## PERSPECTIVE    OPEN

# Global phosphorus dynamics in terms of phosphine

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Since the detection of phosphine in the wastewater treatment plants in 1988, more and more investigations revealed that phosphine is closely related to ecological activities on a global scale. Here, we present perspectives on the whole dynamic cycles of phosphorus, particularly in terms of phosphine and its interactions with natural ecosystems, as well as the impacts from human activities. It may conclude that the phosphine-driving cycles of phosphorus depend on the coordination of human activities with natural ecosystems. Most importantly, the extensive recovery of phosphorus in numerous urban wastewater treatment plants may seriously obstruct its global cycles to catch up with the ecological needs in natural ecosystems. Phosphine gas plays an important role in the biogeochemical phosphorus cycle. Phosphorus might be one of the important elements participating in the global climate change together with carbon and nitrogen.

## INTRODUCTION

In the millions of years' evolution of the global natural ecosystem, the sustainability of this ecological system formed by many element cycles is self-regulated and complex. Most studies focused on the carbon, nitrogen, and sulfur cycles because phosphorus was considered not to exist in gaseous forms. Actually, as one of the critical elements, phosphorus, is cycling in a specific form, i.e., gaseous phosphine ($PH_3$), and getting involved actively in ecological interactions. Now phosphorus might be one of the important elements participating in the global climate change together with carbon and nitrogen.

## OCCURRENCE OF PHOSPHINE

For a long time, the distribution of phosphorus in the cycle of the hydrosphere was thought to be ambiguous and mass-unbalanced, until the detection of phosphine in wastewater treatment plants by Dévai et al. in 1988[1]. With the development of chromatography techniques and sample pretreatment methods, phosphine has been shown to exist universally in the environment. A large number of investigations on the global scope of phosphine have been conducted all over the world[1–55]. Phosphine exists universally in the natural environment with two different forms: free gaseous phosphine and matrix-bound phosphine (MBP). The former has been detected in marsh gas[36], sludge biogas[1], upper troposphere[37], and the atmosphere around the world[33]. MBP has been detected in various types of soils and sediments[14,45,50,54], sewage sludge[5], and feces[55]. It is worth noting that MBP is defined as the non-gaseous reduced phosphorus compounds that are transformed into phosphine gas by acid or alkaline digestion[45]. Thus, MBP does not necessarily refer to the pre-existence of phosphine in the matrix. It generally comprises of phosphine adsorbed by the media, phosphine gas in the interstice, and solid phosphides.

The phosphine concentrations in the atmosphere and the sediments demonstrate significant seasonal variations[24,56,57]. The phosphine concentrations display higher values in the summertime because the high temperature in summer might induce more microbial activity[4]. Besides, the thunderstorm weather during summer create lightning, which strikes the phosphate-containing organic matter (e.g., soil, dust) to form a local phosphate reducing condition[58], favoring the production of phosphine. Since the agricultural practice, specifically fertilization with phosphate-rich fertilizer, is likely to greatly increase phosphine production[59], the impact of the seasonal agriculture activities on the phosphine emission should be analyzed in the future. In addition to the seasonal trend, phosphine concentrations in the atmosphere show an obvious diurnal trend[24]. That is, atmospheric $PH_3$ levels peak during the early morning because phosphine accumulates in the night atmosphere and degraded gradually until noon due to the effects of increasing light intensity that promotes air oxidation[60].

