



# Quantification of N and C cycling during aerobic composting, including automated direct measurement of N<sub>2</sub>, N<sub>2</sub>O, NO, NH<sub>3</sub>, CO<sub>2</sub> and CH<sub>4</sub> emissions



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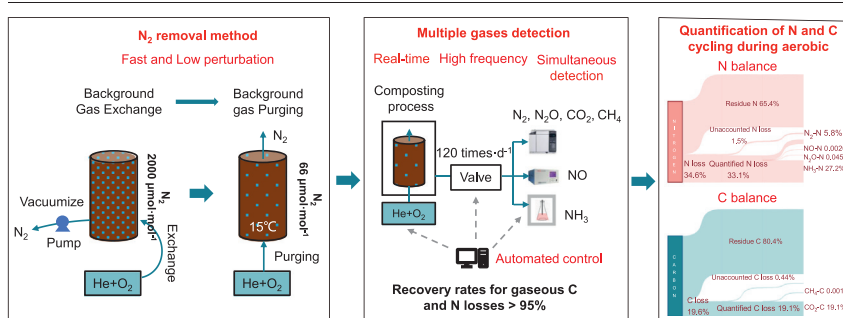
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## HIGHLIGHTS

- Simultaneous measurement of N<sub>2</sub>, NH<sub>3</sub>, NO, N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> emissions in composting
- Measurement frequency of up to 120 times d<sup>-1</sup>
- A fast and low-perturbation N<sub>2</sub> removal method was developed for N<sub>2</sub> measurement.
- N<sub>2</sub> loss from composting was first quantified directly.
- Up to 97.8 % of gaseous C and 95.6 % of gaseous N losses were quantified.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Closing the carbon (C) and nitrogen (N) balance has yet to be achieved in aerobic bioprocess due to current methodological drawbacks in the frequency of sampling and detection and the challenge in direct measurement of instantaneous N<sub>2</sub> emission. To address this issue, a novel system was developed enabling simultaneous and online determination of gaseous C and N species (N<sub>2</sub>, N<sub>2</sub>O, NO, NH<sub>3</sub>, CO<sub>2</sub> and CH<sub>4</sub>) from aerobic composting at a high frequency of 120 times d<sup>-1</sup>. A helium-oxygen gas mixture was used to replace the air in the system to enable direct measurement of N<sub>2</sub> emission, and three different gas exchange methods were assessed in their ability to minimize atmospheric background N<sub>2</sub>: 1) the N<sub>2</sub>-free gas purging method; 2) one cycle of the evacuation-refilling procedure; 3) one cycle of evacuating and refilling followed by N<sub>2</sub>-free gas purging. Method 3 was demonstrated as an optimum N<sub>2</sub>-removal method, and background N<sub>2</sub> concentrations decreased to ~66 μmol·mol<sup>-1</sup> within 11.6 h. During the N<sub>2</sub>-free gas purging period, low temperature incubation at 15 °C reduced CO<sub>2</sub>, CH<sub>4</sub>, NO, N<sub>2</sub>O and NH<sub>3</sub> losses by 80.5 %, 41-fold, 10-fold, 11,403-fold and 61.4 %, respectively, compared with incubation at 30 °C. Therefore, a fast and low-perturbation N<sub>2</sub> removal method was developed, namely the evacuating/refilling-low temperature purging method. Notably, all C and N gases exhibited large within-day variations during the peak emission period, which can be addressed by high-frequency measurement. Based on the developed method, up to 97.8 % of gaseous C and 95.6 % of gaseous N losses were quantified over a 43-day compost incubation, with N<sub>2</sub> emission accounting (on average) for 5.8 % of the initial total N. This system for high frequency measurement of multiple gases (including N<sub>2</sub>) provides a novel tool for obtaining a deeper understanding of C and N turnover and more accurate estimation of reactive N and greenhouse gas emissions during composting.

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## 1. Introduction

Sustainable solid waste management is becoming an increasingly pressing issue facing humanity. The main waste productions are associated with urban, industry, and food production systems. It is estimated that annual solid waste generation will increase drastically by 70 % from 2016 levels to 3.40 billion tonnes in 2050, with approximately 46 % of this as organic waste (Awasthi et al., 2018; Kaza et al., 2018). Of all organic waste management practices, composting represents large anthropogenic sources of carbon (C) and nitrogen (N) losses (Pardo et al., 2015; Awasthi et al., 2018), due to the high substrate availability and microbial activity in compost. If improperly managed, composting can not only cause environmentally damaging pollution but also air quality and human health impacts (Czepiel et al., 1996; McNicol et al., 2020). As estimated, 20–45 % of the initial N is typically lost, mostly (30–70 %) in the form of ammonia (NH<sub>3</sub>), with associated risks to human health and ecosystems. There is also an important loss in the form of nitrous oxide (N<sub>2</sub>O, 0.02–9.9 %), as well as 0.1–12.6 % of the initial C typically lost as methane (CH<sub>4</sub>), both of which are potent greenhouse gases (GHG) with global warming potentials of 268 and 28 times that of carbon dioxide (CO<sub>2</sub>), respectively (Pardo et al., 2015; Cao et al., 2019). Therefore, there is a need to be able to accurately quantify and control these GHG and reactive nitrogen (Nr) emissions from composting for climate neutrality and pollution control. However, characterizing all the forms of gaseous C and N losses from solid waste composting remains a critical knowledge gap in regulating these emissions and developing more effective and targeted reduction options.

Simultaneous measurements of CO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, N<sub>2</sub>O in composting have been made in the past three decades using chamber-based techniques (Pardo et al., 2015). However, these data are subject to high uncertainties, because of: i) the low measurement frequency, which is often limited to daily-to-weekly measurement intervals due to resource constraints, which may result in unrepresentative values and trends, especially in composting, where the microbial C and N turnover is intense; and ii) inability to conduct real-time measurement, owing to sampling-detection separation, possibly resulting in an underestimation of gas concentrations and emissions, given the potential leakage during sample storage and transport. We hypothesized that these current uncertainties can be substantially reduced by using a high frequency automatic sampling and online analyzing system. Development of such a measuring system would help to determine within-day variations and obtain robust estimates of gaseous C and N species from composting.

Simultaneous measurements of all gaseous C and N species from composting have yet to be made. Measurement of dinitrogen (N<sub>2</sub>) and nitric oxide (NO) emissions are particularly challenging, due to their high background concentration (N<sub>2</sub>) or instability in the environment (NO) (Pardo et al., 2015). Lack of measurement of these results in substantial unaccounted N losses (~30 %), which are mainly assumed to be as N<sub>2</sub>, and generally estimated by mass balance approaches (Cao et al., 2019). Emissions of N<sub>2</sub> are environmentally benign, representing the end-product of N cycling and the conversion of Nr forms back to the inert form but such emissions represent a loss of N, and the associated fertilizer value, from compost. Various approaches to measure N<sub>2</sub> production in soil have been developed, such as acetylene-based methods, <sup>15</sup>N tracers, direct N<sub>2</sub> quantification, and mass balance approaches (Butterbach-Bahl et al., 2013). Of these, the direct N<sub>2</sub> quantification methods, including robotized incubation systems (Molstad et al., 2007; Qin et al., 2017) and gas-flow-soil-core techniques (Scholefield et al., 1997; Butterbach-Bahl et al., 2002), are advantageous, being non-destructive and with no isotopic labels or inhibitors being introduced into the soil (Groffman et al., 2006). However, the principles and methods that are used to measure gaseous C and N species from soil are based on static and semi-dynamic chamber techniques, appropriate for measuring gases emitted from soil by diffusion mechanisms (Chadwick et al., 2001) which may not be applicable to aerobic composting, where forced aeration is usually dominant. Dynamic chambers are therefore more appropriate for measurement from composting (Pardo et al., 2015). However, the detection of small and instantaneous changes in N<sub>2</sub> against

the large concentration in ambient air remains a significant challenge for the accurate determination of N<sub>2</sub> emissions.

