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Simultaneous monitoring of phosphine and of phosphorus species in Taihu Lake sediments and phosphine emission from lake sediments

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Abstract. Phosphine (PH_3) was monitored in the Taihu Lake in China by a GC/NPD method, coupled with cryo-trapping enrichment technology. Results showed that PH_3 was universally detected in sediments, lake water and atmosphere of the Taihu Lake area. Total phosphorus (TP_s) and fractions of different phosphorus species in lake sediments were separately measured as dissolved phosphate (DP), phosphorus bound to aluminum (Al-P), iron (Fe-P) and calcium (Ca-P), occluded phosphorus (OP), and organic phosphorus (Org-P) by sequential chemical extraction. High PH_3 levels were correlated with high TP_s values in sediments and with eutrophication at different sites. In addition, a positive linear correlation equation was obtained between the concentrations of PH_3 in lake sediments and of the phosphorus fractions. The resulting multiple linear regression equation is $PH_3 = -165 + 63.3\ \mathrm{DP} + 0.736\ \mathrm{Al\text{-}P} + 2.33\ \mathrm{Ca\text{-}P} + 2.29\ \mathrm{Org\text{-}P}$. The flux of PH_3 across the sediment–water interface was estimated from sediment core incubation in May and October 2002. The annual average sediment–water flux of PH_3 was estimated at ca. 0.0138 ± 0.005 pg dm^{-2} h^{-1}, the average yearly emission value of PH_3 from Taihu Lake sediments to water was calculated to be 28.3 ± 10.2 g year^{-1}, which causes a water PH_3 concentration of up to 0.178 ± 0.064 pmol dm^{-3}. The real importance of PH_3 could be higher, because PH_3 could be consumed in the oxic sediment–water boundary layer and in the water column. Spatial and temporal distributions of total phosphorus (TP_w) and chlorophyll *a* (Chl-*a*) in the water column of Taihu Lake were measured over the study period. Higher water PH_3 has also been found where the TP_w content was high. Similarly, high Chl-*a* was consistent with higher water PH_3. Positive relationships between PH_3 and TP_w (average $R^2 = 0.47 \pm 0.26$) and Chl-*a* (average $R^2 = 0.23 \pm 0.31$) were observed in Taihu Lake water.

Introduction

In the phosphorus biogeochemical cycle in nature, the existence of gaseous PH_3 had been in question during the past decades. In 1988, Dévai et al. believed that 30–45% loss of the total phosphorus in open-air sewage treatment plants could be attributed to release of PH_3 into the atmosphere. After that, improved analytical methods were developed to unambiguously quantify traces of PH_3, 'Free PH_3' gas could be detected in marsh gas (Dévai and Delaune 1995), biogases from landfills, communal waste, animal slurry, river and lake sediments (Glindemann and Bergmann 1995; Glindemann et al. 1996a), and in remote atmosphere (Gassmann et al. 1996; Glindemann et al. 1996b, 2003). Gassmann and Glindemann (1993) and Gassmann and Schorn (1993) revealed that, PH_3 can exist in condensed environmental samples, hidden as 'matrix bound PH_3' in marine sediments, harbor sludge, animal manure, and human faces. Eismann et al. (1997) measured traces of 'matrix-bound' PH_3 in soil. Liu et al. (1999) and Han et al. (2000) detected matrix-bound PH_3 in sediment samples and free PH_3 in ambient air adjacent to a water reservoir and a paddy field in Beijing. Niu et al. (2004) reported the distribution of PH_3 in sediments, lake water and atmosphere in Taihu Lake, China. These investigations reveal that trace PH_3 exists universally in nature.

As for the origin of PH_3 in nature, there is considerable debate. Barrenscheen and Beckh-Widmanstetter (1923) reported that obligate anaerobic bacteria could reduce organic phosphorus compounds to PH_3. Rudakov (1927) claimed to have isolated soil bacteria that reduce phosphate to PH_3, and his claim was supported by the work of Tsubota (1959). But Libert (1927) and Skinner (1968) failed to detect phosphate-reducing bacterial and concluded that evidence for bacterial reduction of phosphate or organically bound phosphorus is still inconclusive. Glindemann et al. (1998) noted that PH_3 is also released from corrosion of phosphorus rich metallic iron, and that process can be accelerated by bacteria. Morton et al. (2003) measured phosphates, phosphites, and phosphides in environmental samples and concluded that PH_3 formation may be caused by some forms of phosphides.

In China, serious lake eutrophication problems have restricted the sustainable development of economies in lake districts and the country (Jin 2000; Yu 2000; Wang and Guo 2000). Phosphorus is the limiting nutrient in most eutrophic lakes in China. The role of phosphorus in eutrophication has been in the forefront of hydrobiological research during recent years. But the existence of PH_3 and its effect on the lake phosphorus cycle has not been considered during past research, and all previous efforts had assumed PH_3 not to be present. Since PH_3 is ultimately converted to phosphate after complex oxidation through hypophosphite and phosphite (Frank and Rippen 1987), if it were released from sediments it possibly play a role in eutrophication (Stigniali et al. 1991). It is therefore useful to study the emission of PH_3 in lakes and its possible link to eutrophication.

