

Tropospheric Phosphine and Its Sources in Coastal Antarctica

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Earlier reports show very low concentrations of phosphine in remote air of the lower troposphere of nonpolar regions, in the low ng m⁻³ range during the night and in the pg m⁻³ range during daylight around noon. In this study, abnormally and unexpectedly high phosphine concentrations (30.0–407.8 ng m⁻³, 11 locations) were found in polar air samples collected on Millor Peninsula, eastern Antarctica and Fildes Peninsula, western Antarctica. The maximum concentration was measured in the atmosphere of penguin colonies. Field phosphine emission rates from four colonies were 8.99 ng m⁻² h⁻¹ (skua colony), 9.56 ng m⁻² h⁻¹ (gentoo penguin colony), 39.96 ng m⁻² h⁻¹ (seal colony) and 63.58 ng m⁻² h⁻¹ (empire penguin colony), respectively. Our air sampling sites are located downwind of two large penguin colonies, indicating that penguin colony emission is the predominant source for atmospheric PH₃ on Millor Peninsula. Laboratory scale incubation of ornithogenic soils amended by penguin guanos yielded a maximum PH₃ production rate of 0.58 ng kg⁻¹ d⁻¹ specifically at low temperature (4 °C). Significant concentrations of phosphine occur in the atmosphere of coastal Antarctica and confirm the existence of a small gaseous link in the phosphorus cycle of the Antarctic tundra ecosystem.

Introduction

Phosphine (PH₃), a widely used gaseous chemical (1), is also an interesting environmental chemical and reactive atmospheric trace gas, which competes with methane and other greenhouse gases for hydroxyl radicals and thus enhances an indirect greenhouse effect (2). Once phosphine enters the atmosphere, it is oxidized by hydroxyl radicals ultimately to nonvolatile and hygroscopic phosphoric acid (1). Phosphine exists in the environment in two different forms: free gaseous phosphine (3, 4) and matrix-bound phosphine (MBP) (5). Gaseous phosphine has been found worldwide in the earth's atmosphere, even at such remote locations as the 1 ng m⁻³ range in the lower (6) and higher (7) troposphere; a diurnal night-time maximum of phosphine in the lower troposphere (6); in surface air of the Northern Sea (8); and

in the urban air of Beijing at the 100 ng m⁻³ range (9). MBP has been defined as phosphine bound to condensed environmental samples (such as lake sediments, animal manure, human feces, etc.), which can be liberated by acid or alkaline digestion (5, 10, 11).

Over the past decade, considerable research efforts have been directed at identifying the emission sources and environmental occurrences of phosphine. Recent studies have demonstrated the effects of phosphine emissions from sewage treatment plants, harbor surface sediments, animal slurry, landfills, communal waste, lake sediments, and paddy fields (3–5, 9–20). Several reports claim that phosphine can be produced by biochemical processes (such as the bacterial reduction of phosphates or natural organophosphorus compounds) (11, 12, 17, 18). Therefore, phosphine emissions and its forming biochemical processes support a gaseous link to the phosphorus cycle in the global environment (7, 18, 21). This is contrary to the common assumption that, unlike carbon, nitrogen, and some other elements, phosphorus can only cycle in different nonvolatile forms of phosphates and phosphonates (22, 23). It is unquestionable that the finding of phosphine is a scientific curiosity.

Recently, high MBP concentrations have been explored in various phosphate-rich biological matrixes (seabird guanos, etc.) of the maritime Antarctic biosphere (24). Earlier field observations showed that penguin guanos and ornithogenic soils (the definition is given in the Supporting Information) are the important emission sources for gaseous hetero-element C-, N-, and S-containing gases (25–27).

It is in question whether seabird guanos and ornithogenic soils may constitute a potentially significant source of free atmospheric phosphine that transports phosphorus beyond the reach of guano deposition. In Antarctic tundra ecosystems, the areas close to penguin colonies are often covered by a dense carpet of vegetation growing in the ornithogenic soils rich in phosphorus. However, the vegetation in most tundra areas does not grow well due to the scarcity of nutrients, including phosphorus (28, 29). Atmospheric phosphine could be a small but significant carrier of the nutrient phosphorus in coastal Antarctica. It is very necessary to explore whether free gaseous phosphine contributes to a certain extent to the geochemical cycle of phosphorus in coastal Antarctic tundra ecosystems.

