



Phosphine in paddy fields and the effects of environmental factors



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HIGHLIGHTS

- We investigated ambient levels of phosphine in paddy throughout rice growing stages.
- Rice plants were discovered as a main transmission way for phosphine in paddy fields.
- The development of rice roots led sharp variations for MBP vertical distribution.
- Acid phosphatase was one of the key environmental factors for MBP in paddy soils.

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ABSTRACT

Ambient levels of phosphine (PH_3) in the air, phosphine emission fluxes from paddy fields and rice plants, and the distribution of matrix-bound phosphine (MBP) in paddy soils were investigated throughout the growing stages of rice. The relationships between MBP and environmental factors were analyzed to identify the principal factors determining the distribution of MBP. The phosphine ambient levels ranged from $2.368 \pm 0.6060 \text{ ng m}^{-3}$ to $24.83 \pm 6.529 \text{ ng m}^{-3}$ and averaged $14.25 \pm 4.547 \text{ ng m}^{-3}$. The highest phosphine emission flux was $22.54 \pm 3.897 \text{ ng (m}^2 \text{ h)}^{-1}$, the lowest flux was $7.64 \pm 4.83 \text{ ng (m}^2 \text{ h)}^{-1}$, and the average flux was $14.17 \pm 4.977 \text{ ng (m}^2 \text{ h)}^{-1}$. Rice plants transport a significant portion of the phosphine emitted from the paddy fields. The highest contribution rate of rice plants to the phosphine emission fluxes reached 73.73% and the average contribution was 43.00%. The average MBP content of 111.6 ng kg^{-1} fluctuated significantly in different stages of rice growth and initially increased then decreased with increasing depth. The peak MBP content in each growth stage occurred approximately 10 cm under the surface of paddy soils. Pearson correlation analyses and stepwise multiple regression analysis showed that soil temperature (Ts), acid phosphatase (ACP) and total phosphorus (TP) were the principal environmental factors, with correlative rankings of $\text{Ts} > \text{ACP} > \text{TP}$.

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1. Introduction

It is well known that phosphorus (P) is an essential nutrient for terrestrial and aquatic ecosystems and plays an important role in plant and microbial nutrition and other geochemical processes (Morton et al., 2003; Geng et al., 2005a). Because phosphate and other oxidation states of phosphorus have been assumed to be the dominant forms of P in the environment, they have been studied more thoroughly. However, reduced phosphine (PH_3 , -3), a natural gaseous carrier of P in its biogeochemical cycle, has begun to receive more attention and its presence has been confirmed in a range of environments in recent years (Devai et al., 1988; Roels and Willy, 2001; Glindemann et al., 2005a; Han et al., 2011b).

Although the mechanisms of phosphine production are still unclear, a number of them have been proposed. Significant evidence demonstrates that the production of phosphine is associated with the microbial reduction of P-containing substances (Rutishauser and Bachofen, 1999; Roels and Willy, 2001; Geng et al., 2005a; Feng et al., 2008b). At the same time, some non-biological pathways for phosphine formation have also been found, such as the corrosion of P-containing metals, mechano-chemical reactions of apatite-bound phosphate and the reduction of phosphate in the atmosphere by light (Glindemann et al., 1998; Glindemann et al., 2004; Glindemann et al., 2005b; Hou et al., 2009).

Some natural environments with significant anaerobic biosphere areas such as lakes (Niu et al., 2004; Geng et al., 2005b; Geng et al., 2010; Song et al., 2011), estuaries (Glindemann et al., 2005a; Hou et al., 2009), coasts (Zhu et al., 2006; Feng et al., 2008a; Li et al., 2010), offshore areas (Hong et al., 2010; Zhu et al., 2011) and wetlands (Devai and Delaune, 1995; Han et al.,

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2011a) are thought to be some of the main sources responsible for the formation and emission of phosphine. As one of the most widely distributed constructed wetlands on the planet, paddies provide a favorable anaerobic environment for the formation and emission of PH_3 . Phosphine has been shown to play an important role in P-cycling in paddy fields, and its existence might have both positive and negative effects on biomass growth and other environmental factors (Han et al., 2000; Roels and Willy, 2001). Phosphine is an intermediate product of anaerobic progress in paddy soils, and its subsequent oxidation to phosphoric acid activates soil P that was originally unavailable to the rice (Han et al., 2000). Phosphine is also a substantial greenhouse gas and competes with methane, nitrous oxide and other greenhouse gases for hydroxyl radicals; as a result, it enhances an indirect greenhouse effect, a phenomenon also known as the coupling effect (Prinn, 1994; Han et al., 2000). The occurrence of phosphine in the biosphere is always accompanied by the presence of methane (Gassmann and Glindemann, 1993). However, there is no significant correlation between the formation of phosphine and methane (Jenkins et al., 2000; Han et al., 2002). An understanding of the behavior of phosphine in paddy fields, including the emission of free phosphine and the distribution of MBP, is necessary to understand the P cycle and the coupling effect between phosphine and other greenhouse gases in paddy fields. Moreover, these studies might help elucidate the mechanism of phosphine formation.