Direct measurement of N<sub>2</sub> emission generally, therefore, requires the replacement of the ambient air with an N<sub>2</sub>-free gas mixture. The evacuating and refilling method (Molstad et al., 2007; Wang et al., 2011) and N<sub>2</sub>-free gas purging method (Butterbach-Bahl et al., 2002; Cardenas et al., 2003) have been developed to achieve this. Shortcomings are mainly associated with (a) the long time needed to establish an N<sub>2</sub>-free atmosphere, (b) poor air tightness, with leakages resulting in ineffective N<sub>2</sub> removal, and/or (c) the high perturbation resulting from C and N losses during the N<sub>2</sub> removal period. Here, a fast and low-perturbation N<sub>2</sub> removal method, with a significantly greater N<sub>2</sub> removal efficiency, was developed to improve the sensitivity and reliability for N<sub>2</sub> emission measurement.

One of the major goals of this study was to develop an automated sampling and analyzing system for the simultaneous measurement of all the gaseous C and N products from composting (CO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, NO, N<sub>2</sub>O, N<sub>2</sub>), as well as oxygen (O<sub>2</sub>) and temperature, with a high sampling and analyzing frequency of 120 times·d<sup>-1</sup>. To achieve this goal, an intelligent temperature-controlled compost incubation system was developed, which allowed simulation of the whole composting process with variable temperature control. We used the system to analyze the temporal dynamics of all C and N gas emissions from composting, and to estimate the impacts of sampling frequency on emission estimates.

## 2. Material and methods

### 2.1. General description of the automated sampling and analyzing system for gaseous C and N

The measurement system comprised a compost temperature intelligent control and incubation unit, an automated gas circuit switching and sampling unit, a multi-gas automatic detection unit, and an automated control unit (Fig. 1). The compost temperature intelligent control and incubation unit includes a biochemical incubator (Yongsheng Instrument, China), six closed composting reactors (Fig. S1) each with a thermal sensor, a gas cylinder providing the through-flow air for composting and six mass flow controllers (MKS Instruments, Inc. USA) regulating the gas flow rate in each reactor. The incubation temperature is computer controlled through a step-wise temperature control program. A total of 10 temperature-change steps can be set, and each step has a temperature control range of 0–99 °C and a maximum time setting of 99 h per step. This design enables automatic temperature control and real-time data recording. The multi-gas automatic detection unit includes a NH<sub>3</sub> absorption device, a gas chromatograph (Agilent 7890B, USA), and a TE 42i NO-NO<sub>2</sub>-NO<sub>x</sub> chemiluminescent analyzer (Thermo Environmental Instruments Inc., USA). Before use, the GC were calibrated with standard gases provided by the National Standard Substances Center of China, and NO analyzer using NIST traceable standard NO gas through multi-point calibrator cum dynamic dilutor (Model 146i, Thermo Scientific, USA). The automated gas circuit switching and sampling unit included: i) a drying unit (Perma Pure LLC, USA) with a double-layer structure, such that as gas passes through the inner tube, water vapor passes through a membrane to the outer tube and is removed by dry gas; ii) a sampling unit comprising three solenoid valves and a multi-positional valve (VICI, Valco, USA), connected to the 1/8th inch stainless steel sampling lines. Automated valve control directed the airflow from each reactor sequentially to the analytical devices with a sampling frequency for all gas samples of 20 times·d<sup>-1</sup> per reactor (Fig. S2). The automated control unit provided overall control of the system via giving/receiving signals to/from i) the multi-positional valve and solenoid valves for setting the target position, ii) the GC for ready signal or to start/stop a method, iii) the NO analyzer for NO concentration or flow rate recording, iv) the compost temperature intelligent control and incubation unit for temperature control and recording, v) the mass flow controllers for flow rate control and recording, and vi) the computer (VMWare ACE) to start/stop data acquisition and system operation.

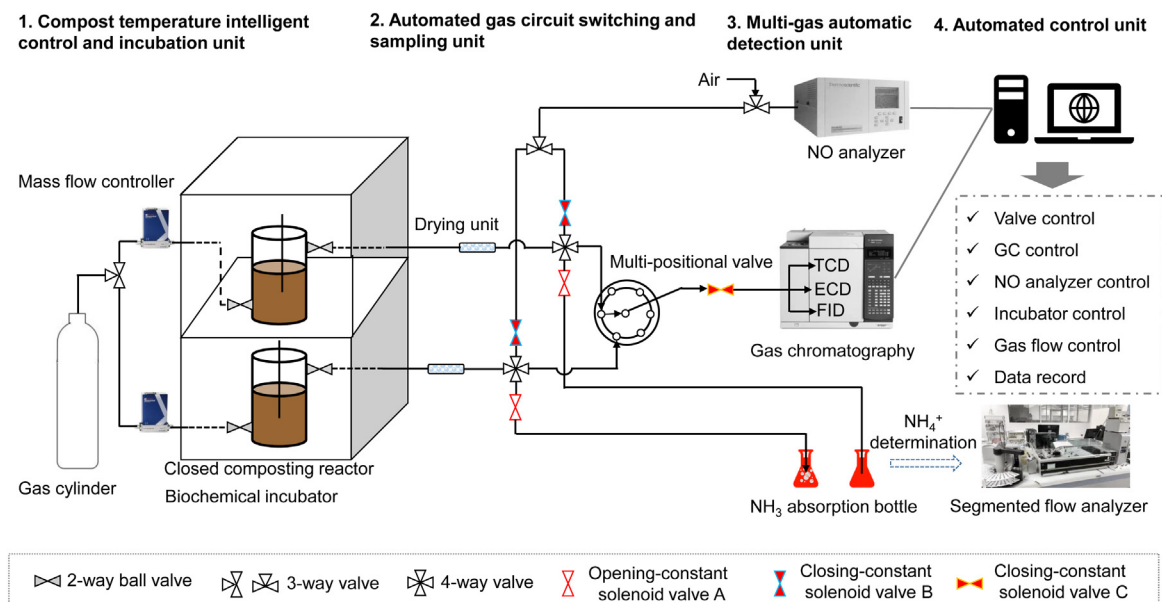


Fig. 1. Schematic representation of the measuring system.