Given the importance of the phosphorus biogeochemical cycle to lake ecosystems, if PH_3 was determined to be present in eutrophic lakes, understanding its production and emission could enhance our understanding of eutrophication. The purpose of this research is to detect PH_3 in eutrophic Taihu Lake, China, and study the relationship between PH_3 and phosphorus species in lake sediments. Second, to measure the flux from sediments by core incubation and estimate the annual emission level of PH_3 to water. Third, to investigate the variation and correlation between PH_3 and TP_w and Chl-*a* in lake water.

Materials and methods

Sampling

Taihu Lake, the third largest freshwater lake in China, is located in the lower reaches of the Yangtze River. The lake covers an area of 2340 km^2 and has a mean depth of 2 m (Chen et al. 2003). It is a component of a large drainage system of 36,500 km^2, which currently serves 33 million people in the Yangtze River Delta. Its waters are used for drinking, flood control, shipping, waste disposal, fisheries, aquaculture and farming. The lake water was oligotrophic in the 1950s, but the increased anthropogenic inputs to the lake have resulted in a deterioration of its water quality in many parts of the lake (Chang 1995). The average value of TN:TP is 35:1, while phosphorus is the limiting factor.

Eight sites were sampled on Taihu Lake (Figure 1). The longitude and latitude at each sampling site are indicated in Table 1. The sampling time was 09:00 in the middle of every month in 2002. Water samples were collected with a 2-dm^3 Niskin type water sampler at each site before sunrise and then drawn in 100-cm^3 airtight polyethylene plastic bottles, taking care not to introduce any air bubbles. The sediment samples were obtained by a Peterson sampler, while the gaseous samples were collected by an airtight plastic syringe near the surface water. All samples (including sediments, water and atmosphere) were collected in three replicates at each site for each sampling period, and stored in the dark at 4 °C. The concentration of PH_3 was determined within 24 h, and the data represented the mean values of three parallel samples. Matrix bound PH_3 was given on a dry weight basis.

PH_3 flux across the sediment–water interface

Sediment samples were collected from site 1# in May and October 2002. Intact sediment cores were obtained with a hand-driven organic glass sampler with a

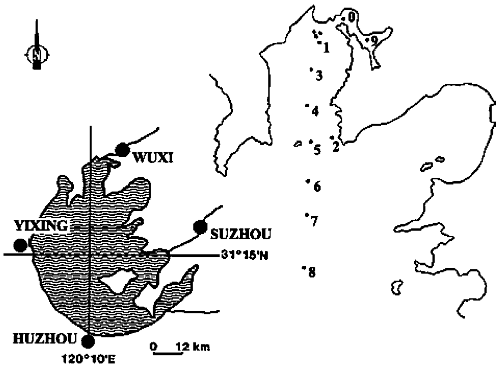

Figure 1. Map of Taihu Lake, showing locations of the sampling sites.

Table 1. Longitude and latitude of sampling sites at Taihu Lake.

No.	Sampling sites	Longitude and latitude
0#	Liangxi River	N31°32′49″ E120°13′38″
1#	Beside the Sanshan Island	N31°30′78″ E120°11′49″
2#	Beside the Fulin Hill	N31°25′42″ E120°12′57″
3#	Two navigation mark	N31°28′60″ E120°11′61″
4#	Three navigation mark	N31°26′84″ E120°11′31″
5#	Four navigation mark	N31°24′69″ E120°11′25″
6#	Zhihugang River	N31°30′31″ E120°07′93″
9#	Wuli Lake	N31°30′78″ E120°15′19″

length of 100 cm and an internal diameter of 6 cm. After extraction, three parallel samplers containing the sediment cores with a height of 45 cm and overlying water were immediately sealed with rubber stoppers taking care not to introduce an air bubbles. Samplers were stored vertically and transported to the laboratory within 6 h. Concurrent water samples were collected; immediately after sampling, the water samples were filtered with 0.45-μm filtration paper to remove the phosphorus adsorbed to particles. Filtrated lake water was stored at 4 °C in the dark.

Release of PH_3 across the sediment–water interface

Laboratory-based sediment core incubation experiments were used to measure the release rate of PH_3. Sediment cores samples were returned to the laboratory and stored in the dark. The overlying water was siphoned off, and filtered lake water was added through a siphon tube until the water height reached 50 cm. The bottom of the core sampler was sealed with a rubber stopper, while the top upper was left open to the atmosphere. Immediately, 30 cm^3 water at sediment–water interface was taken with a syringe for analyzing PH_3 in water. After sampling, another 30 cm^3 filtered water was added immediately to the samplers to maintain a height of 50 cm overlying water. The same process for sampling, supplying overlying water and analyzing PH_3 was carried out at periodic intervals. The experiment was terminated when PH_3 concentration in water remained constant.