From the detection of free phosphine gas (Fig. 1) and MBP concentrations (Fig. 2) in different environments, it can be concluded that the phosphine levels are seriously impacted by human activities. Generally, the concentrations of phosphine in urbanized and populated areas, are higher than those in the natural ecosystems in rural areas. Glindemann et al. found that the phosphine concentration in the air above the urban areas (e.g., Berlin, Hamburg, Beijing) is $0.62–157$ ng/m$^3$ while $0.04–2.03$ ng/m$^3$ in rural air, indicating emission by concentrated human activities[33]. Anthropogenic $PH_3$ production by industry can interfere with the natural cycling of $PH_3$. For example, the exhaust gas from the $PH_3$ fumigation of grain foods in the harbor resulted in high atmospheric $PH_3$ concentrations in Shanghai Harbor[28]. Besides, high $PH_3$ levels are found in paddy fields and eutrophic lakes[13,35,36]. The increased $PH_3$ liberating biological activity in polluted ecosystems with agricultural nutrients, such as the excessive P fertilizer, results in the high $PH_3$ values[59]. Unexpectedly high phosphine concentrations were found in air samples from the poles and the main sources were assumed to be the penguin colonies, guano, and tundra ecosystem[26,61].

## FORMATION AND TRANSFORMATION OF PHOSPHINE IN ECOSYSTEMS

Numerous biological and abiological mechanisms of phosphine formation have been proposed in the literature[2,20,23,58,62–65]. Significant evidence demonstrates that the production of phosphine is associated with the microbial reduction of P-containing substances and most of the results have been summarized in a

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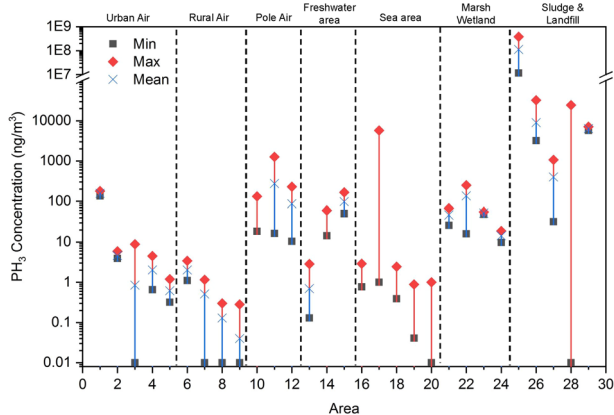
**Fig. 1 Survey of the presence of free phosphine in the environment.** (Urban air[33]: 1. Berlin, 2. Leipzig, 3. East Leipzig, 4. Hamburg, 5. Buenos Aires; Rural air[33]: 6. Leipzig, 7. Hammamet, 8. Israel, 9. Namibia; Pole air[7,27,34]: 10. Arctic Yellow River station, 11. Arctic New Oldsson region, 12. Antarctica Milo Peninsula; Freshwater area[24,35,36]: 13. Lake Taihu (Year 2005), 14. Lake Taihu (Year 2011), 15. Beijing Reservoir; Sea area[28,37,38]: 16. Southwest Yellow Sea, 17. Shanghai Harbor, 18. North-Atlantic Sea, 19. North Sea, 20. Southern Ocean; Marsh Wetland[13,15,36]: 21. Yancheng Reserve, 22. Beijing paddy fields, 23. Jiangsu Paddy fields, 24. Guangzhou paddy fields; 25. Sludge biogas in Hungary[1]; Landfill gas[39]: 26. Beijing, 27. Berlin, 28. Belgium).
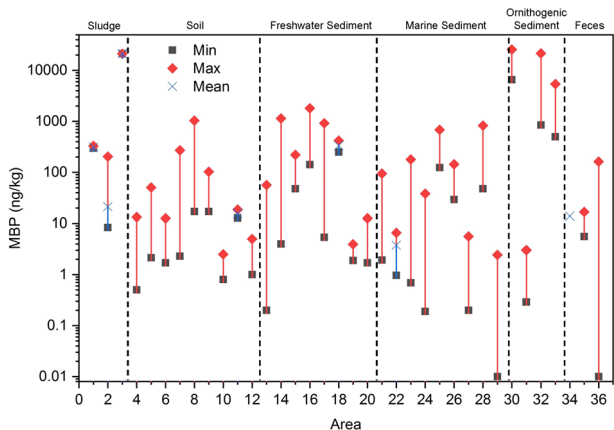