This paper takes advantage of excellent sampling opportunities to study summertime atmospheric phosphine and its sources on Millor Peninsula, eastern Antarctica and Fildes Peninsula, western Antarctica during the 22nd Chinese Antarctic Research Expedition (CHINARE-22). The objectives of this study are (1) to explore and quantify atmospheric phosphine concentrations in Antarctic tropospheric air samples and its affecting climatic factors; (2) to measure in-situ phosphine emission rates from the seabird colonies; and (3) to measure in-vivo phosphine production and emission from the samples of ornithogenic soils incubated in the laboratory.

Materials and Methods

Study Area and Atmospheric Air Sampling. From December 2005 to February 2006, this project was carried out on coastal Millor Peninsula, eastern Antarctica and Fildes Peninsula, western Antarctica. The distribution and description of the sampling sites are given in Figure 1 and in the Supporting Information.

The air sampling frequency at the "normal observation site" (sampling site 4) was once every 4 or 6 days and the sampling time was around 10:00 and 22:00 (local time) to

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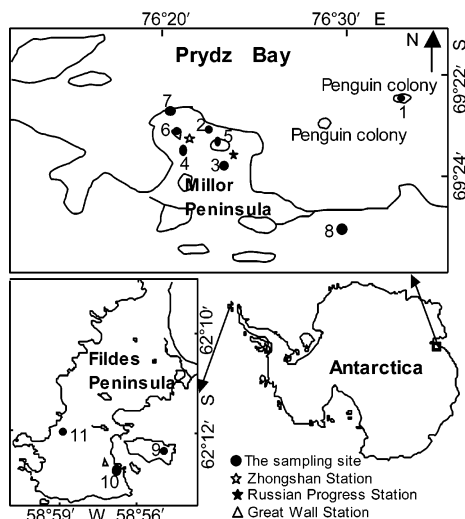


FIGURE 1. Study area and air sampling sites in the coastal Antarctica. These sites can be ordered in three categories: emission sites (1, 2, 5, 6, 9, 10, 11), tropospheric air moderately remote from emission sites (3, 4, 7, 8), and remote tropospheric air (12–19), specifically 1. Empire penguin colony; 2. Saltmarsh of Wolong Beach; 3. Hilltop behind Russian Progress Station; 4. Hilltop behind Zhongshan Station ("normal observation site"); 5. Tuanjie lake; 6. Mochou lake; 7. Nella Bay; 8. Luojiaoshan Glacial; 9. Gentoo penguin colony; 10. Skua colony; 11. Seal colony. In addition, four observation sites of phosphine fluxes were also established at empire penguin colony, gentoo penguin colony, skua colony, and seal colony, respectively. 12–19. Air sampling sites above the Southern Ocean (also evaluated as sites influenced by possible sub-marine emission) (Supporting Information Figure S1).

compare the differences of atmospheric phosphine between two times of day. The sampling season was from December 23, 2005 to February 17, 2006. At other sampling sites, the sampling frequency and time were not regular due to the limited manpower and the severe climatic conditions (Table 1). Samples of air to be tested were sucked into 0.5 L Tedlar sampling bags (7) that keep phosphine stable (see Supporting Information, Table S1), and were stored at -20°C in the dark until laboratory analysis.

Field Phosphine Flux Measurement. The closed-chamber method (13, 16) was used for the measurement of phosphine fluxes from ornithogenic soils in four sea animal colonies (see Supporting Information).

