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Short communication

Supplemental tests of gas trapping device for N_2 flux measurement

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ABSTRACT

The gas trapping device method (GTD) is a relatively new method to measure N_2 flux from waters. However, the non-equilibrium diffusion error and the reliability of GTD method compared to other previously established N_2 flux measurement methods has not been evaluated. In this study, the diffusive error of GTD, coming from non-equilibrium N_2 partial pressure between the headspace inside the gas sample bottle and the air, was estimated using a sterilization experiment. Moreover, the GTD and MIMS methods were compared for measuring N_2 flux from water under similar conditions. The results showed that there were maximum diffusion errors of 2.99% in the sample bottles prefilled with pure Helium, while only 1.09–1.76% diffusion errors in bottles prefilled with other N_2 standard gas (15% or 75%), indicating minor non-equilibrium diffusion errors. N_2 fluxes from water measured by GTD and MIMS methods are quite similar under all three concentrations of nitrate (5.30, 10.55 and 17.25 mg L^{-1}) and two levels of temperature (20 and 30 °C). Therefore, the GTD method offers a reliable alternative method to estimate N_2 flux rate in aquatic ecosystem.

1. Introduction

The N_2 flux rate is the major index to evaluate the denitrification rate and self-purification capability in aquatic ecosystems (Canfield et al., 2010; Collins et al., 2010). Various methods have been developed for measuring N_2 and N_2O flux (Groffman et al., 2006). Recently, a gas trapping device (GTD) method was developed by Gao et al. (2013), using an floating inverted dome device to continuously collect N_2 released from water (Gao et al., 2013; Gao et al., 2016). When using the GTD method, N_2 recoveries of standard gas with known concentrations of N_2 has been proved as high as 99.1%. Moreover, a zero partial pressure experiment indicated that release of the gas from the sterilized water was minor, suggesting the N_2 flux measured by the GTD method should be derived from biological activities.

However, difference (non-equilibrium) of N_2 partial pressure between the headspace inside gas sample bottle and air occurred after gas samples with different N_2 partial pressure has entered into the gas sample bottle. Therefore it is possible that the non-equilibrium diffusion of N_2 flux occurs (Smith and Lewis, 1992; Butterbach-Bahl et al., 2002). According to Fick's law (Nowicki, 1994), there is a concern that the N_2 in the collected gas samples may partially come from the air diffusion (Chanson, 1996; Cole and Caraco, 1998). The GTD method assumed that the non-equilibrium diffusion error was minor and could not affect the estimation of N_2 flux from water body. However, this assumption has not been tested yet.

For direct measurement of N_2 flux from water ecosystem, a well-developed method is membrane inlet mass spectrometry (MIMS) method (Kana et al., 1994; Cornwell et al., 1999; Zhao et al., 2013). Both GTD method and MIMS method could be applied to estimate N_2 flux from microbial activities in aquatic system. The MIMS method estimates the diffusive flux by analyzing the increase of dissolved N_2 in the overlaying water (Mccutchan et al., 2003; Groffman et al., 2006), while the GTD investigates the bubble gas from the aquatic system (Gao et al., 2013). Both GTD and MIMS methods calculate N_2 flux according to difference value rather than absolute value. The weight difference of a gas sample bottle before and after the experiment is used in the N_2 flux calculation formula of GTD method, while slope value of line regression between dissolved N_2 concentration in overlying water of the incubation tube and incubation time is used in MIMS method (An et al., 2001).

Abbreviation: MIMS, membrane inlet mass spectrometry; GTD, gas trapping device method; GC, gas chromatograph; ECD, Ni63 electron capture detector; TCD, thermal-conductivity detector; DO, dissolved oxygen; ANOVA, analysis of variance; ORP, oxidation reduction potential; Anammox, anaerobic ammonium oxidation.

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Table 1
Main properties of sediment and eutrophic water used in the experiment.

Media	NH_4^+ (mg L^{-1})	NO_3^- (mg L^{-1})	TOC/Organic matter	TN (N mg L^{-1})	TP (P mg L^{-1})	pH
Water	2.66 ± 0.05	1.07 ± 0.03	8.40 ± 0.76[a]	4.55 ± 0.09	0.52 ± 0.03	7.4 ± 0.06
Sediment	6.28 ± 0.33	2.80 ± 0.50	7.97 ± 0.22[b]	4.92 ± 0.11	1.39 ± 0.05	6.75 ± 0.13

[a] Means the TOC concentration (mg L^{-1}) in the water.
[b] Means the organic matter concentration (%) in sediment.

Thus, it is possible that the N_2 flux measured by the two methods is similar under still water body. Therefore, the reliability of GTD method for N_2 flux measurement could be compared to MIMS method under similar experimental conditions, which is critical for extensive application of the GTD method.

