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Production and emission of phosphine gas from wetland ecosystems

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Abstract

Phosphine is a part of an atmospheric link of phosphorus cycle on earth, which could be an important pathway for phosphorus transport in environment. Wetland ecosystems are important locations for global biogeochemical phosphorus cycle. In this study, production and emission fluxes of free phosphine from four wetlands types in southern China were observed in different seasons. The results showed that the concentration of phosphine liberated from wetlands was at pg/m^3–ng/m^3 level. The emission concentrations of different wetlands followed the sequence: paddy field (51.83 ± 3.06) ng/m^3 ⩾ marsh (46.54 ± 20.55) ng/m^3 > lake (37.05 ± 22.74) ng/m^3 ≫ coastal wetland (1.71 ± 0.73) ng/m^3, the positive phosphine emission flux occurred in rice paddy field (6.67 ± 5.18) ng/(m^2·hr) and marsh (6.23 ± 26.9) ng/(m^2·hr), while a negative phosphine flux of (–13.11 ± 35.04) ng/(m^2·hr) was observed on the water-air interface of Lake Taihu, suggesting that paddy field and marsh may be important sources for phosphine gas in atmosphere, while lake may be a sink of atmospheric phosphine gas during the sampling period. Atmospheric phosphine levels and emission flux from Yancheng marsh and rice paddy field varied in different seasons and vegetational zones. Both diffusion resistance in aqueous phase and temperature were dominating factors for the production and transportation of phosphine to atmosphere.

Key words: phosphine; flux; wetland ecosystems
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Phosphine (PH_3), a highly toxic reducing gas, is proved to be a ubiquitous trace gas in atmosphere and a significant constituent of the phosphorus biogeochemistry cycle (Geng et al., 2005a; Zhu et al., 2009). Large areas of wetlands may be major sources responsible for the emission of phosphine (Dévai and Delaune, 1995; Han et al., 2000; Liu et al., 1999; Niu et al., 2004; Zhu et al., 2006), producing enough PH_3 into the atmosphere to influence the biogeochemical cycles of phosphorus (Glindemann et al., 2005). However, the source and distribution of PH_3 in natural environment still remain unclear. So far, limited research has been conducted to investigate the fate of PH_3 gas in various wetland ecosystems. Monitoring the concentrations and fluxes of PH_3 gas in different sources are of prime important to understand the sources and sinks of PH_3 in environment. In this article, four typical wetland ecosystems including paddy field, swamps, numerous eutrophic lakes and coastal shallow, were investigated to explain the natural volatile phosphorus emissions and transports in natural environment, and the concentrations and fluxes of PH_3 gas from such wetlands were systemic monitored for the first time.

Four typical wetland ecosystems in Jiangsu Province, Eastern China, were selected in this study. Yancheng Nature Reserve, along the southeast coast of the Yellow Sea, is the largest natural coastal wetland with typical floral succession. According to the salinity of surface water and vegetation types, the investigation was divided into four typical zones: Mudflat zone, Suaeda glauca Bge zone, Spartina alterniflora zone and Reed zone. Gas emission from four zones was collected in four seasons.

Lake Taihu (31°21′N, 120°10′E), a typical shallow freshwater lake, located in one of the most densely populated and developed areas of China. In recent years, large amounts of municipal sewage from surrounding cities are discharged into the lake, causing severe lake eutrophication. The samples were collected in spring, 2009 at the site of Meiliang Bay, where blue algal bloom happens frequently.

Coastal zone of Southwest Yellow Sea (31°45′–33°40′N, 121°–122°22′E), was chosen as representative of shallow coastal marsh. The investigation area has a lot of biologically active mariculture areas, with a large amount of organic mariculture sewage input, as a possible link to PH_3 production and emission. Sampling sites include the bays, harbors, and estuaries along the Southwest Yellow Sea, such as Haizhou Bay, Lianyungang Harbor, Old Yellow River mouth, Sheyang River mouth, Radial tidal sand ridges, Lusi Harbor and Yangtze River mouth.

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Measurements were conducted from 1st December 2007 to 26th February, 2008.

A typical paddy field in Jiangdu, was chosen as an artificial marsh. Samples were collected from June to October 2008, covering all the paddy growth stages: before transplanting, transplanting, late tillering, jointing, heading, flowering, milk and ripening.

The PH_3 samples in atmosphere above the shallow sea area were sucked from the outside through stainless-steel tube installed to the sampler and stored in a 0.5 L Tedlar gas bag with polypropylene valves (Glindemann et al., 2003). To avoid the impacts of anthropogenic factors and research ship itself, air samples were collected from the upwind on the fore. All air sample Tedlar bags were preserved under –20°C in the dark until laboratory analysis. It has been proved that atmospheric PH_3 concentration was stable under such preservation conditions (Zhu et al., 2007).

A closed-chamber method was adopted to measure the PH_3 emission in the swamp, lake and paddy field (Han et al., 2000). In this study, the stainless-steel chamber (50 cm × 50 cm), which could avoid PH_3 photodegradation were wrapped with quilt to maintain the temperature inside the chamber. During sampling in swamp and paddy field, the opened-bottom chamber (50 cm × 50 cm × 100 cm) equipped with two fans and a water groove on the top was inserted into soils for 20 cm. Air sample inside the chamber was taken at 10 min intervals by using a 60-mL plastic syringe for one hour. Before sampling, fans were turned on to stir the air in the chamber. As for the lake, a shorter chamber (50 cm × 30 cm × 50 cm) equipped with an inner tube was used to collect the atmospheric above the water. Three parallel experiments were conducted. All air samples were stored in 0.5 L Tedlar gas bags in the dark until laboratory analysis within 48 hr.

