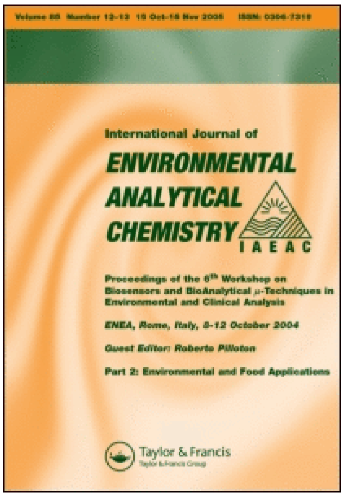

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Geng, Jinju , Niu, Xiaojun , Wang, Xiaorong , Edwards, Marc and Glindemann, Dietmar(2010) 'The presence of trace phosphine in Lake Taihu water', International Journal of Environmental Analytical Chemistry, 90: 9, 737 — 746

To link to this Article: DOI: 10.1080/03067310903013230

URL: http://dx.doi.org/10.1080/03067310903013230

Intern. J. Environ. Anal. Chem.
Vol. 90, No. 9, 10 August 2010, 737–746

Taylor & Francis
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The presence of trace phosphine in Lake Taihu water

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(*Received 5 November 2008; final version received 1 May 2009*)

Phosphine (PH_3) is a natural constituent in phosphorus (P) chemical cycles. The discovery of phosphine will shed new light on the mechanisms of P supplement and biogeochemical cycles. Since phosphine is converted to phosphate after complex oxidation via hypophosphite and phosphite, if it were present in the water column, understanding its production and emission could enhance our understanding of P speciation.

Assuming that phosphine in the gas phase is an ideal gas and at equilibrium between water and gas interface, phosphine in water solution can be quantified from the equilibrated concentration in gas phase using the Henry's Law. Application of this approach to Lake Taihu, China, phosphine in unfiltered and filtered water samples (0.45 µm) was analysed. Results showed that phosphine was universally present in Lake Taihu water. Phosphine concentration in unfiltered water ranged from 0.16 to 1.11 $\mathrm{pg\,L^{-1}}$, and was much less (0.01 to 0.04 $\mathrm{pg\,L^{-1}}$) in filtered samples. Over 90% of phosphine was adsorbed onto or incorporated into suspended materials with $<10\%$ dissolved in the water. Higher phosphine concentrations could be observed in warm seasons. Positive relationships were found between PH_3 and TP (average $R^2 = 0.59 \pm 0.22$) and TSP (average $R^2 = 0.37 \pm 0.13$).

Keywords: phosphine; gas-liquid phase equilibration technique; Lake Taihu; phosphorus cycle

1. Introduction

Phosphine (PH_3) gas is a volatile toxic phosphorus compound used as a dopant in the semiconductor industry and pesticide fumigant in grain storage [1]. The water solubility of phosphine at room temperature is low (partition coefficient gas/water about 5). The rate constant of phosphine oxidation by atomic oxygen is about $5 \times 10^{-11}\,\mathrm{cm^3\,s^{-1}}$, and the average atmospheric half-life is 5–28 h [2]. Phosphine is converted to phosphate in the environment after complex oxidation via hypophosphite and phosphite [3]. However, phosphine can persist for a long time, especially in anaerobic environments, such as freshwater sediments, marshes, swamps and floodplains. There is considerable debate about mechanisms of natural phosphine production. Rudakov [4] claimed to have found

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903013230
http://www.informaworld.com

microbial phosphate conversion to phosphine in manure by analysing phosphine indirectly as water soluble phosphate after oxidation and trapping of biogas, and his claim was supported by the work of Tsubota [5]. Because of their insufficient analytical techniques for phosphine detection, the above mentioned authors could not provide convincing evidence on phosphine formation. The occurrence of biogenic phosphine in natural environment has remained in dispute in later research. Gas chromatography was used as a more sensitive detection method, but biological phosphine production was not detected [6]. Dévai *et al.* [7] were later able to detect phosphine gas as a trace contaminant in biogenic methane produced during sludge digestion. It was proposed that phosphine could be found at detectable levels throughout the hydrosphere.

