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Emission and distribution of phosphine in paddy fields and its relationship with greenhouse gases

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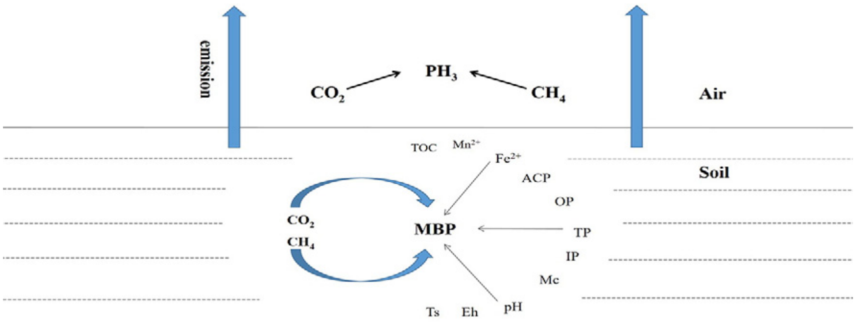
HIGHLIGHTS

- The relationship between CO_2,CH_4 and PH_3 in paddy fields was researched.
- For the emission flux, both CO_2 and CH_4 had a significant positive correlation with PH_3.
- MBP level was positively correlated with soil CO_2 at the late stage of rice growth.
- pH, Eh, TP and ACP were the main environmental factors affecting the MBP level in paddy soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Phosphine (PH_3), as a gaseous phosphide, plays an important role in the phosphorus cycle in ecosystems. In this study, the emission and distribution of phosphine, carbon dioxide (CO_2) and methane (CH_4) in paddy fields were investigated to speculate the future potential impacts of enhanced greenhouse effect on phosphorus cycle involved in phosphine by the method of Pearson correlation analysis and multiple linear regression analysis. During the whole period of rice growth, there was a significant positive correlation between CO_2 emission flux and PH_3 emission flux ($r = 0.592$, $p = 0.026$, $n = 14$). Similarly, a significant positive correlation of emission flux was also observed between CH_4 and PH_3 ($r = 0.563$, $p = 0.036$, $n = 14$). The linear regression relationship was determined as $[PH_3]_{flux} = 0.007[CO_2]_{flux} + 0.063[CH_4]_{flux} - 4.638$. No significant differences were observed for all values of matrix-bound phosphine (MBP), soil carbon dioxide (SCO_2), and soil methane (SCH_4) in paddy soils. However, there was a significant positive correlation between MBP and SCO_2 at heading, flowering and ripening stage. The correlation coefficients were 0.909, 0.890 and 0.827, respectively. In vertical distribution, MBP had the analogical variation trend with SCO_2 and SCH_4. Through Pearson correlation analysis and multiple stepwise linear regression analysis, pH, redox potential (Eh), total phosphorus (TP) and acid phosphatase (ACP) were identified as the principal factors affecting MBP levels, with correlative rankings of Eh > pH > TP > ACP. The multiple stepwise regression model ($[MBP] = 0.456 * [ACP] + 0.235 * [TP] - 1.458 * [Eh] - 36.547 * [pH] + 352.298$) was obtained. The findings in this study hold great reference values to the global biogeochemical cycling of phosphorus in the future.

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1. Introduction

Phosphine (PH_3,-3), as a type of phosphorus-containing compound and a strong reducing agent, has been widely recognized as a gaseous carrier of phosphorus in global biogeochemical cycles. Note that, PH_3 is also highly toxic that possesses acute lethal effects on humans and animals through the inhibition of aerobic respiration (Zhu et al., 2009). In nature, PH_3 exists in two major different forms: gaseous phosphine and matrix-bound phosphine (MBP) (Eismann et al., 1997a; Glindemann et al., 2005). Gaseous phosphine is defined as the amount of phosphine present in gas samples. MBP, referred to the concentrations of phosphine bound to condensed environmental samples including sediments, soils, manures and sludge, can be liberated by acid or alkaline digestion. Also, MBP is the most dominant form of the phosphine in the nature environment (Glindemann et al., 1996; Wang et al., 2016).

Since phosphine was first detected in a sewage treatment plant (Devai et al., 1988), it has been widely observed in global atmosphere (Glindemann et al., 1996; Glindemann et al., 2003), terrestrial soil (Eismann et al., 1997a; Liu et al., 1999), marine environments (Gassmann, 1994; Zhu et al., 2006; Feng et al., 2008a; Hong et al., 2010; Li et al., 2010a, 2010b; Zhu et al., 2011), biogas (Ding et al., 2005), animal slurry or human feces (Glindemann et al., 1996), rock (Glindemann et al., 2005) and wetlands (Han et al., 2000; Niu et al., 2004; Wang et al., 2016). As one of the most widely distributed constructed wetlands on the earth, paddy fields are considered as one of the main sources responsible for the emission of PH_3, especially in China where paddy fields account for about 19% of the total world rice cultivated area of 159 M ha (FAOSTAT, 2012). To date, PH_3 has been detected in Beijing (Han et al., 2000), Nanjing (Han et al., 2011a, 2011b), and Guangzhou (Niu et al., 2013) paddy fields in China. And Wang et al. (2016) studied the MBP distribution in four different paddy soils located in South China. However, these studies only considered the distribution of PH_3 in paddy fields, the reports of the temporal and spatial changes of PH_3 under the global climate change are rare.