After filtrating, it was assumed that the residual phosphorus fraction in the overlying water was negligible. The exchange of PH_3 at the water–atmosphere boundary and the assimilation of PH_3 during the incubation was not considered. The PH_3 flux across the sediment-water interface was by:

$$F = \Delta Q/(A\Delta t) = V\Delta c/(A\Delta t),$$

where F is the PH_3 mass flux or emission rate (pg dm^{-2} h^{-1}); ΔC is the concentration difference between zero and t times (pg dm^{-3}); V is the effective overlying water volume above sediments (dm^3); A is the cross-sectional area between sediment–water interface (dm^2); Δt is the sampling duration time (h); ΔQ is the difference of PH_3 quantity existing at sediment–water interface (pg).

Accordingly, emission quantity of PH_3 from sediments to water column was calculated according to the following equation:

$$Q = FA\Delta t,$$

where Q is the PH_3 quantity emitted from sediment to water (g); F is the emission rate of PH_3 ($g\ m^{-2}\ h^{-1}$); A is the area of the lake (m^2); Δt is the duration time (h).

Determination of PH_3

A gas chromatograph (Agilent 4890 D) was equipped with a capillary column (cross-linked 5% Ph–Me–Silicone, 25 m × 0.2 mm × 0.33 μm film thickness, Hewlett Packard). A Nitrogen-phosphorus-detector (NPD) was used. Two successive capillary cryo-traps (Al_2O_3/Na_2SO_4, cooled down with liquid nitrogen) were used to enrich the PH_3, For details see Glindemann et al. (1996b).

Both the original water samples and the filtered water samples (0.45-μm filtration paper) were measured by using a multiple equilibration technique (McAullife 1971), where the coexisting gas phase concentration is measured to estimate the concentration in water. Briefly, 30 cm^3 samples were equilibrated with 20 cm^3 of high purity nitrogen (N_2) by vigorous shaking in a 60-cm^3 airtight plastic syringe for 5 min, so as to extract PH_3 in the water sample. Then the determination of PH_3 in 20 cm^3 equilibrated N_2 is the same as in gas sample.

Sediment samples were digested with 5 cm^3 of 0.5 mol dm^{-3} H_2SO_4 for 5 min at 100 °C under an anoxic nitrogen atmosphere. The liberated gaseous PH_3 was purged with 50 cm^3 pure nitrogen out to the reaction vessel into a 50-cm^3 disposable polypropylene syringe, from which it was directly transferred into the GC after drying and cryo-trapping (Glindemann et al. 1998). The method for gaseous PH_3 determination is the same as in gas samples.

A sequential extraction method was used to divide total phosphorus (TP_s) in Taihu Lake sediments into six sorts of phosphorus fractions: Dissolved phosphate (DP), phosphorus bound to aluminum (Al-P), iron (Fe-P) and calcium (Ca-P), occluded phosphorus (OP), and organic phosphorus (Org-P). The scheme of successive extraction of different inorganic phosphorus species in sediments is shown in Figure 2. Org-P was analyzed by mineralization at 500 °C in a muffle furnace, following H_2SO_4 solution extraction (Conventional analytical methods of soil agricultural chemistry 1989).

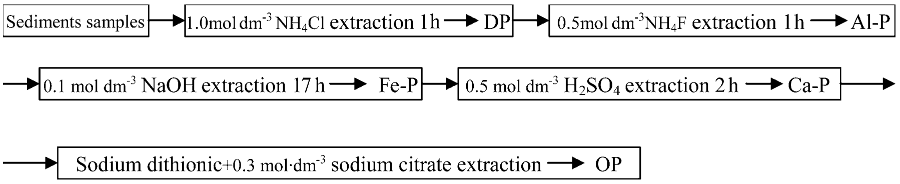

Figure 2. The scheme of sequential extraction of different inorganic phosphorus species in sediments.

Analysis of total phosphorus and Chl-*a* in water column

Total phosphorus in water column (TP_w) was measured colorimetrically by the molybdenum blue method (Jin and Tu 1990). Chl-*a* was determined according to Lorenzen (1967) from spectrophotometeric measurements after extraction with 90% hot ethanol at 80 °C.

Results and discussion

PH_3 in Taihu Lake

The concentrations of PH_3 in various components of Taihu Lake are shown in Table 2. For detailed temporal and spatial distributions of PH_3 see Niu et al. (2004). The data in Table 2 indicate that PH_3 is universally detectable in this eutrophic Taihu Lake. It is found that the concentration of PH_3 in the sediments was much higher than that in the lake water or the atmosphere.

The concentrations of PH_3 in surface water and in bottom water are similar, which may be explained by the shallowness of Taihu Lake. But PH_3 in all samples are much higher than in the same samples after 0.45-µm filtration, which may be attributed to sorption of PH_3 onto particles suspended in the original samples. In lake water, part of the PH_3 dissolves into water, and the other part is adsorbed onto suspended particles (Gassmann 1994).