Spontaneously 'free phosphine' gas was also measured in marsh gas [8] and biogases from landfills, municipal waste, animal slurries, river and lake sediments [9–18]. Phosphine can exist in marine and harbour sediments, animal waste and feces as 'matrix-bound phosphine' [19–21]. Gassmann [22] defined the term 'matrix phosphine' which includes phosphine soluble in water as well as those associated with particulate matter suspended in bottom waters and adsorbed by surface and subsurface sediment. Unfortunately, in that work no phosphine was found in the filtered water samples.

China is confronting serious lake eutrophication, which has restricted sustainable development of economies in lake districts. Phosphorus (P) is the limiting nutrient in most eutrophic lakes in China, often inhibiting primary productivity [23]. The role of P in causing eutrophication has been in the forefront of hydrobiological research in recent years. A full understanding of P cycle in the natural environment requires expanded knowledge of its oxidation–reduction process. However, few publications have been devoted to the existence of reduced phosphine and its effect on the lake P cycle, since all previous efforts assumed that P cycle was limited by P (valence of +5). However, Morton *et al.* [24] pointed out that the reduced P compounds (PH_3, PO_2^{3-} and PO_3^{3-}) can not be analysed by standard P methods and this could cause errors in the P balance of lakes. Recently researches show that reduced P (including phosphorus acid (H_3PO_3), hypophosphorus acid (H_3PO_2) and various forms of phosphides (P(−3)) could be universally detected in the natural environment [25].

Given the impacts of the P cycle to lake ecosystems, if phosphine was determined to be present in lake water, understanding its production and emission could enhance our understanding of P speciation. The existence of phosphine also challenges the current dogma that P in lakes is presented in its most oxidized state (P valence of + 5). This paper will develop multiple equilibration analytical techniques coupled with Henry's law to measure phosphine in lake water, and to detect whether and how it is presented in Lake Taihu, China.

2. Experimental

2.1 *Description and selection of sampling sites*

Lake Taihu is the third largest freshwater lake in China. It is shallow with an average depth of 2.0 m and an area of 2338 km^2. About 40 million people live in the drainage basin (36,500 km^2). More than 200 rivers, streams, canals, and irrigation ditches enter the lake, with a theoretical turnover time of ~308 d. Hydrology of the lake is complicated; it connects with several waterways with frequent changes in flow direction due to seasonal meteorological events and/or topography of catchments. Increasing amounts of domestic and industrial wastewater discharged from nearby cities accelerate eutrophication in the lake, especially in the north. As a result, large cyanobacterial blooms affect drinking water resources, as well as fisheries and aquaculture [26]. Many industrial discharges into Lake Taihu contain pesticides, toxic chemicals or heavy metals [27]. The present study is focused on the northern part of Lake Taihu, Meiliang Bay (Figure 1), which receives large amounts of wastewater from Wuxi, a large city near the lake. Four locations (0#, 1#, 2# and 3#) in Meiliang Bay were selected as sampling sites (Figure 1 and Table 1).

2.2 *Sampling process*

Water samples were collected monthly with a 2 L Niskin-type sampler at 8:00 ~ 9:00 a.m. Sampling was conducted during early morning to minimise sun-light induced phosphine oxidation [28]. Water samples were drawn into 100 mL air-tight polyethylene plastic bottles without introducing air bubbles. Meanwhile, atmospheric samples were collected near the water surface using an air-tight plastic syringe. Samples were stored in a dark refrigerator (temperature +4 °C). Water sampling depth, water quality measurements, and position data for each sampling site are presented in Table 1.

2.3 *Analysis of phosphine in lake water*

Phosphine concentration in water was determined using a multiple phase equilibration technique [29]. Briefly, 30 mL of water were equilibrated with 20 mL high purity nitrogen (N_2) by vigorous shaking in an air-tight plastic syringe for 5 min to extract phosphine. The 20 mL of equilibrated N_2 was injected through a drying tube (NaOH drying agent, Merck, Germany, to remove H_2O, CO_2 and H_2S) into a 6-port valve on a gas chromatograph.