Laboratory Simulation of Phosphine Production. Ornithogenic tundra soils (6 g) were added into 100 mL glass bottles, both filled with high-purity nitrogen and sealed anaerobically. The bottles were incubated statically in a thermostatic chamber in the dark for 72 h; the temperatures were adjusted to 4 and 25°C , respectively. The headspace gas samples were taken every day for analyzing gaseous phosphine (30). The simulation conditions (4°C , dark, anaerobic) are according to tundra covered by accumulated snow and ornithogenic soils or sediments in the summer. The higher temperature of 25°C was selected for comparison. Tundra soils in the coastal Antarctica are covered by accumulated snow during most of every year. The soils under the snow are in almost total darkness in an anaerobic environment, and the soil temperature is very close to 0°C (26, 27).

Since the air temperature rises above 0°C in the Antarctic summer, the ice or snowmelt water can dilute tundra ornithogenic soils; therefore, the effects of water dilution on phosphine production rates were also simulated in the laboratory. A total of 0, 2, 4, and 8 mL clean water together with 5 g of ornithogenic soils were added into four 100 mL brown glass bottles, respectively. The bottles were incubated

anaerobically in the dark at 4°C for 72 h. The headspace gas samples were also taken for analyzing gaseous phosphine (30).

Analysis of Free Phosphine in Air and Other Gas Samples. Phosphine was analyzed at least three times per sample by GC (see Supporting Information).

Analysis of MBP in Ornithogenic Soil or Sediment. A known mass of each soil sample was digested with 5 mL $0.5\text{ M H}_2\text{SO}_4$ for 5 min at 100°C under an anoxic nitrogen atmosphere (24, 30). The liberated phosphine was purged with 50 mL pure nitrogen out of the reaction vessel into a 50-mL disposable polypropylene syringe. The mass of phosphine in this gas (analyzed by GC) divided by the mass of the soil sample yields MBP.

MBP in soil and fecal matter is commonly assumed to include absorbed phosphine, metal-phosphine complexes and inorganic phosphides that can be set free as PH_3 by analytical digestion or through bacterial action (14). MBP was analyzed because it is likely linked to production, consumption, and emission of free phosphine in the guano, ornithogenic soil or sediment. MBP is assumed to indicate a stationary state concentration of phosphine between production and consumption under natural conditions (21).

Environmental Variables. Total phosphorus (TP), inorganic phosphorus (IP), and organic phosphorus (OP) in the guanos, ornithogenic soils or sediments were analyzed in the laboratory (see the Supporting Information). Meteorological data were collected at the weather station of Zhongshan. The average ultraviolet-B (UVB) dose rate data at 9:00–12:00 were obtained by Brewer UVB scan measurements at the ozone observation station of Zhongshan.

Results and Discussion

Atmospheric Free Phosphine at Sampling Site 4 (Moderately Remote from Emission Sites). *Summertime Trend and Daytime Variation:* Atmospheric phosphine concentrations in air samples taken between December 23, 2005 and February 17, 2006 at the normal observation site (sampling site 4) are displayed in Figure 2. Gaseous phosphine was found in nearly all the air samples (except the samples from January 3) around 22:00 ($10.4\text{--}229.0\text{ ng PH}_3\text{ m}^{-3}$). Phosphine concentrations in daytime samples (around 10:00) ranged from 0 (in almost half of the samples) to 121.7 ng m^{-3} . In addition, average PH_3 concentrations around 22:00 were generally higher than those around 10:00 in January and they were almost equal in February (Figure 2a).

The Role of Daytime, Cloudiness, and Snow Cover: Results in Figure 2b combine the evaluation of the influence of different weather and environmental conditions on the atmospheric PH_3 concentrations around 10:00 and 22:00. No phosphine was detected in the air samples around 10:00 on sunny days, suggesting that atmospheric phosphine was degraded between 22:00 and 10:00 due to the effects of increasing light intensity that promotes air oxidation. Phosphine was found in all the 10:00 air samples when it was cloudy or there was light snow fall (average 75.3 ng m^{-3} , range $48.1\text{--}121.7\text{ ng m}^{-3}$). At 22:00, when the bare ground was exposed, the average was 165.8 ng m^{-3} (range $123.4\text{--}229.0\text{ ng m}^{-3}$). But when the ground was covered by accumulated snow, it declined (average 42.3 ng m^{-3} , range $10.4\text{--}73.5\text{ ng m}^{-3}$). In our study area, the ground covered by snow has an average reflectivity of 0.57, significantly higher than the bare ground (an average reflectivity of 0.25) (31). A blizzard or blowing snow weather contributes to surface snow cover for a short period of time and the reflectivity could be up to 0.8, which greatly increases surface effective radiation (31). This likely accelerated the degradation of atmospheric phosphine and led to low concentrations around 22:00 (Figure 2b). Since sunny days are very infrequent in our study area (31, 32), the more common cloudy or snowy days would