**Fig. 2 Survey of the presence of matrix-bound phosphine in the environment.** (Sludge[5,40,41]: 1. WWTP in Beijing, 2. WWTPs in Louisiana, USA, 3. Sewage plant in Beijing; Soil[14,24,34,42–46]: 4. Ardley Island, Antarctica, 5. Arctic Tundra, 6. Beijing paddy, 7. Southern China paddy, 8. Jiangsu paddy, 9. Germany industrial area, 10. Germany rural area, 11. Louisiana marsh, 12. Tropical forest, Mahe, Seychelles; Freshwater sediment[14,24,25,40,47–49]: 13. Hamburg Harbor, 14. Elster River, 15. Elbe River, 16. Lake Illawarra, 17. Taihu Lake, 18. Wulongtang Lake, 19. Shisanling Reservoir, 20. Ming tombs reservoir; Marine Sediment[4,11,47,50–53]: 21. Changjiang River Estuary, 22. South Yellow Sea, China, 23. Southwest Yellow Sea, China, 24. Yellow Sea, China, 25. Coastal agriculture area, Jiaozhou Bay, China, 26. Coastal areas, Jiaozhou Bay, 27. Offshore areas, Jiaozhou Bay, 28. Hamburg, Germany, 29. North Sea, Germany; Ornithogenic sediment[42,54]: 30. Lake Solvatnet, Arctic, 31. Ardley Island, Antarctica, 32. Lake Mochou, Antarctica, 33. Zolotov Island, Antarctica; Feces[55]: 34. Cattle manure, 35. Swine manure, 36. Feces of man).

review by Roels and Verstraete[62]. Biological phosphine formation from mixed bacterial cultures in the lab has been reported in several works[2,20,23,63,64]. This is consistent with the detection of high phosphine levels in natural environments with significant anaerobic biosphere areas, such as eutrophic lakes, coastal areas,

and wetlands[35,36,52,53]. Non-biological pathways for phosphine formation include corrosion of P-containing metals[66], reduction of phosphate by lightning strike[67], and mechanochemical reduction of phosphate in minerals[65]. For example, phosphine is produced when atmospheric lightning strikes the aerosol or soils that contain oxidized forms of phosphorus and chemical reductants[58].

In previous studies, phosphorus usually is thought not to undergo redox reactions and the removal of phosphorus in water occurs only from adsorption, complexation, and precipitation[68]. However, the reduction of phosphate to phosphine occurs commonly in wetlands and paddy fields. It is well-established that the formation of phosphine in nature follows thermodynamics in terms of ORP (oxidation-reduction potential) levels[59]. Anaerobic microorganisms use a sequence of terminal electron acceptors instead of oxygen during their respiration under the anaerobic condition[69]. With decreasing redox potential, they reduce nitrates to nitrogen or $N_2O$, sulfates to sulfides, and carbonate to methane[62,70]. Similarly, the production of $PH_3$ occurs under the reducing conditions while requires more energy and higher reducibility[59]. When redox potential falls below −300 mV, the phosphate may act as an electron receptor and finally get reduced to phosphine[19].

Though the thermodynamics of the production of phosphine by reduction of phosphate is exergonic[71], Bains et al. reported that the phosphine production from phosphite is thermodynamically favored in specific ecosystems[59]. Pasek et al. presented a comprehensive review on the redox chemistry in the phosphorus biogeochemical cycle and proposed that the source of phosphine in the atmosphere is the reduced P compounds, such as phosphite and hypophosphite[72,73]. As shown in Fig. 2, high concentration of phosphine is detected in Taihu Lake and paddy fields, where relatively high levels of phosphite in basal sediments are observed as well[74,75]. Consistently, Sun et al. reported that more phosphine was produced from anaerobic activated sludge with hypophosphite as the inorganic phosphorus source than that with phosphate[63].