## 2.2. Evaluation of the measuring system

Minimizing leakage of the system to guarantee gas tightness is a prerequisite for the measurement of C and N gases (especially  $N_2$ ). To achieve this, huge efforts were made to minimize the leakage through the use of stainless-steel components (e.g., valves, mass flow controller, reactor, gas line), and all connections throughout the system were tested using a liquid leak detector (Snoop, Swagelok, US). To ensure the gas tightness of the reactors, 8-screw fixing lids and O-ring seals were used (Fig. S1), and during incubation the reactors were inverted with the lids immersed under water to reduce potential  $N_2$  diffusion into the reactor. The reliability and repeatability of the measuring system was evaluated using an artificial gas mixture. In detail, stainless steel balls with the same volume as 1.0 kg of compost were placed into each of six reactors and purged with a standard gas mixture for several hours. No significant difference in gas concentrations was observed between the six reactors when constant concentrations were reached (Fig. 2). This confirmed that the developed automatic measuring system could detect compost-derived  $NH_3$ , NO,  $N_2O$ ,  $N_2$ ,  $CO_2$  and  $CH_4$  emissions with good repeatability. Measurement accuracy was confirmed by the high goodness of fit of the standard curves ( $R^2 < 0.999$ , Fig. S3). Using this system, high precision concentration measurements for  $N_2$ , NO,  $N_2O$ ,  $CO_2$  and  $CH_4$  were obtained (Table S2).

## 2.3. Experimental design

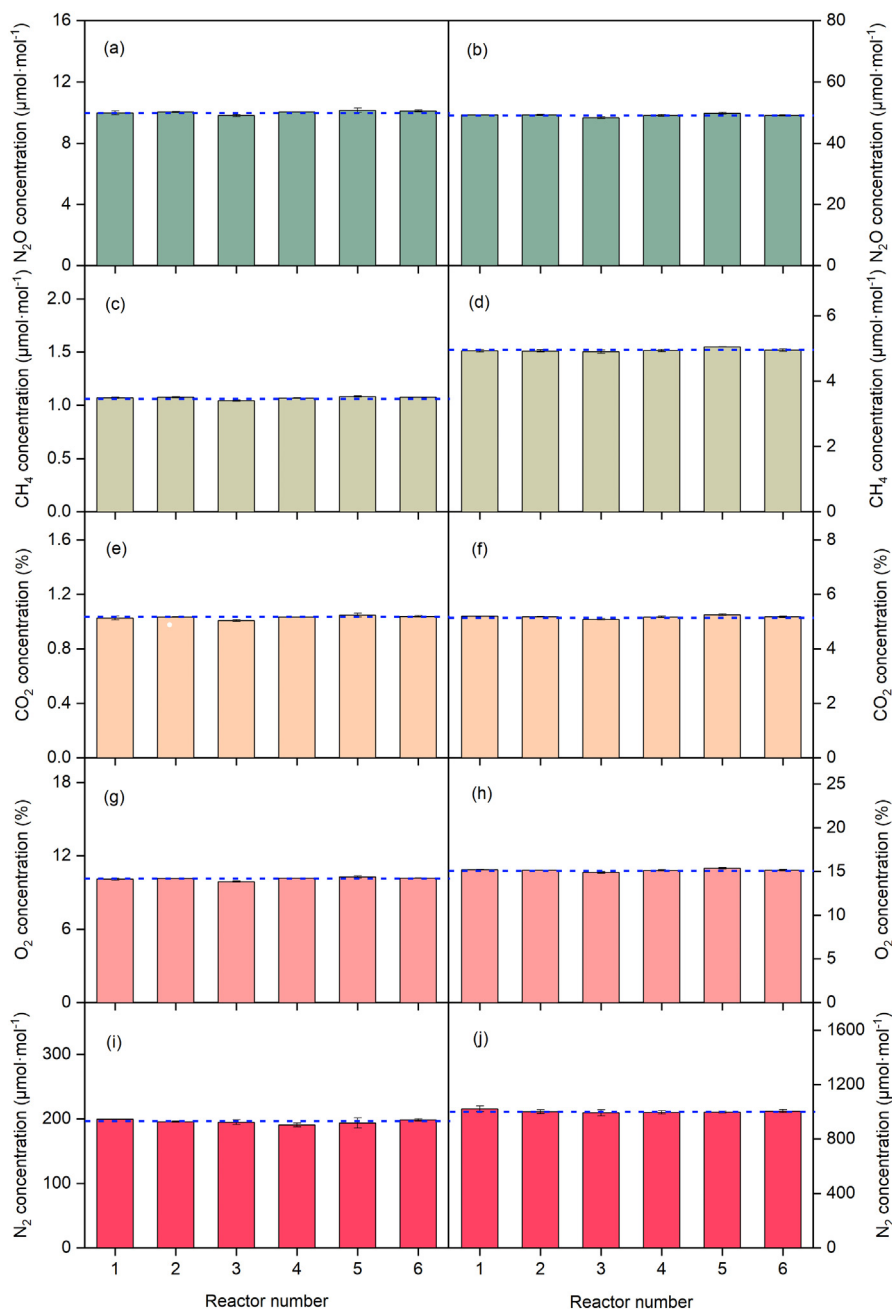
Two experiments were conducted: Experiment 1, to compare different  $N_2$  removal methods and assess the incubation conditions during the  $N_2$  removal phase, and Experiment 2, to quantify all forms of gaseous C and N species from the whole composting process. Fresh poultry manure and sawdust were used as raw material for composting in both experiments. The initial C/N ratio of the feedstock was  $\sim 20$ , with a moisture content of  $\sim 63\%$ .

Experiment 1: Three  $N_2$  removal methods were compared including the evacuating and refilling method, the  $N_2$ -free gas purging method and the evacuating/refilling combined with  $N_2$ -free gas purging method. For the evacuating and refilling method, the number of cycles of evacuating and refilling to reach a constant  $N_2$  concentration in the replacement atmosphere was assessed. In detail, 1.0 kg autoclaved compost (autoclaved at  $121^\circ C$  for 3 h and then incubated at  $25^\circ C$  for 21 h, 3 cycles) was put into duplicate reactors and then evacuated and refilled with the 79 %  $He$  and 21 %  $O_2$  atmosphere for different numbers of cycles (1, 2 or 3 cycles),

and then connected to the measuring system inside the incubator for gas concentration detection. Replacement of the  $N_2$ -rich atmosphere was conducted by repeatedly evacuating the reactor ( $\sim 200$  Pa) for  $\sim 5$  min using a vacuum pump (RV12 Edwards, UK) connected to a pressure meter, and refilling with a 79 %  $He$  and 21 %  $O_2$  gas mixture. The refilling procedure produces an overpressure, which was released by opening the outlet valve for several seconds. To investigate the perturbation effect of the evacuating and refilling procedure on microbial respiration, two closed reactors containing compost with no evacuation/filling procedure were included as control in the experiment and  $CO_2$  concentrations from these closed reactors were measured at hours 0, 1, 2, 3, 4. For the  $N_2$ -free gas purging method, 1.0 kg compost was put into duplicate reactors which were then purged with a make-up atmosphere containing 79 %  $He$  and 21 %  $O_2$  at a flow rate of  $80\text{ mL}\cdot\text{min}^{-1}$  (equivalent to an aeration rate of  $0.2\text{ L}\cdot\text{min}^{-1}\cdot\text{kg}$  dry matter for composting) until a constant  $N_2$  concentration was reached. For the evacuating/refilling combined with  $N_2$ -free gas purging method, 1.0 kg compost was put into duplicate reactors which were evacuated and refilled with the 79 %  $He$  and 21 %  $O_2$  atmosphere and then purged as above until a constant  $N_2$  concentration was reached. From these experiments we were able to evaluate the minimum time needed to fully and reliably replace  $N_2$  and the  $N_2$  removal effect.