TABLE 1. Atmospheric Phosphine in Coastal Antarctica and above the Surface of Southern Ocean

sampling location	sampling time	sampling number (n)	phosphine (ng m ⁻³)
sea animal colony eastern Antarctica			
1. empire penguin colony, Prydz Bay	10:00, December 2005	4 (2 locations)	407.8 ± 8.4
1. empire penguin colony, Prydz Bay	10:00, January 2006	4 (2 locations)	195.8 ± 39.6
western Antarctica			
9. penguin colony, Ardley Island	10:00, January 2006	2 (2 locations)	161.6 ± 31.5
10. skua colony, Fildes Peninsula	10:00, February 2006	2 (2 locations)	76.0 ± 19.0
11. seal colony, Fildes Peninsula	10:00, January 2006	2 (2 locations)	371.3 ± 76.8
Millor Peninsula, near empire penguin colony, eastern Antarctica			
4. Hilltop behind Zhongshan Station	10:00, December 2005 – February 2006	9	41.9 ± 44.6
	22:00, December 2005 – February 2006	12	79.9 ± 72.2
2. saltmarsh of Wolong Beach	18:00, January 2006	4	271.8 ± 7.1
3. hilltop behind Russian Progress Station	22:00, February 2006	4	115.2 ± 19.3
5. Tuanjie lake	17:00, January 2006	4	50.9 ± 3.6
6. Mochou lake	22:00, December 2005	6	31.0 ± 15.5
7. Nella Bay	17:30, January 2006	2	30.0 ± 13.2
8. Luojiashan Glacial southern ocean	22:00, January 2006	2	38.2 ± 6.3
12. 69.17°S, 76.15°E	22:00, December 2005	1	147.9 ± 4.4
13. 65.60°S, 76.63°E	22:00, December 2005	1	1.32 ± 0.9
14. 63.07°S, 89.05°E	22:00, December 2005	1	0
15. 61.93°S, 95.53°E	10:00, December 2005	1	0
16. 60.68°S, 101.40°E	22:00, December 2005	1	0
17. 57.10°S, 110.33°E	23:00, December 2005	1	0
18. 54.32°S, 114.72°E	10:30, December 2005	1	0
19. 51.13°S, 114.68°E	22:00, December 2005	1	0

^a Note: the sampling location labels are the same as those in the Supporting Information Figure S1; The sampling number indicates the number of Tedlar air bag; No label of location number indicates one location.

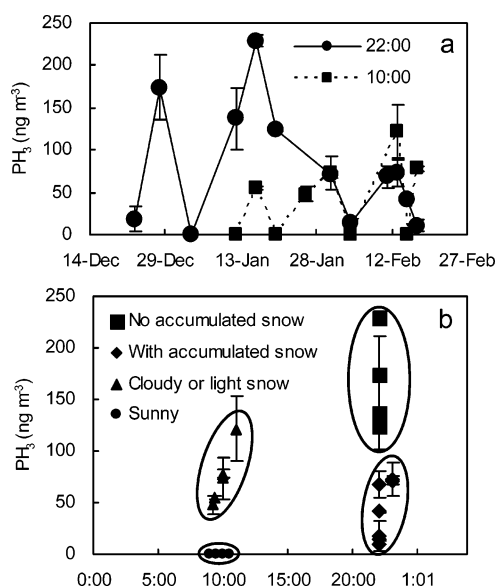


FIGURE 2. Variations of atmospheric PH₃ concentrations at the normal sampling site 4 (hilltop behind Zhongshan Station). (a) Seasonal summer trend and daytime differences at 10:00 and 22:00; (b) Daytime differences at 10:00 and 22:00 and the role of cloudiness and snow.

allow atmospheric phosphine to flow out of the seabird colonies and to migrate with the wind direction toward the normal sampling location before its ultimate oxidation (see subsequent results).