Table 2. PH_3 concentrations in Taihu Lake.

	PH_3		
	Maximum	Minimum	Mean value
Sediments (ng $kg^{-1}{}_{(dry)}$)	919 ± 195	5.39 ± 0.79	161 ± 149
Surface lake water (ng m^{-3})	1.25 ± 0.09	0.098 ± 0.009	0.38 ± 0.25
Bottom lake water (ng m^{-3})	1.41 ± 0.79	0.10 ± 0.039	0.38 ± 0.26
Filtered lake water (ng m^{-3})	0.04 ± 0.00	0.005 ± 0.00	0.02 ± 0.01
Atmospheric air (ng m^{-3})	2.85 ± 0.08	0.13 ± 0.01	0.70 ± 0.54

Four representative sites (0#, 3#, 6# and 9#) were selected to investigate the distributions of different phosphorus species and PH_3 in Taihu Lake sediments. The order of the annual average value of TP_s in different sites was: 0# (666 mg kg^{-1}) > 6# (408 mg kg^{-1}) > 9# (273 mg kg^{-1}) > 3# (194 mg kg^{-1}). The distribution of TP_s was attributed to a different degree of eutrophication at the sampling sites. The sampling sites could also be ranked in the following order of their decreasing averaged PH_3 contents: 0# (563 ng kg^{-1}) > 6# (235 ng kg^{-1}) > 9# (170 ng kg^{-1}) > 3# (35.1 ng kg^{-1}). The data indicate that the PH_3 content rose and fell according to the TP_s content. The highest level of matrix bound PH_3 detected coincided with the highest total phosphorus concentration in the sediment.

The comparison of different phosphorus species in sediments showed that Fe-P is the most important (20–70%) mass fraction of TP_s in sediments. The mass percentage of Ca-P and Al-P of the TP_s content is approximately 10–40% and 10%, respectively. DP and OP are of minor importance. The uneven distribution of different phosphorus species may be caused by a different environmental deposition. Owing to lack of sufficient data, the distribution rule of PH_3 and different phosphorus species in lake sediments could not be well explained at present.

A correlation between PH_3 and different phosphorus species in lake sediments is shown in Figure 3. A positive correlation exists between PH_3 and TP_s, as well as inorganic phosphorus. There was no strong correlation between PH_3 and Org-P (R^2 was only 0.063). It was assumed that PH_3 in sediments may be related to the phosphorus content of sediments.

The data were also processed by step-by-step multiple regression analysis with the software SPSS ‘Statistical Package for the Social Science’ statistical packages for the best fit of phosphorus fractions and PH_3. The best fitting multiple linear regression equation was:

$$\mathrm{PH_3} = -165 + 63.3\mathrm{DP} + 0.736\mathrm{Al\text{-}P} + 2.33\mathrm{Ca\text{-}P} + 2.29\mathrm{Org\text{-}P}$$

$$(R = 0.68, F = 4.302, p = 0.011, n = 25)$$

In this equation: PH_3, DP, Al-P, Ca-P and Org-P represent the concentration of PH_3 (ng kg^{-1}), DP, Al-P, Ca-P and Org-P (mg kg^{-1}) in lake sediments, respectively. The correlation coefficient $R = 0.68$ given by multiple regression is higher than any R given in Figure 3. This indicates that PH_3 was simultaneously correlated with DP, Al-P, Ca-P and Org-P in sediments.

The measured PH_3 in water and air could be caused by reactive reduced phosphorus species (phosphides, elemental phosphorus etc.) which constitute matrix bound PH_3 in sediments (Glindemann et al. 1998; Morton et al. 2003; Roels and Verstraete 2004). Which phosphorus species was responsible for the formation of PH_3 should be validated by future studies.