Gas samples in 50 mL syringes were purged with pure nitrogen into two successive capillary cryotraps after drying. Then, the rich PH_3 desorbed into a gas chromatograph (Agilent 4890D, USA) for all PH_3 determinations, which was equipped with a capillary column (cross-linked 5% Ph MeSilicone, 25 m × 0.2 mm × 0.33 μm film thickness, Hewlett-Packard, USA) and a thermo-ionicnitrogen-phosphorus-detector.

PH_3 is found in all samples, ranging from (0.14 ± 0.00) to (147.68 ± 50.94) ng/m^3. The detected levels are similar to the results by Glindemann et al. (2005). For different wetlands, PH_3 concentrations have an order of paddy field ⩾ marsh > lake ≫ coastal wetland. The highest PH_3 concentration is found in marsh, while the lowest in coastal wetland. Yancheng marsh and paddy field are almost completely covered with vegetation in contrast with Lake Taihu and shallow sea. The concentrations of PH_3 in marsh and paddy field are also much higher than that in lake and shallow sea area, suggesting that vegetation may accelerate the emission of phosphine into the atmosphere. Han et al. (2000) indicated that PH_3 could be transported through the vascular bundle into paddy stems.

A seasonal variation of PH_3 in different zones of Yancheng swamp wetland is shown in Table 1. The highest PH_3 level occurs in summer, followed in spring, autumn and winter, indicating that temperature may be a major factor affecting PH_3 generation. In summer, bacteria are more active and increasing temperature could accelerate the disintegration of soil organism and the mineralization of N and P (Glindemann et al., 1996; Liu et al., 1999; Song et al., 2006). A significant difference is observed for the average PH_3 concentrations at four sites with different soils and vegetation characteristics. The maximum atmospheric PH_3 level is measured in Suaeda glauca Bge zone, followed by in Spartina alterniflora site and mudflat zone; and the minimum is found in reed zone. Water phase plays an important role in slowing down the diffusion of PH_3 from soil to atmosphere (Eismann et al., 1997). Therefore, PH_3 emission level in reed zone covered with water around the whole year is much lower than that in other three zones with less water or without water.

The two PH_3 level peaks are observed at late tillering stage and jointing stage, with the values of (105.3 ± 125.9) ng/m^3 and (116.3 ± 12.9) ng/m^3, respectively, whereas the lowest value is measured before transplanting stage. In general, PH_3 concentrations in flourishing stages are higher than those in slowly growing stages. A significant positive correlation is found between temperature and PH_3 concentration ($r = 0.57$, $n = 32$, $p < 0.005$).

Positive PH_3 flux is found in rice paddy field and swamp, while negative PH_3 flux is observed in lake, indicating that paddy field and marsh may be important places responsible for PH_3 production and emission to atmosphere, while lake may be served as a pool of atmospheric PH_3 gas. Phosphine might be an important gas pathway for phosphorus transport in eutrophicated lakes. The negative flux of PH_3 in the lake also may be the reason of the low atmospheric PH_3 concentration.

Swamp is a source of atmospheric PH_3, showing a distinct spatial and temporal variation. Among the four different vegetation zones, the highest PH_3 average flux 60.25 ng/(m^2·hr) is observed in Spartina anglica zone, while the lowest value –45.87 ng/(m^2·hr) is in reed zone. The PH_3 average flux in Spartina anglica zone is higher than that in mudflat zone, indicating that wetland plants may be a controlling factor. PH_3 release from soils to the atmosphere depended on a balance of the production and

Table 1 Seasonal variation of phosphine above different vegetation zones of marsh (ng/m^3)

	Mudflat zone	Suaeda glauca Bge zone	Spartina alterniflora zone	Reed zone
Spring	47.94 ± 0.98	147.07 ± 101.40	74.19 ± 52.26	34.83 ± 23.91
Summer	138.59 ± 12.75	147.68 ± 50.94	141.55 ± 45.24	55.07 ± 13.65
Autumn	17.79 ± 1.07	2.60 ± 0.89	2.31 ± 0.40	5.60 ± 2.72
Winter	2.81 ± 0.45	2.26 ± 2.04	2.40 ± 2.41	4.16 ± 2.18
Seasonal average	51.53 ± 3.59	74.90 ± 12.33	54.94 ± 2.25	24.91 ± 10.61

depletion processes, which can be stimulated by manures or chemicals that could be produced by soil microorganisms, as well as by root exudates or their microbial degradation (Hou et al., 2009; Eismann et al., 1997). As compared with cool seasons, the release of phosphine in warm seasons is enhanced, it is likely due to the higher temperature (Geng et al., 2005b), therefore, PH_3 flux in summer is the highest (345.31 ± 100.34) ng/(m^2·hr).

Results suggest that large areas of artificial paddy fields could be sources of phosphine emissions. PH_3 fluxes in paddy field have a fluctuation pattern. A positive emission flux appears at late tillering stage, jointing stage and ripening stage, when the field is not covered with water. A significantly positive correlation between the emission flux and temperature during the whole rice growing period is also found in the study ($r = 0.51$, $n = 32$, $p = 0.003 < 0.05$).

As a result, we can speculate that the PH_3 gas above marine waters and lake originates from the emission of nearby paddy fields and swamps. Atmospheric PH_3 will be oxidized into water-soluble phosphate, which precipitates into lakes and coastal marine waters via rain (Lewis et al., 1985). Consequently, it may contribute to lake eutrophication or red tide in coastal water.

From this study, we can draw the conclusions that PH_3 emission varies in different wetland ecosystems. The release of phosphine in study areas correlate with temperature and water. In addition, the atmosphere can carry gaseous phosphorus to other places affecting phosphorus distribution at the global scale.

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