The Role of Environmental Air Temperature and UV Radiation: As can be seen in Figure 3a, no significant correlation was obtained between atmospheric phosphine concentrations at 10:00 and air temperature on Millor Peninsula since phosphine concentrations may be predominantly impacted by light intensity, and a temperature effect

was not evident. In addition, atmospheric phosphine concentrations show a significant negative correlation with the ultraviolet-B (UVB) dose rate around 10:00 (Figure 3b). That is clearly indicating phosphine oxidation mediated by the solar UVB-radiation, which transforms phosphine back to phosphate (6, 9).

A significant correlation exists between phosphine concentrations at 22:00 and air temperature (Figure 3c), indicating that atmospheric phosphine levels could be related to local temperature, which mediated the production and emission of phosphine in the Antarctic environment. Earlier researches also showed that the atmospheric phosphine concentration is higher in the warm period, with more microbial or chemical activity (6, 9). Therefore, temperature may be one of the main factors affecting atmospheric phosphine concentrations when the light factor (favoring oxidation of PH₃) is unimportant in the coastal Antarctica. Similarly, Zhu and Sun (26) found that CH₄ emissions significantly correlated with PT₀ (precipitation—surface soil temperature) at the maritime Antarctic tundra. Parsons et al. (33) reported that CO₂ emissions were associated with increases in soil temperature in Antarctic Dry Valley ecosystems and they further proposed temperature-driven physical influences on CO₂ flux. These influences have also been observed in numerous systems from snowpacks to wetlands to soils (26, 27, 34): Temperature may affect diffusion processes over soil or porous media such as snow (26, 27), influence advection and gas transport over a surface (26, 33), or influence the solubility of a gas in water (34). Temperature-mediated physical processes could also affect the PH₃ flux from the tundra ecosystems (such as sea animal colonies).

Prevailing Wind Direction and Atmospheric Mobility of Phosphine: The prevailing wind direction during the atmospheric sample collection period on Millor Peninsula was from the northeast (see Supporting Information Figure S2) where two large penguin colonies are located (Figure 1). These

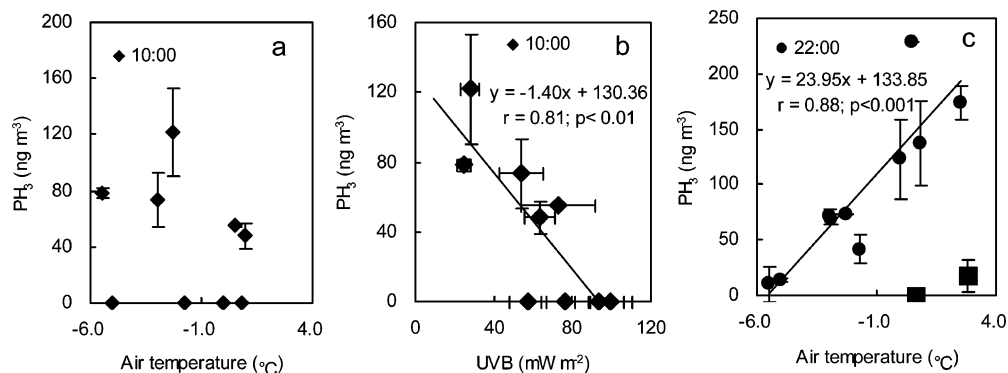


FIGURE 3. Relationships between atmospheric PH_3 concentration, air temperature, and UVB dose rate at sampling site 4. (a) PH_3 and air temperature at 10:00; (b) PH_3 and UVB dose rate at 10:00; (c) PH_3 and air temperature at 22:00 (two outlier samples indicated by squares exempt from correlation).