It is important to maintain optimal incubation conditions during the  $N_2$ -free gas purging period to allow a full assessment of gaseous C and N losses; therefore, an assessment of the effect of incubation temperature during this period was included. Briefly, compost feedstock of 1 kg was placed into the reactor, and after the evacuating and refilling procedure it was purged for several hours with a make-up atmosphere containing 79 %  $He$  and 21 %  $O_2$  at a flow rate of  $80\text{ mL}\cdot\text{min}^{-1}$  until a constant  $N_2$  concentration was reached. During the  $N_2$ -free gas purging period, the incubation temperature was set to either  $15^\circ C$  (the lower limit of the incubator) or  $30^\circ C$ , in triplicate. Concentrations of  $NH_3$ ,  $N_2$ ,  $N_2O$ , NO,  $CH_4$ ,  $CO_2$  and  $O_2$  were analyzed until the  $N_2$  reached a constant concentration to compare the gaseous C and N losses at different incubation temperatures.

Experiment 2: Compost feedstock (1 kg) was placed into each of five replicate reactors. After  $N_2$  removal using the developed method (evacuation-refilling followed by purging), the incubation temperature was set to simulate the whole composting process according to the results from a previous composting experiment (Cao et al., 2020), and concentrations of  $NH_3$ ,  $N_2$ ,  $N_2O$ , NO,  $CH_4$ ,  $CO_2$  and  $O_2$  were measured. Incubation temperature increased to  $50^\circ C$  over the first day (mesophilic phase), was then stabilized at  $50^\circ C$  for 10 days (thermophilic phase), and then dropped to  $30^\circ C$  over



**Fig. 2.** Gas concentrations after system stabilization of  $\text{N}_2\text{O}$  (a and b),  $\text{CH}_4$  (c and d),  $\text{CO}_2$  (e and f),  $\text{O}_2$  (g and h) and  $\text{N}_2$  (i and j) from repeatability tests ( $n = 3$ ; error bars show standard error of mean values); the blue dotted line indicates the concentration of the standard gas:  $10 \mu\text{mol}\cdot\text{mol}^{-1}$  (a),  $49 \mu\text{mol}\cdot\text{mol}^{-1}$  (b),  $1.03 \mu\text{mol}\cdot\text{mol}^{-1}$  (c),  $4.96 \mu\text{mol}\cdot\text{mol}^{-1}$  (d),  $1.05 \%$  (e),  $5.06 \%$  (f),  $10 \%$  (g),  $15 \%$  (h),  $202 \mu\text{mol}\cdot\text{mol}^{-1}$  (i),  $997 \mu\text{mol}\cdot\text{mol}^{-1}$  (j).

2 days (cooling phase) and was finally stabilized at  $30^\circ\text{C}$  for 30 days (curing phase). The compost samples were analyzed for moisture content, and total C and N content at the start and end of composting. Total C and N contents of initial and final feedstock were as shown in Table S1. A parallel incubation with stainless steel balls of the same volume as the compost was used as a control to quantify the baseline gaseous concentrations over time, during which the  $\text{N}_2$  concentration stabilized at  $66 \mu\text{mol}\cdot\text{mol}^{-1}$ . This value was assumed as the inherent  $\text{N}_2$  concentration of the purging gas, since it could not reasonably be further reduced. These baseline concentrations were subtracted from the measured gas concentrations from the compost reactors when calculating emissions. To determine variability during the hotspot period of  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$  emissions, compost ( $1.0 \text{ kg}$ ) containing high  $\text{NO}_2^-$  content ( $2.8 \text{ g}\cdot\text{kg}^{-1}$ ) from the curing phase was incubated in

triplicate at  $30^\circ\text{C}$  for  $\sim 400 \text{ h}$ . It has been reported that the  $\text{N}_2\text{O}$  emission peak occurred when  $\text{NO}_2^-$  accumulated (He et al., 2001; Cao et al., 2021).

#### 2.4. Sample analysis

Moisture content was determined by drying fresh samples in triplicate at  $105^\circ\text{C}$  in an oven for  $\sim 24 \text{ h}$ . Gas concentrations in the air flow from the gas cylinder ( $c_{\text{background}}$ ,  $\mu\text{mol}\cdot\text{mol}^{-1}$ ) and reactors ( $c_{\text{exhaust}}$ ,  $\mu\text{mol}\cdot\text{mol}^{-1}$ ) were analyzed using a thermal conductivity detector (TCD) for  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$ , a flame ionization detector (FID) for  $\text{CH}_4$ , an electron capture detector (ECD) for  $\text{N}_2\text{O}$ , and a TE 42i  $\text{NO-NO}_2\text{-NO}_x$  chemiluminescent analyzer for  $\text{NO}$  quantification. For determination of  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$ , gases were first separated by a molecular sieve before entering the TCD,



and pure He was used as the carrier and back-purge gas. The air was passed through a trap containing boric acid (2 %, w/v) to absorb  $\text{NH}_3$  and the  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  concentration in the acid was determined using a segmented flow analyzer (AutoAnalyzer San ++, Skalar, Netherlands). Total C and N content of the compost were determined with an elemental analyzer (Vario EL CHNOS, Elementar Analysensysteme GmbH, Germany). The  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$  emission rates ( $F$ ,  $\text{mg}\cdot\text{h}^{-1}\cdot\text{kg}^{-1}\text{DW}$ ) were calculated according to Eq. (1):

$$F = \frac{v \cdot 60 \cdot (c_{\text{exhaust}} - c_{\text{background}}) \cdot M \cdot P \cdot 10^{-3}}{dm \cdot R \cdot (273.15 + T)} \quad (1)$$

where  $v$  is the flow rate ( $\text{L}\cdot\text{min}^{-1}$ );  $M$  is the molecular weight of gas molecules ( $\text{g}\cdot\text{mol}^{-1}$ );  $dm$  is dry weight of the compost (kg);  $P$  is the standard atmospheric pressure,  $1.013 \times 10^5$  Pa;  $R$  is the universal gas constant,  $8.314 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ , and  $T$  is compost temperature ( $^\circ\text{C}$ ).

## 2.5. Statistical analysis

Concentrations and emission rates were averaged to produce means and standard errors. Gas concentration data were recorded online and saved in spreadsheet format (EXCEL) for subsequent data processing. The change in gas concentrations was obtained, and some obvious deviation points were removed as abnormal values. A total of 3873, 3678, 3852, 3851, 3854, 3851 available data points can be used to calculate the emission rate of  $\text{N}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{O}_2$ , respectively. The cumulative gaseous C and N losses from composting were calculated by integrating the individual emission rate measurements over the total measuring period.