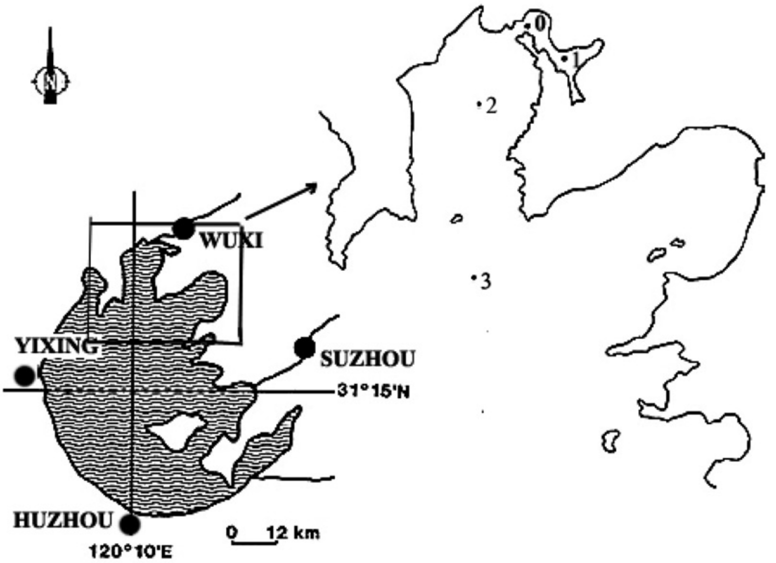

Figure 1. Map of Lake Taihu, showing locations of the sampling sites.

Table 1. Sampling description and some properties of water samples in Lake Taihu.

No.	Sampling sites	Longitude and latitude	Water depth (m)	Total P ($mg\,L^{-1}$)	Total soluble P ($mg\,L^{-1}$)
0#	Liangxihe	N31°32′49″E120°13′38″	1.75 ± 0.35	0.26 ± 0.04	0.125 ± 0.055
1#	Wuli Bay	N31°30′78″E120°15′19″	2.30 ± 0.09	0.20 ± 0.05	0.055 ± 0.023
2#	Two navigation mark	N31°28′60″E120°11′61″	2.53 ± 0.15	0.09 ± 0.03	0.029 ± 0.019
3#	Zhihugang	N31°20′31″E120°07′93″	1.88 ± 0.15	0.17 ± 0.04	0.112 ± 0.069

Phosphine in the N_2 was enriched in two successive capillary cryo-traps (Al_2O_3/Na_2SO_4 capillary columns: 80 cm × 0.53 mm, trap 1; 20 cm × 0.32 mm, trap 2, Hewlett Packard, both temperatures were controlled at $-60\ ^\circ C$ with liquid nitrogen) and desorbed into the gas chromatograph column. The retention time for phosphine is about 1.5 min [9].

The gas chromatograph (Agilent 4890D) was equipped with a capillary column (cross-linked 5% Ph-Me-Silicone, 25m × 0.2 mm × 0.33 μm film thickness, Hewlett-Packard). A nitrogen-phosphorus-detector (NPD) was used. Gas chromatograph conditions: Oven temperature was 40 °C isothermal; carrier gas pressure was 150 kPa and $2.0\,mL\,min^{-1}$ nitrogen. NPD gas flows: $4.5\,mL\,min^{-1}$ for hydrogen, $20\,mL\,min^{-1}$ for nitrogen as make-up gas, and $120\,mL\,min^{-1}$ for air. Every sample was measured at least three times. The detection limit for phosphine in gas phase was 0.1×10^{-12} (v/v), phosphine concentration was determined by comparison with a standard. Phosphine (10×10^{-12} (v/v) in N_2, certified) purchased in pressure cylinders from the Nanjing Special Gas Plant was used as standards.

3. Results

3.1 *Calculation of Henry's law constant for phosphine*

Assuming that phosphine in the gas phase is an ideal gas and at equilibrium between the water and gas interface, phosphine in solution can be quantified from the equilibrated concentration in gas phase using Henry's law:

$$P = KC_w$$

where K ($Pa \cdot L\,pg^{-1}$) is Henry's law constant, C_w ($pg\,L^{-1}$) is the equilibrium concentration of phosphine in the water, and P (Pa) is the phosphine partial pressure in N_2 in equilibrium with the water sample.