TABLE 2. Matrix-Bound Phosphine (MBP), Total Phosphorus (TP), Organic Phosphorus (OP) in Coastal Antarctic Biosphere^a

	MBP ^a (ng kg ⁻¹)	TP (g kg ⁻¹)	OP (g kg ⁻¹)	OP/TP (%)	MBP/TP ($\times 10^{-9}$)	MBP/OP ($\times 10^{-9}$)
empire penguin guano	2.54	67.5	3.6	5.33	0.04	0.71
gentoo penguin guano	6.21	84.3	3.8	4.51	0.07	1.63
ornithogenic soil 1	13.34	9.7	4.5	46.39	1.38	2.96
ornithogenic soil 2	4.57	12.6	4.9	38.89	0.36	0.93
ornithogenic soil 3	1.27	3.0	1.2	40.00	0.42	1.06
ornithogenic sediment 1	1.57	30.5	6.9	22.62	0.05	0.23
ornithogenic sediment 2	3.04	35.3	7.6	21.53	0.09	0.40
ornithogenic sediment 3	2.14	50.0	4.6	9.2	0.04	0.47
krill ^b near Fildes Peninsula		34.2				

^a The sampling number $n = 3$. ^b The data for krill are from the ref 37.

colonies are important emission sources of PH_3 (see subsequent results) that cause high PH_3 accumulation in adjacent air (Table 1). On the other hand, no phosphine was detected in the very remote air above the surface of the Southern Ocean (range from 51 °S to 65 °S) that is not impacted by the penguin colonies (Table 1, Figure S1), which indicates that the sub-marine biosphere does not emit phosphine. This is all indicating that the emissions from penguin guanos may be the predominant sources of phosphine in adjacent air (Table 1) that is moderately remote from this natural source. The source of phosphine in these air samples is unlikely the ground of the normal observation site itself, because it is located on a rocky hilltop.

Millor Peninsula is located within the Antarctic Circle. It has the characteristics of a dry and cold polar continental climate (32). Strong UV radiation is very evident due to the occurrence of the Ozone Hole (35). Earlier related laboratory experiment shows that atmospheric phosphine can be relatively mobile because it can survive daylight much longer in the very clean and dry air due to a lack of UV-induced oxidants (7). Our study area has a very clean atmosphere with an average visibility of 31 km and low relative humidity of 57% in the summer (32). Therefore the dry, cold and very clean atmospheric conditions (see Supporting Information Figure S3) on Millor Peninsula may prolong the life of atmospheric PH_3 , which leads to the accumulation of PH_3 from penguin colonies in the coastal Antarctic atmosphere (Table 1 and Figure 2).

Atmospheric Phosphine Concentration at Different Emission Sites. Average PH_3 concentrations in air adjacent to several suspected emission sites in coastal Antarctica and above the surface of the Southern Ocean are listed in Table 1. Atmospheric PH_3 concentrations above the ground in the middle of sea-animal colonies ranged from 76.0 to 407.8 ng m⁻³ with an average of 242.5 ng m⁻³. The highest PH_3 concentration was found in the Empire penguin colony, about 5 km away from Millor Peninsula. A high atmospheric average PH_3 concentration was also found at a saltmarsh of Wolong

Beach (217.8 ng m⁻³), above the surfaces of Tuanjie lake (50.9 ng m⁻³), Mochou lake (31.0 ng m⁻³), Nela Bay (30.0 ng m⁻³), and Luojiashan Glacier (38.2 ng m⁻³). Out of eight air samples from above the surface of the Southern Ocean, phosphine was detected in only two samples, of which a significant concentration (147.9 ng m⁻³) was found at the sampling site nearest to a penguin colony (Figure S1 and Table 1).

It is surprising that the PH_3 concentration in the remote and cold (i.e., biologically less productive) Antarctic atmosphere is in the order of 100 times higher than earlier reported air or even biogas PH_3 data (6, 7, 9, 15) from regions remote from and near industry.