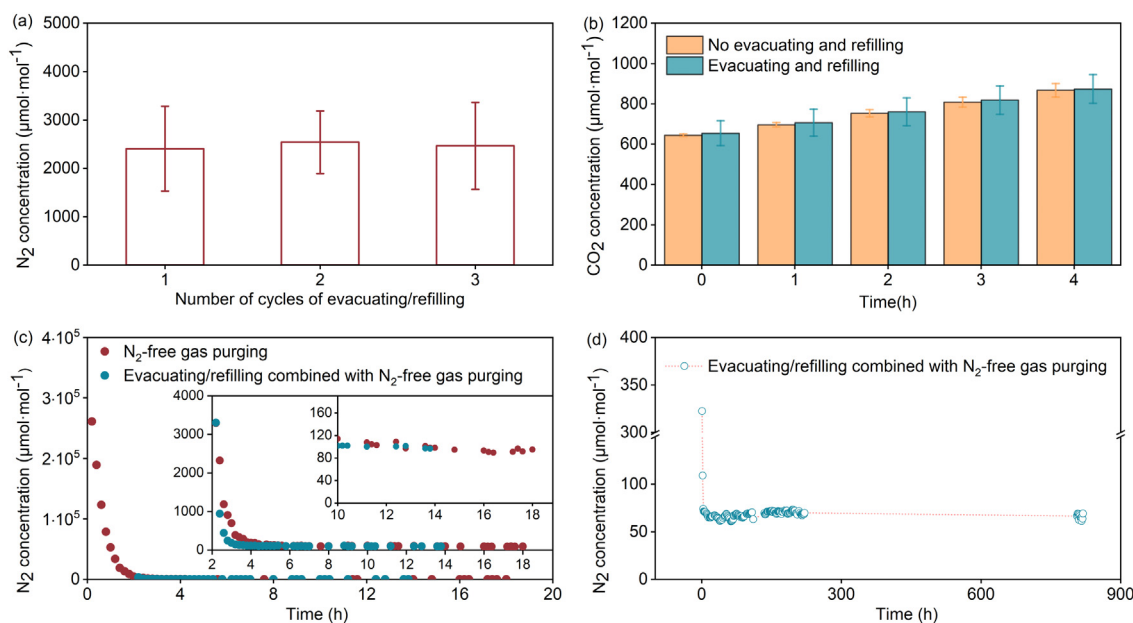
## 3. Results and discussion

### 3.1. Experiment 1. Comparison between different $\text{N}_2$ removal methods

A shortcoming of the traditional  $\text{N}_2$ -free gas purging technique used for soil is the relatively long time (16–48 h) needed to complete the gas exchange process. In the present study, purging for ~14 h was required to achieve a constant concentration (Fig. 3c). The time required to replace the original atmosphere of the intact cores with the artificial  $\text{N}_2$ -free

atmosphere depends on the feedstock type, headspace volume and flow rate. Using this procedure, the moisture content of compost was not affected significantly (before purging: 63 %; after purging: 62 %). An alternative method, also developed previously (Molstad et al., 2007; Qin et al., 2017), requires much less time (~3 h) for soil gas exchange through repeated evacuation and refilling rather than purging with  $\text{N}_2$ -free gas. In the present study, results showed that one cycle of the evacuation-refilling procedure removed 99.7 % of the original  $\text{N}_2$ , leaving a residual  $\text{N}_2$  concentration of  $2400 \mu\text{mol}\cdot\text{mol}^{-1}$ ; further cycles of evacuating and refilling did not result in further decrease in the residual  $\text{N}_2$  concentration (Fig. 3a), suggesting that one cycle was sufficient. The number of cycles of evacuating and refilling (one) and time taken (~10 min) were much less than described previously (3–5 cycles and ~3 h) (Qin et al., 2017) due to the use of a higher capacity vacuum pump ( $12 \text{ m}^3\cdot\text{h}^{-1}$ ) and gas exchange needle diameter (3.175 mm) than that used before ( $5.1 \text{ m}^3\cdot\text{h}^{-1}$  and 0.4 mm). Moreover, the evacuation-refilling procedure had no significant impact on the microbial respiration (as indicated by  $\text{CO}_2$  production) in the compost (Fig. 3b), suggesting that the impacts on general microbial activity could be considered negligible. However, a background  $\text{N}_2$  concentration of  $2400 \mu\text{mol}\cdot\text{mol}^{-1}$  would still present difficulties in detecting  $\text{N}_2$  emissions generated by composting. The residual baseline  $\text{N}_2$  concentrations obtained using the evacuating and refilling method were significantly higher than those using the  $\text{N}_2$ -free gas purging method (Fig. 3), which emphasizes the need to combine these two methods for a better  $\text{N}_2$  removal effect in a shorter time.

To decrease the background  $\text{N}_2$  concentration further, following one cycle of evacuation-refilling, the reactor containing compost was purged with a 79 % He and 21 %  $\text{O}_2$  gas mixture until the  $\text{N}_2$  concentration in the effluent gas remained constant. Here, a mixture of He and  $\text{O}_2$  rather than pure He was used, because cumulative losses of  $\text{N}_2$  and  $\text{CH}_4$  would be severely underestimated under anaerobic conditions during the  $\text{N}_2$ -free gas purging period (Cardenas et al., 2003; Liao et al., 2013). After one cycle of evacuation-refilling, the  $\text{N}_2$  concentration stabilized after ~11.6 h (Fig. 3c), representing the minimum time needed to fully and reliably remove and replace the inside atmosphere of the reactor. Compared to the  $\text{N}_2$ -free gas purging method, the evacuating-refilling and  $\text{N}_2$ -free gas purging method developed in the present study can shorten the  $\text{N}_2$  removal time by 2.2 h, although the residual  $\text{N}_2$  concentrations were comparable



**Fig. 3.**  $\text{N}_2$  concentration as a function of the number of evacuating/refilling cycles with  $\text{N}_2$ -free gas (79 % He, 21 %  $\text{O}_2$ ) (a); the degree of perturbation of the evacuating/refilling procedure on microbial respiration (b) as indicated by  $\text{CO}_2$  concentrations (mean  $\pm$  the standard error) from reactors containing compost measured at 0, 1, 2, 3 and 4 h; impact of  $\text{N}_2$  removal method ( $\text{N}_2$ -free gas purging or evacuating/refilling combined with  $\text{N}_2$ -free gas purging) on reactor  $\text{N}_2$  concentration (c), inserts showing greater detail; changes in  $\text{N}_2$  concentration over time with  $\text{N}_2$ -free gas purging after evacuating/refilling reactors containing stainless steel balls (d).

(Fig. 3). With this method,  $N_2$  concentration stabilized at a lower value ( $\sim 66 \mu\text{mol}\cdot\text{mol}^{-1}$ , Fig. 3d) compared with the evacuating and refilling method. This combined evacuation-refilling followed by  $N_2$ -free gas purging method therefore gives better ability to detect instantaneous production of  $N_2$  from aerobic composting, given the relatively low baseline  $N_2$  concentration. Here, we have demonstrated a fast and effective  $N_2$  removal method; however, the time required for the evacuating/refilling and  $N_2$ -free gas purging may need varying according to the feedstock type (Butterbach-Bahl et al., 2002; Qin et al., 2017).