In this study, phosphine emission samples at different depths of paddy soils during the entire period of rice growth were collected, and the values of Ts, TP, ACP and eight other environmental factors were measured. Our objectives were: (1) to investigate the seasonal changes in ambient phosphine (PH_3) levels, phosphine emission fluxes from paddy fields and the contribution rate of rice plants to phosphine emission fluxes; (2) to investigate the seasonal changes and the distribution characteristics of MBP in paddy soils; (3) to analyze the relationships between MBP and related environmental factors and to identify the principal factors involved in the process.

2. Materials and methods

2.1. Site description

Field studies were carried out at one of the teaching and research paddy fields of South China Agricultural University, located at Ningxi ($23^\circ14'34''\text{N}$, $113^\circ37'59''\text{E}$) in the Zengcheng city of Guangzhou, China. The region has a humid and subtropical monsoon climate, with an annual mean temperature of $20\text{--}22^\circ\text{C}$, more than 1953.5 h of sunlight, an annual average rainfall of 1800 mm and a frost-free period of 346 d. Double-cropping of paddies is the typical method of planting in this region. The field studies were carried out from mid-August (when the late rice is sown) to mid-November (when the rice is harvested).

2.2. Field experiments

Field studies were implemented from 7 August to 20 November of 2012. No chemical fertilizer was applied during this period. Flooding (20 July) was performed before transplantation (8 August). The dates of various field practices and the rice growing stages are listed in Table 1.

2.3. Sample collection

The closed-chamber method was used for the collection of gas samples to measure phosphine concentrations and emission fluxes from the paddy field (Han et al., 2000). Three parallel plots were

Table 1

Rice growing stages and field practice.

Events	Dates
1st Flooding practice	20 July
Flooding collection	7 August
Transplanting practice	8 August
Transplanting collection	14 August
Tillering collection	28 August
2nd Flooding practice	3 September
Joining collection	9 September
Heading collection	26 September
Flowering collection	24 October
Drainage practice	1 November
Ripening collection	13 November
Harvest	20 November

employed for each collection. To distinguish the contribution of paddy soil and rice plants to phosphine emission fluxes, certain modifications were applied to the traditional static chamber technique (Byrnes et al., 1995; Jia et al., 2001). Gas samples were collected by syringes from 10.00–13.00 h, taken back to the laboratory and measured for 6 h. Soil cores 30 cm long were taken from each plot with a stainless steel column sampler (AMS, 209.51, American) at 10.00 h. The eight stages of paddy growth were divided into 0- to 5-, 5- to 10-, 10- to 15-, 15- to 20-, 20- to 25- and 25- to 30-cm segments, respectively. Three parallel soil cores were collected in each sampling. After collection, soil samples were immediately sealed in plastic bags, preserved in the dark at 4°C and analyzed within 24 h.

2.4. Determination of phosphine

An acidic digestion procedure was applied to soil samples to liberate the mixture-bound phosphine (Han et al., 2000). Both gas samples and liberated mixture-bound phosphine samples were analyzed with a gas chromatography–flame ionization detector (GC–NPD, Agilent 7820A) coupled to two successive capillary cryo-traps for enrichment; this method has been widely used in recent years (Niu et al., 2004).

2.5. Determination of environmental factors

The field determination of pH, soil redox potential (Eh) and Ts was performed with a soil pH meter (Spectrum, IQ 170, American) as soon as each paddy soil sample was collected. Soil gravimetric moisture content (Mc) was measured by drying the soil samples at 105°C for 12 h.

Soil P fractions were measured as TP, inorganic phosphorus (IP) and organic phosphorus (OP) fractions with the ammonium molybdate spectrophotometric method after digestion (Aspila et al., 1976; Zhu et al., 2011).

Phosphatase mineralizes organic P into phosphate and is involved in the soil P cycle (Zhu et al., 2011). Because the investigated paddy soils were slightly acidic, ACP levels were determined using phenyl phosphate disodium. Two milliliters of 0.1 M acetic acid buffer (pH 5.0) and 2 mL of substrate were added to 2.5 g of dry soil sample and incubated at 37°C for 3 h. A spectrophotometer (Agilent, 8453, American) was used to determine the phenol level in the filtrate at 578 nm (Zhu et al., 2011).

All of the paddy soil samples were sieved through a $70\text{ }\mu\text{m}$ mesh and ground to powder. Soil aliquots of 0.5 g were precisely weighed, digested with a multi-acid ($\text{HNO}_3\text{--HCl--HF--HBO}_3$) total digestion procedure (Sastre et al., 2002), and determined by inductive coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Fisher Scientific).

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