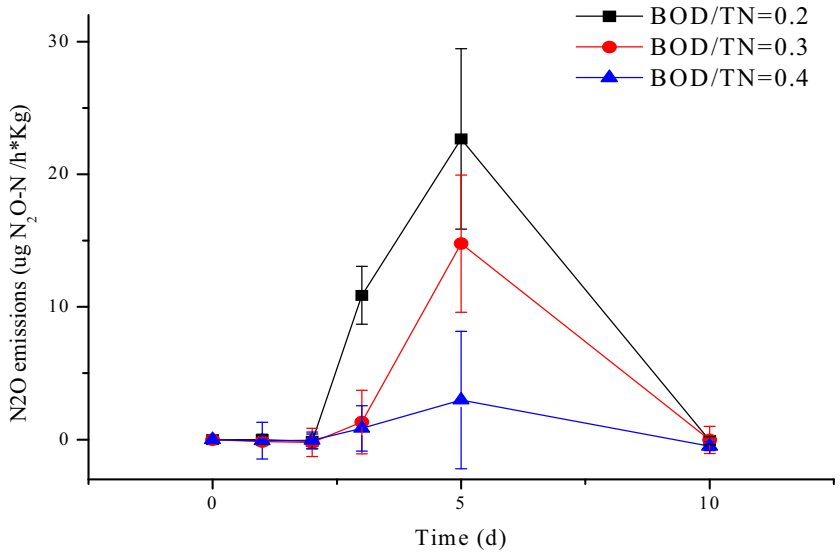

Fig. 4. Influence of BOD/TN ratios on nitrous oxide emission flux; the square, circle and triangle indicate leachate with 0.2, 0.3 and 0.4 BOD/TN ratios respectively.

Table 3
Nitrogen removal efficiency after incubation of three parts.

Leachate	NO_3–N	NH_3–N/NO_2–N (Mixed)	NO_2–N	NH_3–N	N-load*	BOD/TN
Part 1	67.1 ± 10.6%	47.8 ± 9.0%	63.8 ± 14.6%	22.5 ± 9.3%	180	n.d.
Part 2	52.1 ± 25.6%	49.3 ± 10.3%	42.9 ± 7.3%	41.2 ± 18.2%	90	n.d.
	61.8 ± 12.7%	49.4 ± 12.8%	49.4 ± 18.8%	45.4 ± 9.9%	180	n.d.
	72.6 ± 11.3%	57.6 ± 7.1%	55.9 ± 11.4%	29.9 ± 11.9%	360	n.d.
Part 3	61.8 ± 12.4%				180	0.2
	69.9 ± 10.6%				180	0.3
	74.6 ± 12.1%				180	0.4

n.d: not determined.
* N-loading rate unit is mg N/kg-soil.

observations made in a field test of completely nitrified leachate recirculation where no significant N_2O release was recorded in the first week (Tallec et al., 2009). Increasing of the loading rate also tripled emission fluxes in day 5 (from ~3 μg N/kg-soil · h to ~10 μg N/kg-soil · h). These values were similar to the results of incubation tests of landfill cover soil, ranging from 2 μg N/kg-soil · h to 16 μg N/kg-soil · h, under 100 mg nitrate–N/kg-soil the loading rate (Zhang et al., 2008). This direct proportionality between nitrogen loading rate and emission was also observed in simulated landfill bioreactors, attributed to limited denitrification by low dissolved oxygen (DO) and carbon content (Giraldo, 2009). However, the flux was still lower than from nitrite containing leachate. This is probably because of the low reproduction rates of facultative anaerobes (denitrifiers) at low DO, which reduced nitrate reduction rates and consequently nitrite accumulation (Sun et al., 2013). In addition, the significant N_2O flux reduction (Fig. 4), companied by BOD/TN ratio increase of nitrate type leachate, was also observed. This implies that heterotrophs were responsible for the denitrification.

