Estimation of N_2 and N_2O production in a eutrophic river using a newly developed gas trap device

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Abstract
Biogenic gas production in a eutrophic pond located in the subtropical climate zone of China was quantified using a newly developed gas-trapping device. This device allows for a vertically resolved collection and subsequent analysis of biogenic gases (N_2, O_2, N_2O and CH_4). Determining the vertical structure of gas production is especially relevant in stratified water bodies as it allows to link the stratification of physicochemical parameters with the gases produced. The investigated pond exhibited strong thermal stratification in temperature, DO, pH, nutrients and Chlo-α during summer and autumn, but not in winter. Gas production was greatest at the sediment-water interface and in the surface layer and small in the middle layer. Gases produced at the surface were mainly N_2 and O_2, whereas the latter is likely to stem from photosynthetic activity as gas production followed a diurnal cycle. At the sediment-water interface, the collected gas was mainly composed of N_2 and CH_4. Our results highlight the vertical heterogeneity of gas production and underline the value of vertically-resolved sampling which is made possible with the presented gas-trapping device.
Key Words
Biogenic gases, N_2O, CH_4, N_2, ponds, stratification, measurement techniques

Introduction
Small and shallow water bodies are often ecological hotspots (Downing, 2010) that exhibit high rates of biogeochemical activities, yet have not received much attention. In China and many other countries, many man-made ponds were created for farming purposes (e.g. fish farming, irrigation water storage, storm retention/detention and recreation) (Xie et al., 2004; Casey et al., 2006; Zheng et al., 2009). These shallow water bodies in China received considerable loads of nutrients (Herbecket al., 2013), leading to the increased occurrence of harmful algal bloom. As a consequence, the internal biogeochemical processes of these eutrophic ponds seem to undergo different trends compared to less eutrophic ecosystems.
The changes of physiochemical parameters are likely to be coupled with the dynamics of biological processes that trigger the gas emission, e.g. N_2O and N_2 production from denitrification and CH_4 production processes (Ferrón et al., 2012; Sims et al., 2013; Hernandez-Paniagua et al., 2014). The biological process of denitrification has been shown to be closely correlated with nutrients and physiochemical conditions, e.g. DO, pH and temperature (Hargreaves et al., 1998). In eutrophic ponds, strong stratification may cause the heterogeneous distribution of nutrients, carbon, light intensity, DO, pH and temperature along the vertical profile of the water column. This, in turn, likely causes a heterogeneous distribution of biogenic gases like N_2, N_2O and CH_4 as well. However, there is still a major lack of method to study the diurnal dynamics of gas production and its spatial heterogeneity. Therefore, we used a newly developed a gas-trapping device for vertically resolved collection and subsequent analysis of biogenic gases (N_2, O_2, N_2O and CH_4). We tested the hypothesis that strong stratification of physicochemical characteristics in a hyper-eutrophic pond would lead to a heterogeneous distribution of biogenic gas production along the vertical profile of the water column. This study will provide important insights into the dynamics of stratification and de-stratification in eutrophic pond waters, and its consequences for the biogeochemical functioning of the water body.

Methods
Diurnal dynamics of physicochemical parameters and gas production in the vertical profile of the water column in a eutrophic pond located at Jiangsu Academy of Agricultural Sciences (JAAS, 32◦02N, 118◦52E), Nanjing, China were monitored during different seasons in 2013 with significant variation of temperature, e.g. summer (35-38℃), Autumn (22-28℃) and winter (5-10℃). Stratification was sampled as a function of time and depth in order to characterize large density gradients and chemical gradients that develop in the shallow water column. Therefore, sampling was performed at a vertical resolution of centimeters (intervals of every 0.2 m). In order to *in situ* monitor DO, pH and temperature

(T℃), a water quality field meter and a light meter were located at the fixed depths in the water column every 4 hours. At the same time, latex tubes connected to a vacuum pump were located at the same intervals of depth in water column to collect water samples. The collected water samples were analyzed with concentrations of NO_3^-, NH_4^+, total dissolved nitrogen (TDN), PO_4^{3-} and total dissolved nitrogen (TDP).