The detailed process for Henry's law constant is described as the following: at a definite temperature (about 25 °C), part of the water sample was placed under ultraviolet light for 24 h so that phosphine was broken down by light, then 30 mL of the radiated sample were mixed with 20 mL phosphine (equipped in N_2) of known concentration, and the mixture was shaken vigorously in an air-tight plastic syringe for 5 min. The following determination of phosphine in the gas phase of headspace was conducted in a way identical to the determination of phosphine in air. Thus, the Henry's law constant can be calculated as the following:

$$K = \frac{P}{C_w} = \frac{m_N RT}{MV_N} \times \frac{V_w}{m_T - m_N}$$

where m_T (pg) is the total mass of phosphine, m_w (pg) is the equilibrium mass of phosphine in water. m_N (pg) is the mass of phosphine in equilibrium N_2, V_N(L) is the volume of equilibrium N_2, V_w(L) is the volume of water, M is the molecular weight of phosphine.

Assuming K is constant across the phosphine concentration in this study, the concentration of phosphine in actual sample was calculated according to Henry's law constant:

$$C_s = \frac{m_N}{V_w} + C_w = \frac{m_N}{V_w} + \frac{m_N RT}{MV_N K} = \left(\frac{1}{V_w} + \frac{RT}{MV_N K}\right) m_N$$

where C_s(pg L^{-1}) is the concentration of phosphine in water sample, K is Henry's law constant, the other symbols are described as above.

3.2 *Recovery rate and relative standard deviation (RSD) for analysis of trace phosphine*

Recovery was measured by adding standard phosphine (10×10^{-12}(v/v)) to actual gaseous sample obtained from site 0#, then proceeding with the experimental method. The recovery rate was 101.1%. Thirty mL of phosphine standard (10×10^{-12}(v/v)) was analysed five times in parallel (phosphine concentration in unit of pg L^{-1}), and the RSD% was 3.7%.

3.3 *Phosphine in Lake Taihu water*

Phosphine results as a function of sampling time in Lake Taihu (Figure 2) indicated that phosphine in unfiltered samples from all sampling sites were 20–30 times higher than filtered samples.

Phosphine concentration in unfiltered samples ranged from 0.16 to 1.11 pg L^{-1} with a mean of 0.49 ± 0.04 pg L^{-1}. After filtration (0.45-μm), highest and lowest phosphine concentrations were 0.04 pg L^{-1} and 0.01 pg L^{-1}, respectively, with a mean of 0.02 ± 0.002 pg L^{-1}. Over 90% of phosphine in lake water was removed by filtration. This was attributed to sorption of phosphine onto particles suspended in unfiltered samples [22]. Results suggest that phosphine is quantifiable in this eutrophic lake, and over 90% of phosphine was adsorbed onto or incorporated into suspended materials with less than 10% dissolved in the water phase (Figure 2).

3.4 *Total phosphorus and total soluble phosphorus in Lake Taihu water*

Temporal and spatial distributions of total phosphorus (TP) and total soluble phosphorus (TSP) in Lake Taihu water are displayed in Figure 3. The highest TP concentration of 0.47 mg L^{-1} occurred in October at site 0#, while the lowest of 0.018 mg L^{-1} was in May at site 2#. A similar fluctuating pattern seen in TP was observed in TSP. The annual average concentration of TSP ranged from 0.029 to 0.12 mg L^{-1}, with a maximum of 0.18 mg L^{-1} at site 0# in July and a minimum of 0.017 mg L^{-1} at site 2# in June.

Positive relationships were found between PH_3 and TP (average $R^2 = 0.59 \pm 0.22$) and TSP (average $R^2 = 0.37 \pm 0.13$) (Figure 4). This suggests that the PH_3 was closely linked to the P cycle.