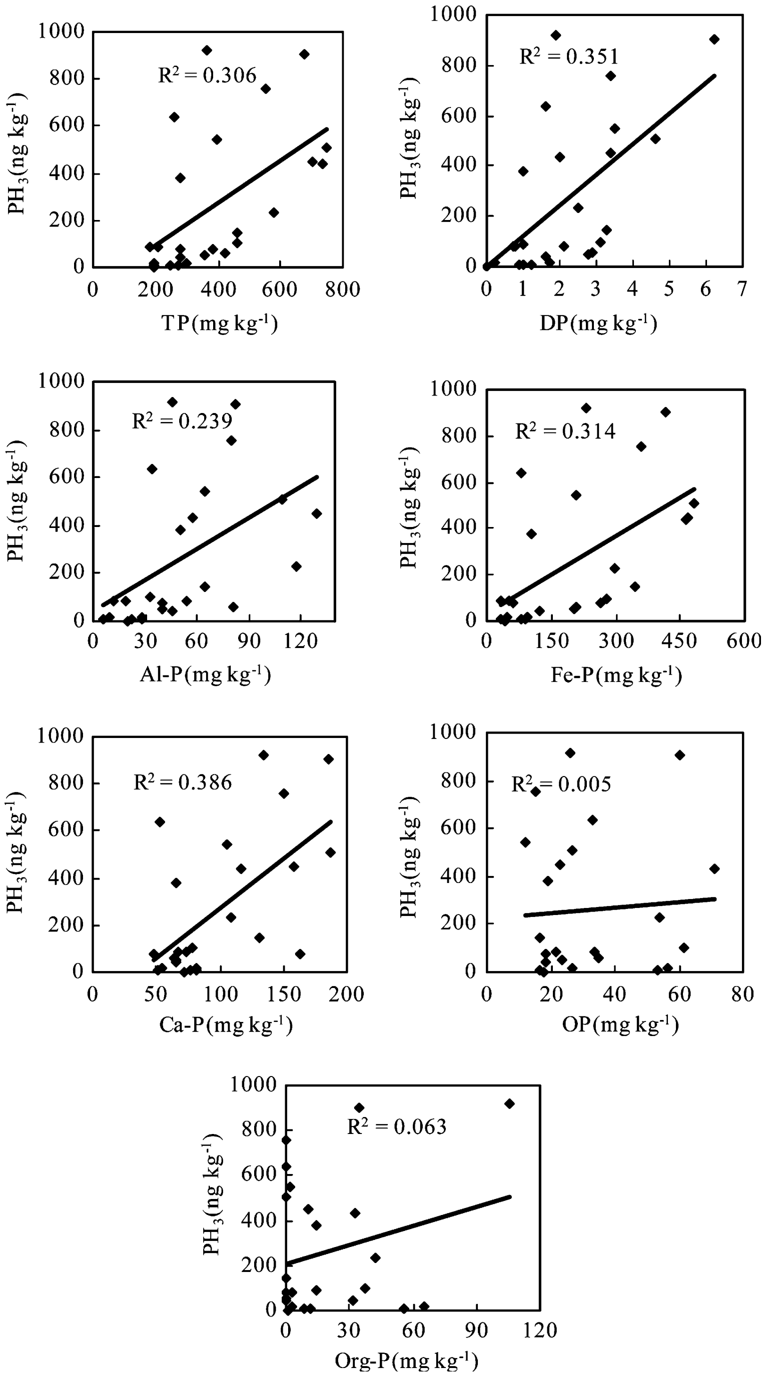

Figure 3. Correlation between PH_3 and different phosphorus species in sediments of Taihu Lake.

PH_3 fluxes

A sharp increase in the concentration of PH_3 in overlying waters was observed at the beginning of the experiment of the core incubation experiments, and then the increase in PH_3 concentration slowed down and achieved a water PH_3 maximum equilibration concentration of 0.34 ± 0.029 pg dm^{-3} after 64 h in May and after 102 h in October (Figure 4). The release pattern over time and the equilibration concentration of water PH_3 were similar in May and in October.

The emission rates of PH_3 at the sediment–water interface are presented in Figure 5. In May, the flux of PH_3 increased quickly and achieved a maximum flux of 0.024 ± 0.003 pg dm^{-2} h^{-1} at 20 h, and then it decreased gradually to 0.008 ± 0.0002 pg dm^{-2} h^{-1} and remained constant during the following time. The average emission rate was 0.016 ± 0.0043 pg dm^{-2} h^{-1}. A similar pattern was observed in October: The flux of PH_3 increased at first with a highest emission rate of 0.015 ± 0.0001 pg dm^{-2} h^{-1} at 42 h, and the average emission rate was 0.0115 ± 0.0027 pg dm^{-2} h^{-1}.

Both the PH_3 concentration and the emission flux were higher in May than in October, which may be explained by the higher temperature in May (25 °C) compared to October (15 °C), speeding up the emission of PH_3 from lake sediments (Han et al. 2000) or the formation of PH_3 in sediments (Gassmann 1994).

Estimated annual PH_3 emission from sediments to water

The estimated annual average PH_3 flux of 0.0138 ± 0.005 pg dm^{-2} h^{-1} allows us to evaluate the magnitude of PH_3 in the phosphorus biogeochemical cycle of

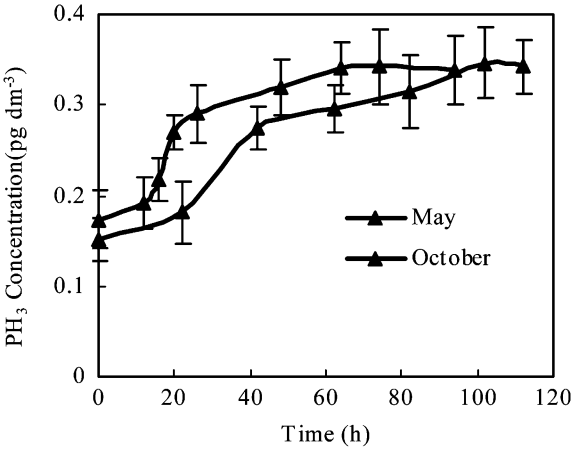

Figure 4. Variation of PH_3 concentration at sediment–water interface of core samples.