In recent years, greenhouse effect, as the main cause of global warming, has been continuously attracting increasing attentions globally. CO_2 and CH_4 are two of the most important greenhouse gases, which account for the major enhancement of the natural greenhouse effect (Yang et al., 2015). Unfortunately, long-term records showed that the concentration of CO_2 in the atmosphere has risen steadily since the preindustrial period (Cheng et al., 2005). The concentration of CO_2 was 280 μmol/mol in preindustrial times, and it was predicted to reach levels of 450–550 μmol/mol by 2100 (IPCC, 2007). CH_4 is a another crucial gas with high global warming potential, which is responsible for approximately 20% of the anthropogenic global warming effect. Over the last 150 years, the concentration of atmospheric methane has risen from 0.75 to 1.73 μmol/mol (Lelieveld et al., 1998). Both CO_2 and CH_4 have significant effects on phosphorus cycling in ecosystems. It was well established that elevated CO_2 significantly decreased soil available phosphorus contents in farmland (Yu et al., 2016) and increased the phosphorus contents of paddy plants (Yang et al., 2007). Eismann et al. (1997a, 1997b, 1997c) discovered that there was a significant positive correlation between CH_4 and PH_3 in the process of manure fermentation. PH_3 is an important carrier in the process of phosphorus cycling, and it will inhibit the growth of soil microorganisms, disturb the microenvironment of plant root zone. Furthermore, as a lively reducible gas, PH_3 can compete with CH_4 and other greenhouse gases for accepting hydroxyl radicals, thus having a coupled greenhouse effect (Han et al., 2000). Therefore, the study of CO_2 and CH_4 on the role of PH_3 is meaningful. To the best of our knowledge, barely little research efforts have been devoted to investigate the relationship between CO_2, CH_4 and PH_3 in paddy fields. This is the primary motivation of our current study.

In this study, the emission fluxes of CO_2, CH_4 and PH_3 were measured. The contents of SCO_2, SCH_4, MBP, and other environmental variables were also assayed. The objectives of this study are: (1) to quantify and study the relationship between the emission fluxes of CO_2, CH_4 and PH_3 from paddy fields; (2) to compare the concentration of SCO_2, SCH_4 and MBP at different depths of paddy soils during the entire period of rice growth; (3) to discuss the principal environmental parameters affecting MBP distribution in paddy soils. The results of this study can shed light on further investigations regarding the impact of global greenhouse effect upon phosphorus cycle involved in phosphine.

2. Materials and methods

2.1. Site description

Field studies were conducted at one of the teaching and research paddy fields of South China Agricultural University, located at Ningxi (23°14′34″N, 113°37′59″E) in the Zengcheng district of Guangzhou, China. Zengcheng has a subtropical monsoon and humid climate, with an annual average temperature of 20–22 °C, an annual relative humidity of 78%, an annual mean rainfall of 1800 mm and >1953.5 h of sunlight per year. Paddy soils are developed from red soil. Double-cropping of paddies is the traditional method of planting in this area.

2.2. Field experiments

Field studies were carried out from 19 August to 21 November of 2016. During the whole sampling period, the experimental paddy fields were kept in the traditional tillage mode, no chemical fertilizers and pesticides were applied. The dates of different rice growing stages and field practices are given in Table 1.

2.3. Sample collection

The gas samples above the soil were collected to measure emission fluxes from the paddy field by closed-chamber method. The method has been proven effectively for flux measurements of CO_2, CH_4, and PH_3 (Han et al., 2000; Huttunen et al., 2003; Gupta et al., 2007). This technique was described in detail by Streever et al. (1998). Two parallel sites were employed for each collection. Carbon dioxide and methane inside the soil were collected by self-made soil gas samplers consisting of collecting trachea ($L = 15$ cm; $\Phi = 21$ mm), airway ($L = 50$ cm), waterproof breathable membrane ($\Phi = 3$ μm), rubber stopper, cap, air vent ($\Phi = 0.5$ mm) and three-way valve. The self-made soil gas samplers were placed at depth of 0- to 5-, 5- to 10-, 10- to 15-, 15- to 20-, 20- to 25- and 25- to 30-cm in the soil. Gas samples were collected by syringes from 15:00 to 18:00, injected into high purity nitrogen purged Tedlar bags immediately, taken back to the laboratory and measured for 24 h. Three replicate soil samples at one site were collected by a stainless steel column sampler (AMS, 209.51, American) at 16:00. The seven stages of paddy growth were classified into 0- to 5-, 5- to 10-, 10- to 15-, 15- to 20-, 20- to 25- and 25- to 30-cm segments. All soil samples were immediately taken into teflon casings after collection, then stored in the dark at −20 °C until further analysis.

2.4. Determination of PH_3, CO_2 and CH_4

Both CO_2 and CH_4 were analyzed by a gas chromatograph (Agilent 7820 A, USA) equipped with a thermal conductivity detector (TCD)

Table 1
Rice growing stages and field practice.

Events	Dates
Transplanting practice	19 August
Tillering collection	6 September
Jointing collection	18 September
Heading collection	6 October
Flowering collection	29 October
Ripening collection	13 November
Harvest	21 November