The major objectives of the present study were to (1) test the diffusive error of GTD derived from non-equilibrium of N_2 partial pressure between the headspace inside the gas sample bottle and the air, and to (2) test the reliability of the GTD for N_2 flux measurement by comparing with MIMS methods under still water body conditions in lab.

2. Material and methods

2.1. Sterilization experiment for non-equilibrium diffusive error check

200L containers, with the open top, were filled with water for the error check. Before the experiment, the water was sterilized with ClO_2 (20 mg kg^{-1}) to minimize the gas production from microbial activities in water, and then was kept at 15 °C in lab for ten days to achieve the gas equilibrium of water with atmosphere. After that, the GTDs were placed in the water as described in Gao et al. (2013). Then, about 100 ml standard gas was piped into the collecting dome of GTD, which would enter into the sample bottle subsequently. Three standard gases were selected in the test, with the gas composition of 75.32% N_2, 0.50% CO_2, 4.99% CH_4 and 19.19% H_2 in standard gas I, 15.50% N_2, 2.01% CO_2, 43.30% CH_4 and 39.19% H_2 in the standard gas II, and 99.99% He_2 in standard gas III. All standard gases were purchased from the 55th Institute of China Light and Power Group Corporation (Nanjing, China).

The N_2 concentration variation of standard gas in the sample bottles was used as the index of non-equilibrium diffusive errors from the GTD method. Gas samples were collected at 0, 20, 40, 60, 80,100, 120, 140, 160 and 180hr after the standard gas was piped into the GTD. All treatments had four replications.

2.2. Comparison of GTD method with MIMS method

2.2.1. Sediment and water preparation

Sediment and eutrophic water used in this experiment were collected from a eutrophic pond located in Jiangsu Academy of Agricultural Sciences, Nanjing, China. The sediment collected from the pond was mixed fully and sieved with 4 mm mesh to remove the impurities. The main properties of the sediment and overlying water were listed in Table 1.

2.2.2. Comparison experiment

The whole experiment was carried out in the laboratory of the Institute of Soil Science, Chinese Academy of Sciences (ISSAS) at carefully maintained temperatures (20–30 °C). Three treatments (i.e. T1, T2 and T3) with different temperature and nutrients conditions were listed in Table 2. All treatments had three replications. Before the experiment, the same sediment, with 20 cm thickness, was fully mixed and placed evenly at the bottom of water container of GTD method and core tubes of MIMS devices. Subsequently, the same eutrophic water was carefully placed on the sediment. Then, the two methods were started simultaneously after ten days to minimize the man-made interference, and ended at the same time after the experiment. The sampling arrangement of the two methods was listed in Table 2. Sample bottle volume of GTD method was enough for storing bubble gas collected from water. Rubber stoppers in the incubation core tubes of MIMS were sealed tightly during the whole experiment. All the overlying water samples were collected and analyzed immediately.

2.2.3. Net N_2 flux determination by GTD method and MIMS method

The detailed description of the GTD method and calculation of N_2 flux was described in Gao et al., (2013). The gas samples were analyzed using a Gas Chromatography (GC-2010, Shimadzu Corp., Japan) (Liu et al., 2015). Net N_2 flux by MIMS method was determined as described in Li et al. (2013). The detailed information of GTD and MIMS methods was shown in the supporting information.

2.3. Methods for analysis of water and sediment samples

Water samples were analyzed for the concentrations of NH_4^+, NO_3^-, TN, TP using a flow injection analyzer (Skalar Analytical, Breda, The Netherlands). The water temperature (t °C), dissolved oxygen (DO), pH and redox potential were measured using a portable meter (YSI Pro Plus, USA). The nutrients background in sediment samples were analyzed according to standard method (APHA, 2005).

2.4. Statistical analysis

Analysis of variance (ANOVA) was performed using Statistical software (SPSS18.0), and the graphs were created by Sigmaplot12.0.

Table 2
The sampling arrange of the MIMS method during comparison experiments and condition parameters of water.

Test No.	Temperatures	NO_3^-	NH_4^+	TN	TP	MIMS sampling time[a]
T1	20	5.30 ± 1.07	10.86 ± 0.08	18.33 ± 1.00	0.65 ± 0.15	0,2,4,6,8,24,48,96,120,144,168,192,216,240,264,288
T2	30	10.55 ± 0.51	4.28 ± 0.02	15.36 ± 0.10	0.1 ± 0.00	0,2,4,6,8,24,48,96
T3	30	17.25 ± 1.70	6.23 ± 0.04	25.71 ± 1.68	0.16 ± 0.00	0,2,4,6,8,26

[a] Means that MIMS sampling time was set at different time points during the whole treatment process. The sampling time of GTD method was set at the end of each treatment process.