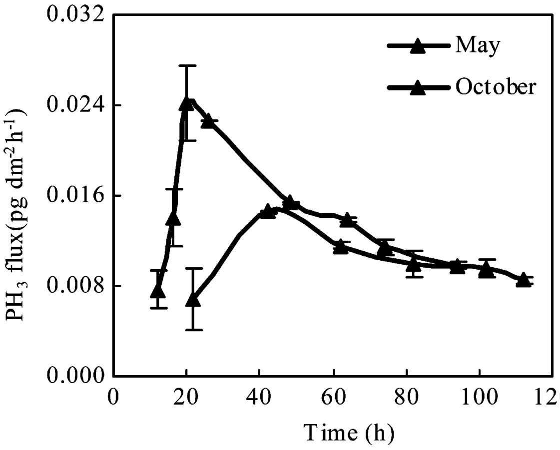

Figure 5. Variation of PH_3 emission rate at sediment–water interface of core samples.

Taihu Lake. For the year 2002, it was estimated that 2340 km^2 of Taihu lake sediments will release 28.3 ± 10.2 g PH_3 to the lake water based on our laboratory experiment (Table 3). The result was only 5 times lower than the PH_3 emitted from a landfill (160 g $year^{-1}$) (Roels and Verstraete 2004). PH_3 release rates measured in a sediment core exclude turbulent diffusion in the upper sediment boundary layer, and therefore may underestimate the real flux under field conditions (Portielje and Lijklema 1999).

An estimated PH_3 release of 28.3 ± 10.2 g $year^{-1}$ would lead an annual concentration of PH_3 in Taihu Lake water of 46.7×10^8 m^3 and up to 0.178 ± 0.064 pmol dm^{-3} (Table 3). This calculation is assuming that all PH_3 released from sediments will build up this concentration in water as observed in our laboratory incubations. This result was one order of magnitude higher than in field measurements, where a mean concentration of 0.011 pmol dm^{-3} was found (Table 2). These lower field concentrations could from either particle sorption or PH_3 released to the atmosphere.

Both the laboratory and the field concentrations of PH_3 may understate the real flux of PH_3, if there is any consumption of PH_3 or of its subsequent oxidation products by algae or microorganisms. In an attempt to understand this process, we grew algae in the laboratory (*Microcystis aeruginosa)* and

Table 3. Estimation of PH_3 emission at sediments–water interface.

Time	F_{max}(pg dm^{-2} h^{-1})	F_{min}(pg dm^{-2} h^{-1})	F_{mean}(pg dm^{-2} h^{-1})
May	0.024 ± 0.003	0.008 ± 0.0002	0.016 ± 0.0043
October	0.015 ± 0.000	0.008 ± 0.0002	0.0115 ± 0.0027
Annual	F_{mean}(pg dm^{-2} h^{-1})	Q_{mean}(g $year^{-1}$)	Conc.$_{mean}$(pmol dm^{-3})
	0.0138 ± 0.005	28.3 ± 10.2	0.178 ± 0.064

added PH_3, hypophosphite (PO_2^{3-}) and phosphite (PO_3^{3-}). After 7 days of incubation, our investigations reveal that the addition of PH_3 (0.0054–0.0432 mg dm^{-3} in water), PO_2^{3-} (0.034–0.274 mg dm^{-3}) and PO_3^{3-} (0.026–0.211 mg dm^{-3}) can all accelerate the growth of algae compared to blank experiment (unpub. data). Addition of PH_3 induced a greater growth of *Microcystis aeruginosa* than addition of PO_2^{3-} or PO_3^{3-}. It is possible that these compounds were oxidized to phosphate before they were utilized, although it has been proven that bacteria can utilize reduced phosphorus compounds directly (Casida 1960; Malacinski and Konetzka 1966).

The present work measured the PH_3 flux from sediments through the water column (resulting in an increase in the PH_3 concentration in water). This is likely only a small part of the total PH_3 flux. It is also necessary to measure the consumption rate of PH_3 by oxidation and possible microbial consumption in the water column and in the oxic sediment–water boundary layer. These boundaries (only a few mm thick) are known to be very productive, and the microorganisms (bacteria and algae biofilms on sediment surface particles) could consume most PH_3 before it can be released into the water column. These biofilms do over time degrade, and release their phosphorus into the water, where it can supply nutrient for the growth of algae. The total PH_3 flow may be higher compared to our water remaining concentration measurements, future method improvements are necessary to measure the importance of PH_3 more accurately.

Some PH_3 in the water may be released to the atmosphere. The diffusion flux of PH_3 at the sediment–water interface is much lower than that at the water–gas surface. The average PH_3 flux of 0.0138 pg dm^{-2} h^{-1} from Taihu Lake sediments was found to be approximately 1000-fold lower than the PH_3 flux of 17.8 pg dm^{-2} h^{-1} from paddy fields to the atmosphere (Han et al. 2000).