A remaining issue is the choice of incubation conditions during the  $N_2$ -free gas purging phase, given that some perturbation and C and N losses are unavoidable. Under incubation at  $30^\circ\text{C}$ , the compost temperature sharply increased from  $19.5$  to  $32.7^\circ\text{C}$  within 4 h, and then slowly increased to  $34.7^\circ\text{C}$  over the next 8 h (Fig. S4). The compost temperature increased above the set temperature because of the heat released through the degradation of carbon substrates. However, under incubation at  $15^\circ\text{C}$ , the compost temperature increased slightly from an initial  $21.6^\circ\text{C}$  during the first 1.5 h, and then dropped to  $19.1^\circ\text{C}$  in the following 10.5 h. Production of  $\text{CO}_2$  and  $\text{NH}_3$  at  $15^\circ\text{C}$  were significantly lower than at  $30^\circ\text{C}$  incubation, by 80.5 and 61.4 %, respectively (Fig. 4), because of greater microbial activity at the higher incubation temperature. As expected,  $\text{O}_2$  concentration gradually increased to  $>15\%$  under  $15^\circ\text{C}$  incubation; however, at  $30^\circ\text{C}$ ,  $\text{O}_2$  concentrations sharply declined to values close to 0 within 3 h. The more anaerobic conditions at  $30^\circ\text{C}$  favored the production of  $\text{NO}$  (by 10-fold),  $\text{N}_2\text{O}$  (by 11,403-fold) and  $\text{CH}_4$  (by 41-fold), suggesting that the main drivers of C and N losses at the initial stage of composting are the availability of easily degradable C substrates and  $\text{O}_2$  concentration. These results suggest that a low temperature during  $N_2$ -free gas purging can reduce perturbation and C and N losses. The effects of lower temperature could be tested in the future, but the minimum incubation temperature of the present system is  $15^\circ\text{C}$ . Nevertheless, we demonstrated a fast and low-perturbation  $N_2$  removal method, namely the evacuating/refilling-low temperature purging method. In principle, the developed  $N_2$  quantification method can also be applied for other solid or liquid media (e.g., sediment and waste-water processing), which would improve the understanding in quantifying and regulating these emissions and developing more effective and comprehensive reduction options in wider terrestrial and aquatic ecosystems. Moreover, it is feasible to combine the present measuring system with other instruments (e.g., IRMS) to study microbial source partitioning of  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$ , which could inform the development of more targeted mitigation strategies in composting. The developed robotized system and method would be of great interest to many environmental scientists and agricultural scientists, who focus on atmospheric pollution and biowaste treatment.

### 3.2. Experiment 2. High-frequency and real-time measurement of $\text{NO}$ , $\text{N}_2\text{O}$ , $\text{N}_2$ , $\text{CO}_2$ , $\text{CH}_4$ and $\text{NH}_3$ over the whole composting process

Storage of gas samples in bags prior to transport and analysis in a laboratory, as has typically been used in studies of emissions during composting, can be associated with losses and thereby underestimate emissions. Therefore, real-time in-situ determination of  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{CH}_4$  concentrations is preferable. Moreover, microbial C and N turnover is intense in composting, and changes in environmental variables (e.g., temperature Fig. S5) are large. However, resource constraints often limit the sampling frequency to once or twice per day, resulting in estimates of C and N balance that are associated with high errors. Few studies have reported a full N balance from composting, with, in many cases, substantial unaccounted N losses ( $\sim 30\%$  of initial N) (Cao et al., 2019). Within-day variation in  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$  emissions was evident in the present study (Fig. 5a, c, e, g, i), especially during the peak emission period, with mean coefficient of variation values of 13.4, 23.1, 14.0, 36.7 and 11.4 %, respectively. These results suggest that emission estimates based on infrequent sampling, as is typical, will be associated with large uncertainties. It should be noted that part of the within-day variation in  $\text{N}_2$  emission are attributed to the limitations of GC-TCD (Agilent Technologies) sensitivity,

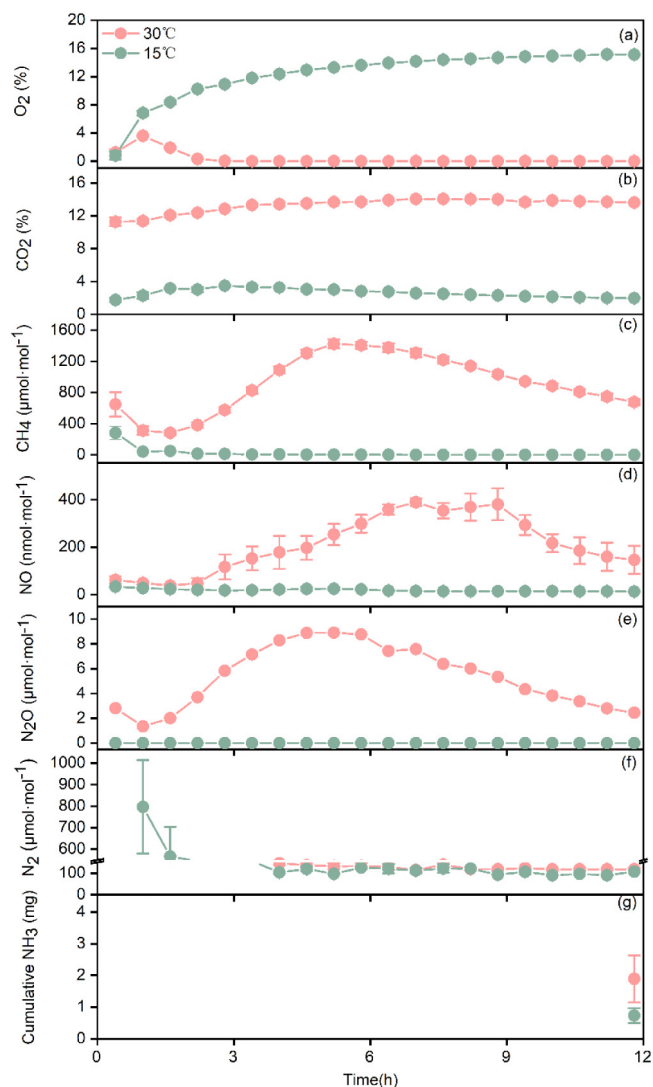
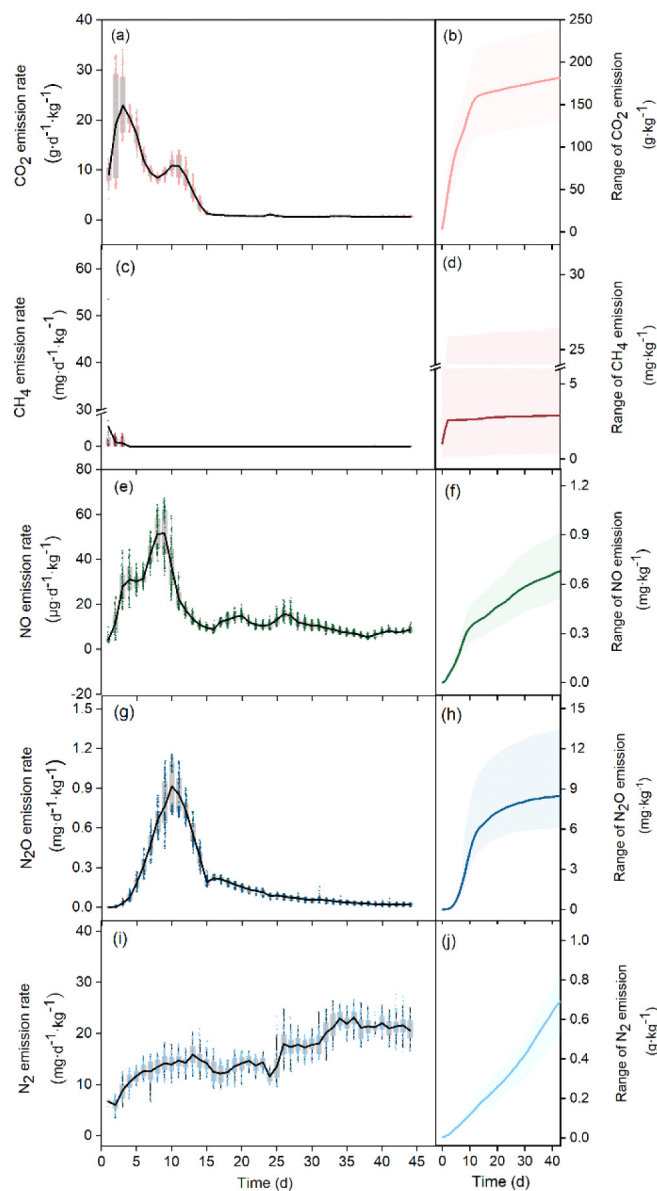