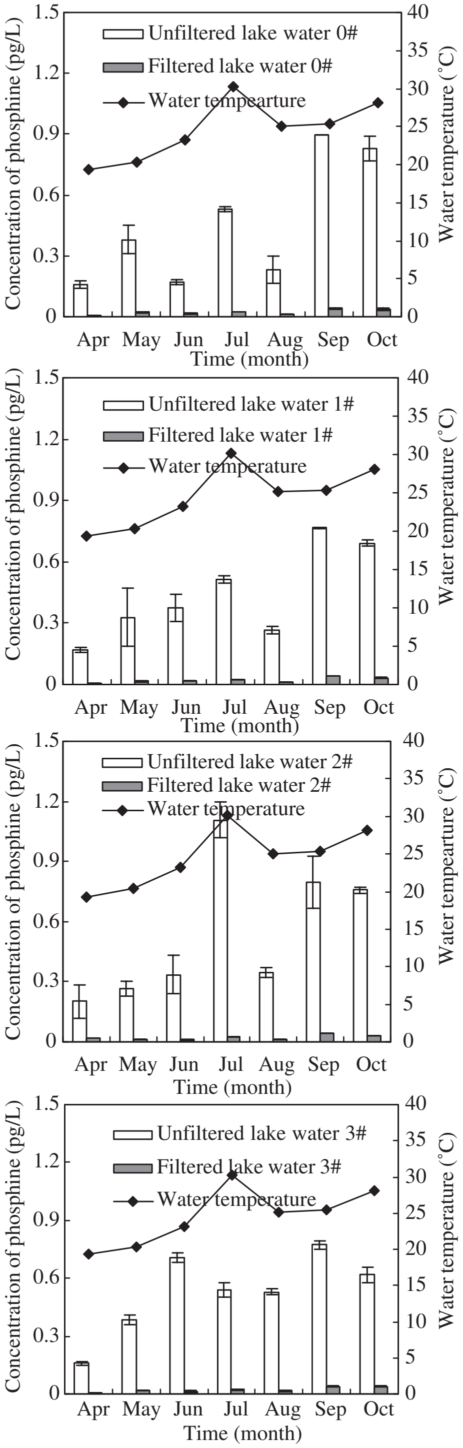

Figure 2. Phosphine in water of Lake Taihu.