About 10% of the phosphorous in the atmosphere exists as phosphine[59,73]. Most phosphine is formed in soil, sediments, sludge, or landfill, and prefers to adsorb in the media at a matrix-bound status. Then most phosphine may transform back to phosphates for use by natural plants or microbes[76], and the rest may emit from lower layers to surface layers and eventually into the atmosphere.

The living plants in wetlands transfer atmospheric oxygen through aerenchyma to the rhizosphere, keeping a high ORP level in their root areas[77]. The rhizospheric ORP ranges from 130 to 350 mV in daily time, creating an aerobic microenvironment that is more oxidizing than bulk water (−220 ± 22 mV)[78,79]. Though the oxygen transportation of plant to roots increases the rhizospheric ORP[80] and barely changes the total anaerobic environment in the bulk water, this favors the uptake of P by the plant. Such aerobic conditions may allow phosphine to transform back to phosphates and promote the utilization of phosphorous by plants. On the other hand, if the plants become dead, with no oxygen transporting to the rhizosphere, there will be an anaerobic condition with ORP <−300 mV. In this case, some available phosphates will be reduced back to phosphine, which may emit into the atmosphere.

It is estimated that there are about 40,000 ton/year of phosphine released to the atmosphere[81]. At certain temperature and under lightning conditions, most of the gaseous phosphine will be oxidized to phosphorus oxides[26,82], which might be deposited in clouds or rainwater[58,83], becoming a major source of phosphorus for the ecosystems that are poor in phosphorus[84].

From Fig. 3, it is found coincidentally that the concentrations of $PH_3$, which are in the sediments, bottom water, and surface water from Taihu Lake of China and in the atmosphere above it, as well as the phosphorus deposition rate, have almost the same monthly
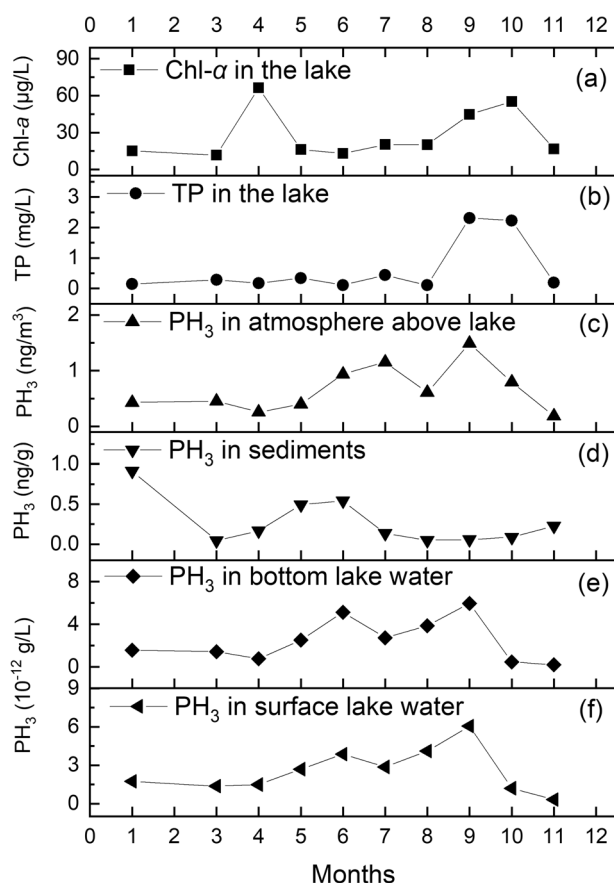
**Fig. 3  Variations of PH₃ distribution, total phosphorus (TP) and Chl-α concentration in Taihu Lake**[25,35,85]. (**a**) TP dry deposition rate in the lake; (**b**) PH₃ in atmosphere above the lake; (**c**) Chl-α concentration in the lake; (**d**) PH₃ in surface lake water; (**e**) PH₃ in bottom lake water; and (**f**) PH₃ in sidements.