Fig. 4. Changes in concentration of  $\text{O}_2$  (a),  $\text{CO}_2$  (b),  $\text{CH}_4$  (c),  $\text{NO}$  (d),  $\text{N}_2\text{O}$  (e) and  $\text{N}_2$  (f) and cumulative emission of  $\text{NH}_3$  (g) during  $\text{N}_2$ -free gas purging when incubated at  $15^\circ\text{C}$  and  $30^\circ\text{C}$ ; data presented are mean values ( $n = 3$ ) with standard error bars.

which had been previously used for  $\text{N}_2$  emission in soil (Molstad et al., 2007; Wang et al., 2011). In the present study, linearity of the detector was observed between 1 and  $1000 \mu\text{mol}\cdot\text{mol}^{-1}$ . These results further suggest that the developed system could reliably detect compost-derived  $\text{N}_2$  emission. For better data quality and reliability, it seems feasible to improve the detector sensitivity and/or adjust the background  $\text{N}_2$  concentration in the purging gas mixture. Cumulative emission of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{N}_2$  over the 43-day incubation were 181.8, 2.89, 0.68, 8.48 and  $0.69 \text{ g}\cdot\text{kg}^{-1}$  dry matter, respectively, with potential quantitative ranges based on using a single daily highest or lowest emission rate of 130.9–241.0, 0.34–26.50.51–0.91, 6.06–13.4 and 0.52–0.83  $\text{g}\cdot\text{kg}^{-1}$  dry matter, respectively (Fig. 5b, d, f, h, j). Increasing the sampling frequency, especially at the time of peak gaseous emissions, will therefore greatly reduce the uncertainty associated with the estimate of cumulative emission.

The measuring frequency of multiple gaseous C and N species using the automated system was  $120 \text{ times}\cdot\text{d}^{-1}$  ( $20 \text{ times}\cdot\text{d}^{-1}$  per reactor, 6 reactors) in the present study, significantly higher than that reported for soil incubation systems ( $6\text{--}10 \text{ times}\cdot\text{d}^{-1}$ , Cardenas et al., 2003; Liao et al., 2013) and was maintained across the whole composting period. Emission rates of  $\text{CO}_2$  increased sharply at day 1 to  $1.28 \text{ g}\cdot\text{h}^{-1}\cdot\text{kg}^{-1}$ , and subsequently decreased to low values ( $\sim 0.03 \text{ g}\cdot\text{h}^{-1}\cdot\text{kg}^{-1}$ ) by day 15 (Fig. S6a). These results indicate that the easily degradable C substrates have been consumed during



**Fig. 5.** Emission rates of CO<sub>2</sub> (a), CH<sub>4</sub> (c), NO (e), N<sub>2</sub>O (g) and N<sub>2</sub> (i) over the incubation period; within-day variations in the measured values are presented by boxplot, and the daily means are connected by the line. Cumulative emissions of CO<sub>2</sub> (b), CH<sub>4</sub> (d), NO (f), N<sub>2</sub>O (h) and N<sub>2</sub> (j), the lines representing cumulative emission calculated by integrating the individual emission points over the total measuring period, and shaded areas representing potential quantitative ranges of cumulative emission calculated by integrating the daily minimum or maximum values over the total measuring period.

the initial stage, which also led to a consequent decline in O<sub>2</sub> concentrations (Fig. S5). These results confirm that the microbial activity typically associated with composting occurred in this laboratory incubation. The more anaerobic condition facilitates the production of CH<sub>4</sub>, NO, N<sub>2</sub>O and N<sub>2</sub>. Specifically, significant CH<sub>4</sub> emission peaks were observed immediately after the onset of composting, whereas after day 2 the CH<sub>4</sub> emission rates decreased by two orders of magnitude coinciding with the resumption of higher O<sub>2</sub> concentrations. Under O<sub>2</sub>-limited conditions, NO, N<sub>2</sub>O and N<sub>2</sub> emission rates peaked, with the main microbial pathway being attributed to heterotrophic denitrification (Cao et al., 2021). Peak N<sub>2</sub> emission was markedly later than NO and N<sub>2</sub>O emission, which could be attributed to the expression of N<sub>2</sub>O reductase lagging behind that of NO<sub>2</sub><sup>-</sup> and NO reductase when O<sub>2</sub> becomes limiting (Molstad et al., 2007). Emission rates of N<sub>2</sub> increased over time, because nitrifiers were active and the production of

NO<sub>x</sub><sup>-</sup> provided substrate for denitrification (Mahimairaja et al., 1995; Hellmann et al., 1997). The peak N<sub>2</sub> emission was higher by factors of approximately 1 and 2 than that of N<sub>2</sub>O and NO. As shown in a previous study (Mahimairaja et al., 1995; Cao et al., 2021), N loss during denitrification of manure composting was mostly as N<sub>2</sub> rather than N<sub>2</sub>O. The C and N balances for the composting process were closed in this study (Fig. 6). On average, 19.6 % of the initial TC was lost. Most of this C loss was in the form of CO<sub>2</sub>-C, with negligible loss as CH<sub>4</sub>-C. On average, 34.6 % of the initial TN was lost, comprising NH<sub>3</sub> (27.2 %) > N<sub>2</sub> (5.8 %) > N<sub>2</sub>O (0.045 %) > NO (0.0026 %), indicating an almost complete denitrification process in the present composting system, as evidenced by the high N<sub>2</sub>/(NO + N<sub>2</sub>O + N<sub>2</sub>) ratio (99 %, on average). However, the N<sub>2</sub>/(NO + N<sub>2</sub>O + N<sub>2</sub>) ratio was low (16 %) during the hotspot period of NO and N<sub>2</sub>O emissions (Fig. S7), highlighting the crucial role of NO and N<sub>2</sub>O reduction in controlling Nr gas emissions. In view of uncertainties in the measurements, the calculated average recovery rates of C and N in gaseous products of >95 % demonstrate that the measuring system is suitable for studying the dynamics and quantification of total gaseous C and N emissions from composting. Here we provide a solution for high-frequency and real-time measurement including N<sub>2</sub>. Further improvement depends on the performance optimization of relevant instruments and parts (e.g., moisture removal). Another improvement would be to replace helium with argon to reduce cost.