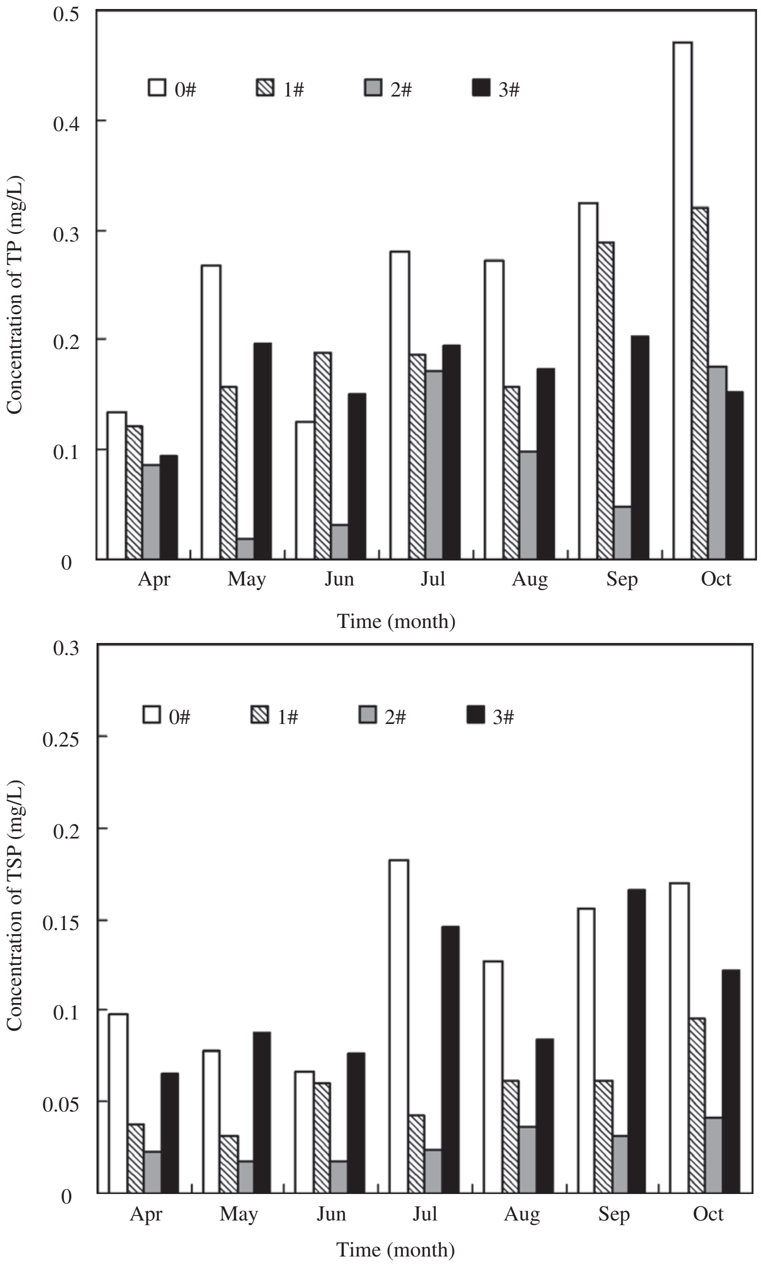

Figure 3. Variation curves of TP and TSP in water of Lake Taihu.

4. Discussion

A method was developed capable of quantifying trace phosphine in lake water by equilibration with headspace gas. This capability may improve understanding of the P cycle in lakes. Phosphine may be produced by microbial activities in lake sediment. However, these microbial activities can occur only in reducing