variation patterns[25,85]. The positive correlation between the phosphine and Chl-a has been reported in several studies[35,50]. It is speculated that phosphine plays an important role in the algal bloom or eutrophication in the lake. Phosphine is produced in sediments, then releases into water and sequentially emits into the atmosphere. Later, mainly in spring and autumn, phosphine may return to the lake water as dry deposition of phosphorus. Consequently, the release of phosphorus from sediments and the dry deposition of phosphorus into the water body would result in algal blooming as indicated by the Chl-a distribution pattern in Fig. 3[35]. In this regard, phosphorus becomes a renewable resource. When phosphorus is not needed, it transforms to phosphine under anaerobic conditions and emits into the atmosphere; in reverse, phosphorus goes back to the ecosystem via dry deposition or rainfall.

## IMPACT OF ENGINEERING ACTIVITIES ON CLIMATE CHANGE IN TERMS OF PHOSPHINE

Another issue that is overlooked by scientists is the influence of regional engineering activities on the phosphorus cycle in terms of phosphine. It was reported that Gobi Desert in the northwestern of China is gradually turning green, mainly attributed to the foundation of Three Gorges Reservoir project. This project transports massive amounts of water vapor to the northwestern areas[86], probably carrying phosphine, phosphorus oxides as well as plant seeds in the troposphere. Several studies demonstrate that the foundation of Three Gorges Reservoir affect the precipitation, drought, heat wave, local temperature, humidity,

and even induce the extreme weather in reservoir regions[86–88]. Therefore, large-scale hydraulic engineering projects may dramatically influence the regional even global climate change. Another grand hydraulic project under planning in China is the Hongqi River water transfer proposal. As shown in Fig. 4, the 6188-km-long Hongqi River will be starting from southeastern Tibet Plateau[89], which is going to supply 60 billion m³ water per year to the northwestern inland of China. It could be expected that this grand project will cause an inevitable and marked impact on the phosphorous cycle and the ecosystems.

Phosphine is a reactive atmospheric trace gas, which competes with methane and other greenhouse gases for hydroxyl radicals that are produced by the light degradation of ozone[22]. Therefore, the presence of phosphine in the atmosphere induces the consumption of ozone, extends the residence time of greenhouse gases, and indirectly enhances the greenhouse effect[90]. Moreover, phosphine is easily converted into phosphoric acid or phosphate ions in the presence of oxygen and solar radiation[60]. The phosphoric acid could provide condensation nuclei for cloud formation in the upper troposphere and subsequently influence the global climate[37,58]. The phosphate ions will deposit to the land and lakes, playing an important role in the biomass growth in phosphorus-limited areas.

## PERSPECTIVES ON FUTURE RESEARCHES

Currently, phosphorus is still considered as a rare resource to be recovered from engineering facilities, such as municipal wastewater treatment plants[91]. However, the concentration of total phosphorus in raw wastewater is around 10 mg/L, and recovering such highly dissipated phosphorus to pure phosphate requires concentrating for over $10^5$ times. This is an irreversible process that costs more than gains according to the thermodynamic law. Thus recovering phosphorus directly from wastewater is not feasible[92]. Undoubtedly, the regional recycle of phosphorus as happened in municipal wastewater treatment plants may benefit local farmlands or gardens. However, the accumulation of phosphorus in local areas might result in a runoff of phosphorus during the rainfall season and endanger the local water body due to eutrophication[93].

In global ecosystems, the wastewater treatment plant plays a role as a decomposer. If the researchers turn it to be a producer for phosphorus recovery or energy production, the loss will outweigh the gain. Instead, modifying the conventional wastewater treatment processes into a mode that transforms more phosphates into phosphine would benefit the ecological cycle of phosphorus. In this way, all the wastewater treatment plants would become an essential part of the global phosphorus cycle.