MBP and Phosphorus in Guano, Soil, and Sediment.

Results in Table 2 show that the guano and ornithogenic samples with high total (TP) and organic (OP) phosphorus content contain also the highest MBP content (up to 13 ng kg⁻¹), particularly a high quotient MBP/OP. MBP has also been detected in similar solid matrixes of the Antarctic biosphere (24).

Even low concentrations of MBP could be important, assuming they indicate a stationary state concentration of phosphine between production and consumption under natural conditions (21).

It is assumed that the source of the high P content in these samples is Antarctic krill (34.2 g kg⁻¹ TP), the predominant food source of penguins (28, 36, 37). It is possible that microbial processes in the intestines of penguins and subsequently in soils could produce phosphine. MBP could also be produced in an abiotic way from inorganic phosphate minerals like apatite, struvite, and brushite in the Antarctic ornithogenic soils or sediments (28, 38). Geochemically or microbially mediated deterioration of the MBP could cause the subsequently reported fluxes (Table 3) of free gaseous phosphine into the atmosphere as found in the air samples (Table 1).

In Situ Phosphine Fluxes from Tundra Ornithogenic Soils. Results in Table 3 show that phosphine is emitted in-

TABLE 3. Emission Flux of Phosphine from the Antarctic Biosphere Compared with Other Biospheres

biosphere	location	flux (ng m ⁻² h ⁻¹)	sampling numbers (n)
Antarctic biosphere			
skua colony	Fildes Peninsula, Antarctic	8.99 ± 1.6	2
gentoo penguin colony	Ardley Island, Antarctic	9.56 ± 2.7	2
seal colony	Fildes Peninsula, Antarctic	39.96 ± 4.5	2
empire penguin colony	Prydz Bay, Antarctic	63.58 ± 2.9	2
other biosphere			
Louisiana saltmarsh ^a	Louisiana U.S.	0.91–6.52	2
soil of brackish marsh ^a	Louisiana, U.S.	0.42–3.03	2
soil of paddy field ^b	Beijing, China	–13 to –22	144
intertidal mud flat area ^c	North Sea, German bight	4500	

^a The data are from ref 13. ^b The data are from ref 16. ^c The data are from ref 21.

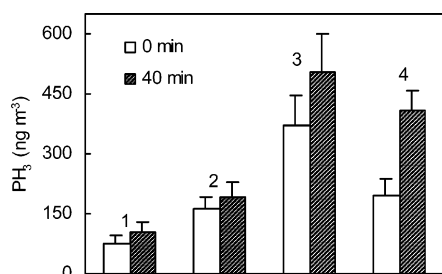


FIGURE 4. Increase of phosphine concentration within 40 min in closed chambers set up in-situ on ornithogenic soils of four animal colonies. 1. Skua colony; 2. Gentoo penguin colony; 3. Seal colony; 4. Empire penguin colony. Two repetitions were taken at each colony.

situ under the Antarctic environmental conditions from the ornithogenic soils of four animal colonies at a rate in the order of 10–100 ng m⁻² h⁻¹. These emission rates are significantly higher than those from the literature (saltmarsh and paddy fields). The emissions from these ornithogenic soils of the four colonies notably increase the concentration of phosphine in the closed chambers (*t*-test for four colonies: *t*₁ = 11.31, *p* < 0.01; *t*₂ = 6.40, *p* < 0.05; *t*₃ = 24.18, *p* < 0.01; *t*₄ = 76.45, *p* < 0.001) and the highest value reached 550.0 ng m⁻³ (Figure 4). Similarly, high N₂O and CH₄ emissions from ornithogenic soils have also been observed in the

summertime of the coastal Antarctica (26, 27). Combined with the exploration of high phosphine emission rates from ornithogenic soils, we propose that the emissions from penguin colonies might be the predominant sources for atmospheric phosphine at the analyzed coastal Antarctic locations.