Distributions of PH_3, TP_w and Chl-a in Taihu Lake water column

Temporal and spatial distributions of PH_3, TP_w and Chl-*a* in Taihu Lake water column are displayed in Figure 6. Over the period studied, the annual average water PH_3 concentration varied between 0.30 ± 0.15 and 0.45 ± 0.26 ng m^{-3}. The highest PH_3 concentration of 1.41 ± 0.79 ng m^{-3} occurred in October at site 9#, while the lowest of 0.10 ± 0.039 ng m^{-3} was in April at 4# (Figure 6a). A similar fluctuating pattern seen in PH_3 was observed in Chl-*a* (Figure 6c). The annual average concentration of Chl-*a* ranged from 13.1 ± 8.3 to 56.5 ± 37.3 μg dm^{-3}, with a maximum of 128.6 ± 42.5 μg dm^{-3} at site 9# in October and a minimum of 2.79 ± 0.36 μg dm^{-3} at 4# in January. The values of TP_w seemed to follow a similar pattern with a sharp rise in September and October at all stations (Figure 6b). The average yearly TP_w value of the stations ranged from 0.40 ± 0.19 to 0.78 ± 0.26 mg dm^{-3}, the highest is 2.69 ± 1.53 mg dm^{-3}, and the lowest is 0.039 ± 0.02 mg dm^{-3}. This distribution may be caused by a different degree of eutrophication at the sampling

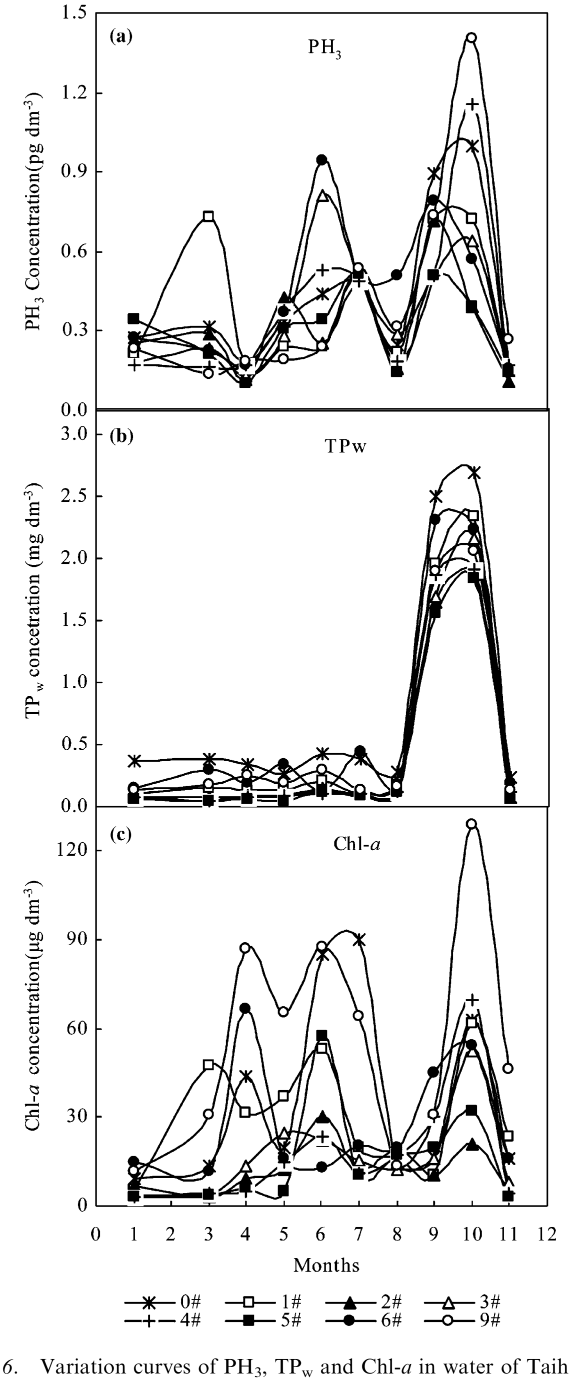

Figure 6. Variation curves of PH_3, TP_w and Chl-*a* in water of Taihu Lake.

sites. High water PH_3 coincided with high TP_w content, e.g. at 0# and 6# sites. High Chl-*a* also correlated with high PH_3, such as at 0# and 9# sites.

Positive relationships were found between PH_3 and TP_w (average $R^2 = 0.47 \pm 0.26$) and Chl-*a* (average $R^2 = 0.23 \pm 0.31$) (Figure 7). This suggests that the PH_3 was closely linked to the P cycle.