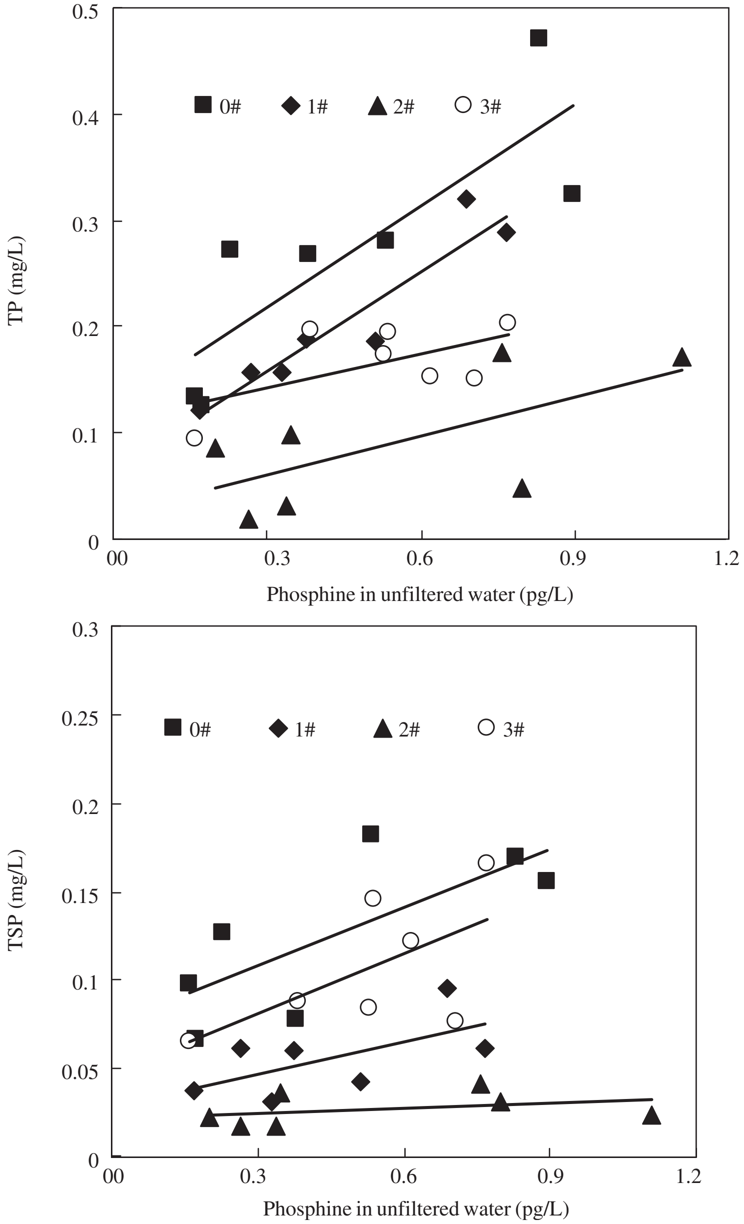

Figure 4. Correlation between TP, TSP and PH_3 in water of Lake Taihu.

environments at appropriate temperature and are limited if the microorganisms are strictly anaerobic (Table 2). Previous research [10] showed that atmospheric phosphine concentration is higher in warm seasons, which could indicate a correlation with higher microbial or chemical activity. Phosphine concentrations were higher in July, September and October than other months in the present study (Figure 2).

Table 2. Survey of the formation of phosphine by microbe activity.

Origin	Phosphine concentration	References
Manure or sludge	$98 \sim 692\,\mathrm{pg}$	[30]
Biogas	$0 \sim 382\,\mathrm{mg\,m^{-3}}$	[11]
Sediments, manure or soil	$0 \sim 964\,\mathrm{ng\,kg^{-1}}$	[31]
Mixed acid fermentors (*Escherichia coli*, *Salmonella gallinarum*, and *Salmonella arizonae*) and solvent fermentors_(*Clostridium sporogenes*, *Clostridium acetobutyricum* and *Clostridium cochliarium*)	$0 \sim 76\,\mathrm{pg\,mL^{-1}}$	[32]
Sewage sludge cultures	$5 \sim 100\,\mathrm{pg}$	[33]
Anaerobic digesters	$0 \sim 212 \times 10^{-12}$ (v/v)	[10]
Animal slurry	$0 \sim 14621 \times 10^{-12}$ (v/v)	[9]
Anaerobic mixed bacterial culture (fecult medium)	$0 \sim 186.7\,\mathrm{ng\,kg^{-1}}$	[19]

Lewis *et al*. [34] found that the peak value of the lake surface P sedimentation was usually observed in every midsummer, and the P sediments were primarily soluble P compounds which may be derived from the gaseous P compounds produced by metabolism of microorganisms. These P substances can be removed by filtration. It is not known if phosphine transport is sufficient to support an algae bloom. To quantify the contribution of phosphine to internal P budgets in lakes, it is necessary to examine phosphine flux and oxidation rates to phosphites and phosphates. However, there is no doubt that phosphine is present.

Filtration removed suspended particles from water samples. Phosphine in filtered samples depends on its solubility in water, which is related to air temperature and atmosphere pressure, etc. Phosphine concentration in filtered samples was low. Thus, phosphine in lakes may be associated with matrix bound phosphine absorbed onto suspended particles in water. While filtration method itself maybe remove phosphine by sorption or possible aeration. In this study, the Henry's law only allows to calculate both the soluble phosphine in water and the desorbed phosphine from suspended particles, if part of phosphine failed to be desorbed from suspended particles, it could not be detected by Henry's law. The results of this research maybe underestimate the actual phosphine content in water samples. The partitioning of phosphine to particles is also deserving of additional research.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 20607009), National Key Basic Research Project (No. 2008CB418003), Natural Science Foundation of Jiangsu Province of China (No. BK2008276), International Foundation of Science (No. A/4425-1), Research Fund for the Doctoral Program of Higher Education of China (No. 200805611054), Open Foundation of Engineering Center of Water Treatment and Water Environment Remediation, Ministry of Education (No. WTWER0715), and Key Laboratory of Environmental Protection and Eco-Remediation of Guangdong Regular Higher Education Institutions (No. G01N9080050). We are grateful to Ms. Feng Jianfang for helpful hints concerning phosphine detection. We also express our gratitude to the reviewers and editors for their valuable comments on the paper.

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