Compared with other leachates, the ammonia type leachate did not stimulate N_2O emission. The increasing loading rate did not impose any significant effects either (less than 1 μg N/kg-soil · h). This is not surprising considering that production of N_2O from ammonia requires O_2 (Fig. 1), which was absent from the headspace in our incubations. N_2O surges caused by ammonia and methane co-oxidizing bacteria have been observed, but the flux was consistently below 4 μg N/kg-soil · h when the nitrogen loading rate was 100–130 mg ammonia–N/kg-soil (Yu et al., 2009; Zhang et al., 2009), which also agrees with our results. Even if small amount of ammonia could be oxidized by these bacteria, the high NH_3–N loading rate of leachate can strongly inhibit responsible enzyme (*NirK & NorB*) for denitrification in AOBs (Kool et al., 2011), therefore substrates (NO) for the production of N_2O were barely provided in this experimental condition (Fig. 1).

4.2. Evaluation of nitrogen removal of different simulated leachates

Nitrogen removal in ammonia type leachate was low, and doubling of the loading rate (180 to 360 mg N/kg-soil) almost halved the removal efficiency (Table 3). This indicates that nitrogen removal capacity was saturated. The landfill bioreactor did not perform effective ammonia reduction under anaerobic conditions. Instead of removal, the running landfill sites usually encounter the high NH_3–N residual problem in leachate after long time recirculation (Shao et al., 2008; Zhong et al., 2009). The limited capacity results from poor nitrification since ammonia oxidizing bacteria and archaea require oxygen for ammonia oxidation. However, the observed NH_3–N removal can presumably be ascribed to absorption by the soil particulates as a part of polydentate ligands or humic substances (Hartley et al., 2014; Havelcova et al., 2009).

By contrast, the nitrogen removal efficiency of the nitrite and mixed leachate was greater than the ammonia leachate. Removal efficiency in nitrite based incubations both ranged from 40% to 60% (Table 3). Denitrification is known to be performed by both heterotrophic and autotrophic denitrifiers, and the collaboration can lead to high removal efficiency even at the low organic content leachate from aged landfill (Sun et al., 2014). Moreover, compared with nitrite only, mixed (nitrite plus ammonia) leachate performed slightly better with statistic difference ($p < 0.05$) in Part 2, probably due to less inhibition caused by the lower nitrite content.

The highest nitrogen removal efficiencies belonged to bottles fed with nitrate type leachate, up to ~70% at maximum (Table 3), and doubling nitrate loading resulted in a 10% nitrogen removal efficiency increase. Indeed, nitrified raw leachate showed higher nitrogen removal efficiency in the anaerobic than the aerobic zone of landfill sites (Shao et al., 2008). This is because nitrate would be highly favored as electron accepter in the absence of oxygen (Khdyer et al., 1982). Notably, this efficiency increase did not induce pronounced N_2O surges. The specific maximum total N_2O emission of nitrite type leachate (<4 mg N/kg-soil) during the 5-day experiment accounted for ~1% of the total nitrogen loaded, which is equivalent to about 1.5% nitrogen was removed as N_2O. However, the mixed (and nitrite) type leachates' total N_2O emissions were ~40 and ~50 mg N/kg-soil respectively, and this means that ~40% nitrogen (removed) emitted as N_2O. Similar to nitrite, nitrate can also be reduced by both autotrophic and heterotrophic denitrifying bacteria. The experiments in Part 3 showed that degradable carbon content played a pivotal role, indicating that the main microorganisms responsible for denitrification are typically heterotrophs (Lee et al., 2002; Xie et al., 2013). Carbon source is insufficient in our experiments, however, the autotrophic denitrifiers could still offset the loss, where the aged (45 years old) landfill bioreactor still possessed 3.8 mg N/kg-soil capacity of denitrification (Jokela et al., 2002). Further, the stepwise increment in nitrogen removal in Part 2 implied the existence and potential role of other possible pathways in carbon source limited scenarios, in which sulfur plays a role as potential electron donor (Flere and Zhang, 1998; Zhang and Lampe, 1999).

5. Conclusion

The application of nitrate type leachate for landfill recirculation was proven to be a viable approach to simultaneously enhance nitrogen removal efficiencies and reduced N_2O emission. Study on the four types of leachates indicated that the presence of nitrite could inhibit microbial activities pertinent to N_2O reduction and this issue may be alleviated when the BOD/TN of raw leachate was kept no less than 0.4. The general take-home messages are that: prior to leachate in situ recirculation, sufficient pre-aeration is critical to control N_2O surges, particularly for mature leachate with low BOD/TN ratios, and limited (partial) nitrification in open leachate reservoirs and top soil should be avoided.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.01.021.

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