The vertical distribution of gas production in the water column was assessed based on multiple sampling campaigns by *in situ* trapping the gas production from different depths intervals (0-0.5m, 0.5-1.0m, 0.05 m above the sediment), using a newly developed gas-trapping device (Fig. 1). The gas-trapping device used in this study was adapted from a device recently described by Gao et al. (2013). It was originally developed to *in situ* trap the biological gas production from the whole column of water including sediment, followed by analyses of N_2, N_2O, O_2 and CH_4 composition in the collected gas samples (Gao et al., 2013) using Gas Chromatography. By locating an inverted floating dome at different depths of water instead of beneath the surface of water, gas production from different intervals of depths in the water column was collected by the domes. In winter, gas produced in winter was too minor to be collected and analyzed.

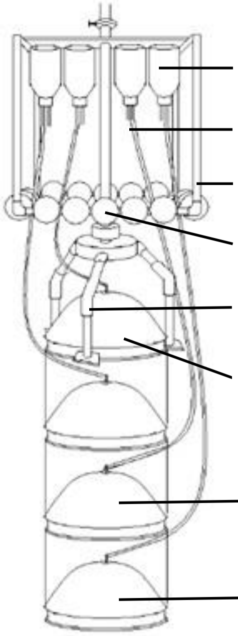

Fig.1 Sketch of gas trapping device to *in-situ* collect gas released from different intervals of water column in eutrophic pond

Results

Diurnal variation of water physical parameters in vertical profile of water column

The results on diurnal variation of water temperature, pH and DO concentration along the vertical profile of water column are shown in Fig. 2 (A–C). In general, obvious diurnal stratification and de-stratification dynamics of water temperature, DO concentration and pH were observed along the vertical profile of water column during summer and autumn, but not in winter. In summer and autumn, the consistent variation of DO concentrations and pH ($p < 0.01$) was observed, with high DO concentrations coinciding with high pH values.

Diurnal variation of N and P in the vertical profile of water column

We observed strong vertical stratification of NO_3^-, NH_4^+ and TDN during summer and autumn, but not in winter. The vertical distribution profiles of NH_4^+ and NO_3^- showed a reversed pattern. The concentrations of NO_3^- decreased with increasing depth, whereas the concentrations of NH_4^+ increased with increasing depth at a vertical resolution of centimeters. In summer and autumn, the vertical distribution and the diurnal cycle of PO_4^{3-} were very similar to those for NH_4^+. The concentration of PO_4^{3-} increased with increasing depths. TDP and PO_4^{3-} concentrations show very similar vertical profile during summer.

Diurnal variation of gas production in vertical profile of water column

The gas fluxes at different depths of the water column were recorded during summer and autumn (Table 1) because gas produced in winter was too minor to be collected and analyzed. The quantity of gas production from sediment was much higher than that from the surface layer in summer; whereas the gas production from surface layer was much higher than that from sediment in autumn. In both seasons, the least gas production was detected within the middle water layers. Gas production from the surface layer was mainly composed of O_2 and N_2, while gas production from the sediment was mainly composed of CH_4 and N_2. Gases produced at the surface were mainly N_2 and O_2, whereas the latter is likely to stem from photosynthetic activity as gas production followed a diurnal cycle (Fig. 3).

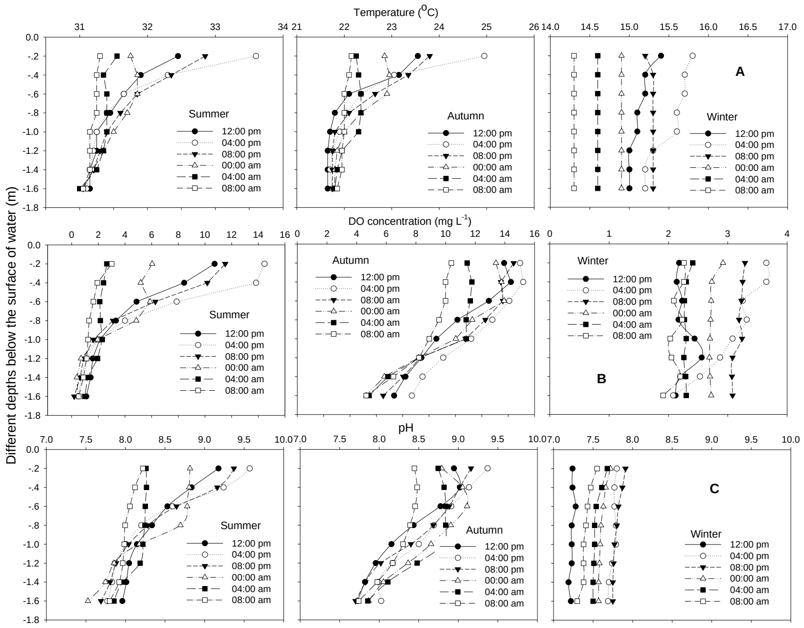

Fig. 2 Vertical profiles of temperature (A), DO concentration (B) and pH (C) at different times of the day during summer, autumn, and winter.