The removal of phosphorus from wastewater by phosphine production is accomplished by the phosphate reducing microorganisms in the inoculum (e.g., animal manure, paddy soil) under anaerobic conditions. In general, PH₃ emission from conventional biological wastewater treatment is less effective (ng-mg/m³)[20]. Scholars tried to improve PH₃ yield in different wastewater treatment process via artificially strengthened anaerobic digestion systems, such as the anaerobic sequencing batch reactor (ASBR)[94], sequencing biofilm batch reactor (SBBR)[95], and microbial electrolysis cell (MEC)[96]. Yang et al. achieved 83% total phosphorus (TP) removal via oxygen-limited membrane bioreactor (OLMBR) and about 19.4% phosphorus was removed by the production of PH₃ gas[97]. In order to find a breakthrough of increasing the phosphine yield, researchers have conducted comparative experiments on the best inoculum sources (e.g., animal manure, paddy soil)[95,98], electron donors (i.e., carbon sources)[2], sources of phosphorus (e.g., phosphate, hypophosphite, lecithin, phosphonoacetic acid)[99,100], investigation of the influencing factors[20,101], as well as isolating the microbial functional bacteria[64,102,103]. The recovery of phosphorus by gaseous phosphine is proposing a different direction

**Fig. 4 The diagram of Hongqi River under planning.** The red lines represent Hongqi River and its tributaries. Map data: Google Maps.

for the removal of phosphorus from wastewater. The potential benefits and differences for doing so are illustrated as follows.

First, phosphorus removal in wastewater treatment plants is generally rather problematic and the significant drawback is the absence of phosphorus redox processes. Phosphorus was wrongly assumed not to undergo redox reactions in transformation and migration processes. As discussed above, when redox potential falls below $-300$ mV, reduction of phosphate to phosphine can take place. If we take advantage of the conversion of more phosphorus to phosphine, it is believed to be a qualitative change of P removal in the wastewater treatment plants (WWTPs) and reduce the amount of phosphorus-rich sludge, saving the cost for the post-treatment of sludge. Second, instead of recovering P as the anthropogenic fertilizers, the redistribution of phosphorus via $PH_3$ transport from rich phosphorus sources could fertilize areas that are poor in phosphorus[26]. Though the atmospheric phosphine is a small contribution to the phosphorus cycle, $PH_3$ might not be insignificant for areas where P limits the biomass stock or phosphine is the main or only source of phosphorus. Through this work, we aim to raise the research attention on the impact of enormous recovery of P from wastewater on P cycle in natural ecosystems and the production of phosphine when designing the removal processes of phosphorus in the wastewater.

Moreover, according to the global budget of atmospheric phosphorus balance, the total global emissions of atmospheric phosphorus was estimated to be 3.5 Tg/yr, of which 2.7 Tg/yr fell down to the land and 0.8 Tg/yr into the ocean[104]. However, the successive cycling activities through phosphine or other pathways remain unexplored. The tentative estimation of the global phosphine budget is provided in Supplementary Table 1. Since the emission of phosphine demonstrates significant spatial variations and the survey about phosphine levels has not been carried out globally yet, it is impossible to estimate the global budget so far. For example, the surface area of global oceans is about $3.6 \times 10^8$ km$^2$ but the existing survey of phosphine levels in

the marine environments is focused on the coastal and offshore areas[28,47,53], which are seriously affected by the human activities. The emission flux data in these areas can barely represent the immense ocean areas. It is anticipated that this work will stimulate more research on the role of phosphine in the global phosphorus cycle.

## DATA AVAILABILITY
The authors declare that all data supporting the findings of this study are available within the paper and its supplementary information file.

## CODE AVAILABILITY
This study does not use any unreported custom computer code or mathematical algorithm that is deemed central to the conclusions.

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## AUTHOR CONTRIBUTIONS

X.Z. proposed the concept and supervised. W.F. created the first draft of the article. The authors contributed in revising and finalizing the manuscript.

## COMPETING INTERESTS

## ADDITIONAL INFORMATION