Laboratory In-Vivo Simulation of Phosphine Production from Ornithogenic Soils. As illustrated in Figure 5a, a higher phosphine production rate was found at 4 °C compared to 25 °C after 72 h of incubation of three ornithogenic soil samples (*t* test for three samples: *t*_{os1} = 6.78, *p* < 0.01; *t*_{os2} = 8.00, *p* < 0.01; *t*_{os3} = 7.74, *p* < 0.01). A microbial or microbially mediated phosphine production could be favored at the low temperature of 4 °C (compared to the high of 25 °C) due to the long-term adaptation of the microorganisms to local low summer temperature and strengthening of microbial or chemical activities at 4 °C (close to natural summertime ground temperature). High CH₄ and N₂O emissions (26, 27) show that microorganisms in such soils are active even when they are snow-covered or when soil temperatures are near 0 °C.

Effect of Soil Dilution with Water. As shown in Figure 5b, dilution of the soils with additional water caused an increase of phosphine production by a factor of about 5 to a level of 0.58 ng kg⁻¹ d⁻¹ after 72 h of incubation. It is concluded that phosphine production in the field will significantly increase during the Antarctic summer when the air temperature rises to above 0 °C and when fresh penguin guanos and ornithogenic soils are diluted by ice or snowmelt water.

Significance of Gaseous Phosphine for Phosphorus Cycling in the Antarctic Tundra Ecosystem. We propose that phosphine emission from penguin colonies is a predominant source for atmospheric phosphine at the analyzed coastal Antarctic locations. This conclusion is based on a combination of the results of phosphine in the air moderately remote from such colonies (Figure 2), phosphine in the air above or adjacent to colonies (Table 1), in-situ phosphine flux from colony soil (Table 3), in-situ phosphine concentration in a chamber above the soil (Figure 4), in-vivo phosphine flux from soil (Figure 5), Matrix-bound phosphine (MBP) and the richness of ornithogenic soils in phosphorus (Table 2).

In addition to migrating into the atmosphere, phosphine could also slowly migrate from ornithogenic soils into different compartments of the soils (21, 24), and such processes would additionally influence the balance of phosphorus in the Antarctic tundra ecosystem.

Our results support the finding of a small gaseous link to the Antarctic phosphorus cycle. The final fate of atmospheric phosphine will be oxidation into water-soluble phosphate, which enters the tundra ecosystem in coastal Antarctica.

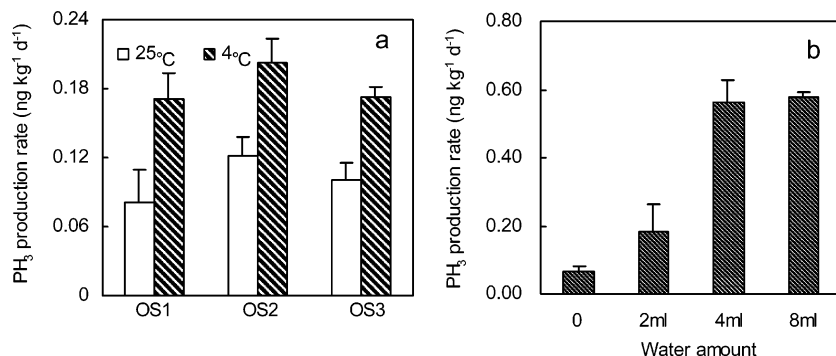


FIGURE 5. Phosphine production rate from ornithogenic soils in-vivo under different experimental conditions. (a) Dependence from temperature at 4 °C and 25 °C (three ornithogenic soil samples OS1, OS2, and OS3, three repetitions) (b) Dependence from amounts of water added into ornithogenic soils (three repetitions).

Phosphine formation and atmospheric phosphine may have significant positive distributing effects on the dissemination of phosphorus in the coastal Antarctica. The redistribution of phosphorus via phosphine from rich phosphorus sources could additionally fertilize tundra areas that are poor in phosphorus. The mechanisms of phosphine formation and the accumulation of environmental PH₃ data deserve more scientific attention.

Acknowledgments

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Supporting Information Available

Additional sampling information, climatic data, and method details (Table S1 and Figures S1–S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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