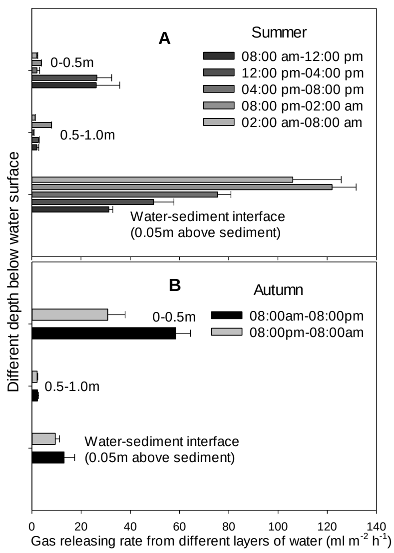

Fig. 3 Diurnal gas production rates from the different layers of water column in summer and autumn

Table 1 Gas quantity, individual gas concentration and flux released from the different depths below the water surface.

Water depths	Gas production rates	Individual gas flux			
	ml m^{2-} h^{-1}	O_2 (mmol L^{-1} m^{2-})	N_2 (mmol L^{-1} m^{2-})	N_2O (umol L^{-1} m^{2-})	CH_4 (umol L^{-1} m^{2-})
	8:00 am-08:00 pm in summer				
Upper layer (0-0.5m)	63.4±6.6	0.08±0.02	1.2±0.2	0.49±0.03	0.04±0.01
Middle layer (0.5-1.0m)	2.4± 0.5	0.003±0.0006	0.3±0.002	0.01±0.001	0.002±0.0001
Bottom layer	14.1±4.7	0.02±0.004	0.02±0.005	0.03±0.003	0.006±0.001
	08:00 pm- 8:00 am in summer				
Upper layer (0-0.5m)	29.4±3.1	0.04±0.01	0.31±0.003	0.12 ±0.02	0.04 ±0.007
Middle layer (0.5-1.0m)	2.3± 0.3	0.002±0.0002	0.014±0.002	0.001±0.0001	0.0009±0.0001
Bottom layer	10.1±1.9	0.002±0.0004	0.012±0.002	0.008±0.002	0.004±0.0007
	8:00 am-08:00 pm in autumn				
Upper layer (0-0.5m)	42.8±6.6	0.96±0.06	1.29±0.09	6.8±0.6	0.08±0.06
Middle layer (0.5-1.0m)	5.1± 1.1	—	—	—	—
Bottom layer	143±0.8	0.16±0.09	1.08±0.17	11.5±1.08	2.7±1.3
	08:00 pm- 8:00 am in in autumn				
Upper layer (0-0.5m)	4.4± 1.0	—	—	—	—
Middle layer (0.5-1.0m)	7.6± 2.0	—	—	—	—
Bottom layer	284±9.6	0.13±0.02	1.2±0.2	21.1±3.0	7.2± 1.4

—: Below the detection limit because the gas production within 4 hours was not enough for the analysis of the gas composition with our methods.

Conclusions

The eutrophic pond can undergo persistent and strong diurnal stratification of a variety of physicochemical factors during summer and autumn despite their shallowness and small size. Thermal stratification led to the stratification of DO, pH and nutrients. The vertical stratification of all physicochemical factors can finally lead to the heterogeneity of gas production (O_2, N_2O, N_2, CH4) along the vertical profile of the water column. The surface water and sediment-water interface can produce much more gas, compared to the middle layers of water column. The O_2 production from algal photosynthesis contributed to the high gas production rates in the surface layer. Other biological processes, e.g. nitrification and/or denitrification, may also have contributed to the heterogeneous gas production as suggested by high N_2 and N_2O fluxes detected in the surface layer and sediment-water interface. The strong stratification in the pond is likely to alter the physicochemical environment and internal nutrient loading, and hence affect water quality, greenhouse gas emission and biological nitrogen transformation processes.

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