PH_3 in various aquatic systems

The levels of PH_3 in Taihu Lake sediments are in the same order of magnitude as those in the Hamburg Harbor, Germany and Wulongtan, China, and are significantly higher than those from the North Sea and Beijing sediments (Table 4). PH_3 in the water of Taihu Lake is 10–100 times lower than that in Hamburg Harbor or North Sea. On the contrary, PH_3 in the atmosphere is higher than in North Sea air, possibly because PH_3 in Taihu Lake water may be the main source of PH_3 to the atmosphere.

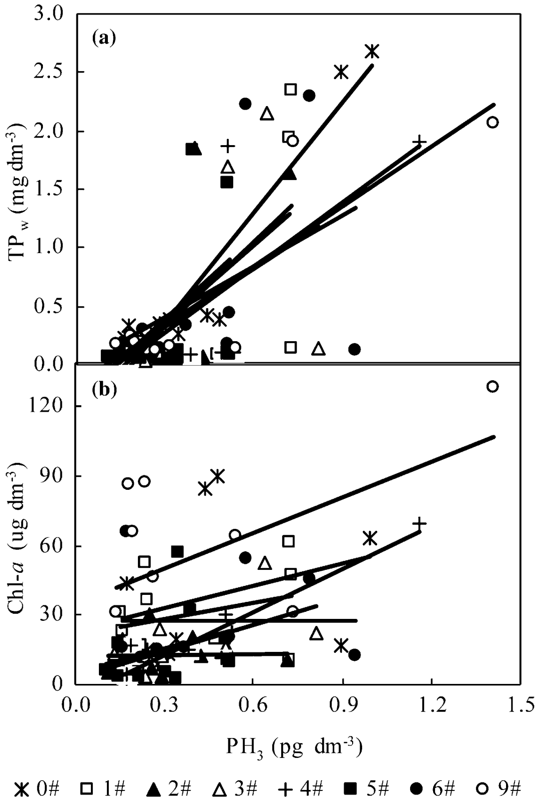

Figure 7. Correlation between TP_w, Chl-*a* and PH_3 in water of Taihu Lake.

Table 4. PH_3 in various aquatic systems.

Origin	Concentration	References
Sediments (matrix bound PH_3)		
Taihu Lake freshwater sediments, China	5.39–919 ng kg^{-1}	This work
Wulongtan freshwater lake sediments, China	335 ng kg^{-1}	Han et al. (2003)
Hamburg Harbor freshwater sediments, Germany	47.6–826 ng dm^{-3}	Gassmann (1994)
Hamburg Harbor freshwater sediments, Germany	0.2–56.6 ng kg^{-1}	Gassmann and Schorn (1993)
Jiaozhou Bay marine sediments, China	685 ng kg^{-1}	Yu and Song (2003)
Jiaozhou Bay marine sediments, China	60–271 ng kg^{-1}	Han et al. (2003)
North Sea marine sediments, Germany	0.01–2.43 ng dm^{-3}	Gassmann (1994)
Jiaozhou Bay pawn pond sediments, China	78 ng kg^{-1}	Han et al. (2003)
Beijing paddy field sediments, China	1.7–12.6 ng kg^{-1}	Liu et al. (1999)
Beijing reservoir sediments, China	1.89–3.92 ng kg^{-1}	Liu et al. (1999)
Water (water soluble PH_3)		
Taihu Lake water, China	0.49–6.93 ng m^{-3}	This work
Hamburg Harbor bottom water, Germany	0- 425 ng m^{-3}	Gassmann (1994)
North Sea bottom water, Germany	0–30.6 ng m^{-3}	Gassmann (1994)
Atmospheric air (free gaseous PH_3)		
Taihu Lake atmospheric air, China	0.13–2.85 ng m^{-3}	This work
North sea atmospheric air, Germany	0.041–0.885 ng m^{-3}	Gassmann et al. (1996)
Beijing paddy field atmospheric air, China	137 ng m^{-3}	Liu et al. (1999)
Beijing reservoir atmospheric air, China	98 ng m^{-3}	Liu et al. (1999)
Louisiana brackish marsh soil, America	0.42–3.03 ng m^{-2} h^{-1} (emission rate)	Dévai and Delaune (1995)
Louisiana salt marsh soil, America	0.91–6.52 ng m^{-2} h^{-1} (emission rate)	Dévai and Delaune (1995)

Conclusions

In summary, a focus on PH_3 and its emission over an annual scale has provided a useful framework for the development of novel phosphorus cycling. Future investigations should investigate other reduced phosphorus species like $PO_2^{3-}$and PO_3^{3-} as contributing to lake eutrophication. A source of PO_2^{3-} and PO_3^{3-} in lake water could be disposal of waste from the phosphorus industry or natural cycling of reduced phosphorus. Furthermore, Morton et al. (2003) pointed out that the reduced phosphorus compounds (PH_3, PO_2^{3-} and PO_3^{3-}) cannot be analyzed by standard phosphorus methods and this could cause errors in the phosphorus balance of lakes. Such reduced phosphorus waste could be a very mobile form of phosphorus that would not precipitate like phosphate does. These results would increase the understanding of the aquatic P balance.

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