Composting, as a main technique for organic waste treatment and resource recovery, which has been identified as an important anthropogenic source of GHG (CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O) and Nr gases (NH<sub>3</sub>, N<sub>2</sub>O) emissions (Pardo et al., 2015; Cao et al., 2019). As a typical aerobic bioprocess, composting represents a significant anthropogenic source with potential to mitigate gas pollutions. Ammonia emission mainly occurred in the thermophilic phase, and the NO and N<sub>2</sub>O emission peaks were greatest during the curing phase (Fig. S7). Despite the negligible NO and N<sub>2</sub>O emissions observed in the present study, these important forms of Nr should not be ignored. If improperly controlled, composting could be a hotspot for NO (~120 μmol·mol<sup>-1</sup>) and N<sub>2</sub>O emissions (~340 μmol·mol<sup>-1</sup>) (Fig. S7a and b), with 3–4 order of magnitude higher concentrations of NO and N<sub>2</sub>O than background levels. These results highlight composting as a hotspot of NH<sub>3</sub> and N<sub>2</sub>O emissions in livestock manure management, which account for >40 % of the total global anthropogenic emissions (Davidson, 2009; Liu et al., 2022).

Composting was estimated as contributing 14 % of anthropogenic N<sub>2</sub>O emissions (Czepiel et al., 1996); however, the time of the peak N<sub>2</sub>O emission event appears uncertain (thermophilic phase, Cao et al., 2020 or curing phase, He et al., 2001) and may be due to the variations in N<sub>2</sub>O production pathways and the microenvironment (Cao et al., 2021). In the present study, N<sub>2</sub>O emissions were mainly related to the enriched NO<sub>2</sub><sup>-</sup> content in the curing phase of composting, indicating that NO<sub>2</sub><sup>-</sup> accumulation plays a crucial role in the hotspot N<sub>2</sub>O emission. The accumulation of NO<sub>2</sub><sup>-</sup> in compost can induce denitrification derived N<sub>2</sub>O emission (Cao et al., 2021), which can be a significant source of N<sub>2</sub>O production. This observation was supported by previous studies (He et al., 2001; Fukumoto et al., 2006), which attributed NO<sub>2</sub><sup>-</sup> accumulation to the unbalanced composition of nitrifying communities in compost. It has been established that NO<sub>2</sub><sup>-</sup>-oxidizing bacteria are more sensitive to environmental factors (e.g., NH<sub>4</sub><sup>+</sup>) than NH<sub>3</sub>-oxidizing bacteria, and NH<sub>3</sub> toxicity can suppress the activity of nitroreductase-associated NO<sub>2</sub><sup>-</sup>-oxidizing bacteria (Breuillin-Sessoms et al., 2017). However, the primary cause of NO<sub>2</sub><sup>-</sup> accumulation still remains to be determined. Moreover, N<sub>2</sub> emissions in Experiment 2 were comparable with those in the supplementary experiment (Fig. S7), despite the latter having a 3–4 order of magnitude higher emission of NO and N<sub>2</sub>O, indicating that NO and N<sub>2</sub>O formation, rather than consumption, dominated the emission. The findings observed in this study have implications for the development of process-based N<sub>2</sub>O mitigation technologies in composting.

#### 4. Conclusions

This study has developed a novel system for simultaneous measurement of NH<sub>3</sub>, NO, N<sub>2</sub>O, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> emissions from solid waste composting.



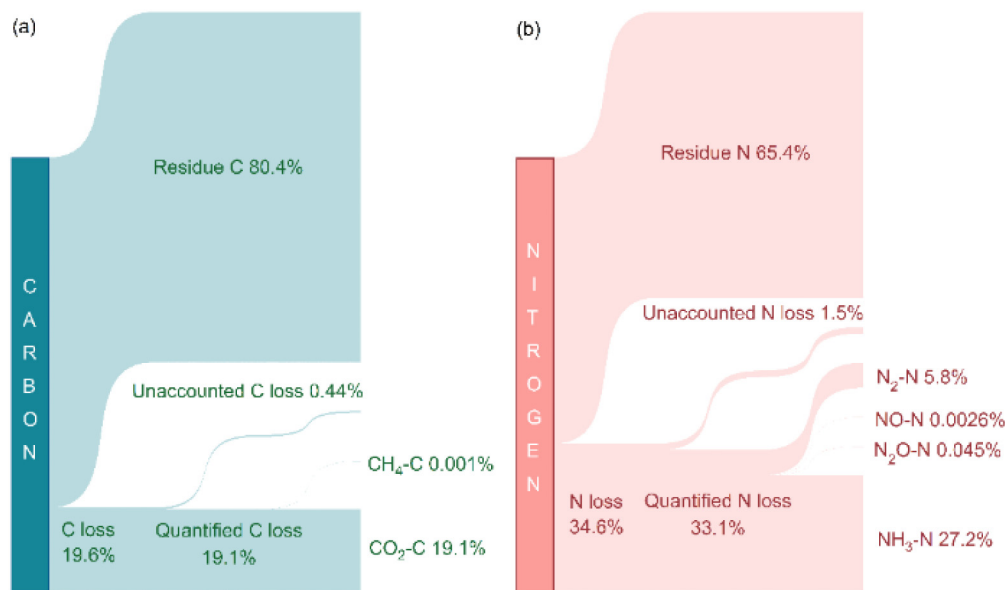


Fig. 6. Carbon and nitrogen balances during composting.

To derive the C and N balance during composting, gaseous C and N species, especially N<sub>2</sub>, were quantified with high detection frequency (120 times·d<sup>-1</sup>). Using the evacuating/refilling-low temperature purging method, background N<sub>2</sub> concentrations decreased to ~66 μmol·mol<sup>-1</sup> within 11.6 h, and the perturbation to the compost (indicated by C and N losses) was significantly minimized. The results presented highlight the constraints in quantifying gaseous losses using current methods, which would affect the accuracy of current estimates and can be addressed through the use of real-time and high-frequency measurement as in the novel developed system. Based on the developed measuring system, over 95 % of gaseous C and N losses during composting were quantified. This study also highlights the importance of aerobic composting as a source of Nr gases (NH<sub>3</sub>, NO and N<sub>2</sub>O) to the atmosphere and of N losses through N<sub>2</sub> emission (5.8 %). Overall, this high-frequency multi-component (including N<sub>2</sub>) gas measuring method can be used to improve the understanding of complex C and N turnover and the estimation of Nr and GHG emissions during waste management.

#### CRediT authorship contribution statement

**Yubo Cao:** Investigation, Writing – original draft, Formal analysis, Data curation, Methodology. **Xuan Wang:** Writing – review & editing, Formal analysis, Supervision, Funding acquisition. **Tom Misselbrook:** Writing – review & editing, Formal analysis, Funding acquisition. **Rui Wang:** Writing – original draft, Methodology. **Xunhua Zheng:** Writing – original draft, Methodology. **Lin Ma:** Supervision, Funding acquisition, Methodology.

#### Data availability

Data will be made available on request.

#### Declaration of competing interest

None.

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#### Appendix A. Supplementary data

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