# Supporting Information

# Tropospheric phosphine and its sources in coastal Antarctica

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12 pages

3 figures

1 table

## Description of study area and the sampling sites

From December 2005 to February 2006, this project was carried out at Chinese Zhongshan Station (69°22′S, 76°24′E) and Great Wall Station (62°13′S, 58° 56′W), respectively (Figure S1). Zhongshan Station is located on the coastal Millor Peninsula, eastern Antarctica. A large Empire penguin colony and an Adélie penguin colony in Prydz Bay, are located about 5 km and 1 km, respectively, to northeast of this peninsula. There are several lakes on this Peninsula, such as Mochou Lake and Tuanjie Lake, and the sediments in these lakes have been confirmed to be impacted by the depositions of seabird guanos (*1*). Russian Progress Station is located about 500 m to southeast of Zhongshan Station. There is a small salt marsh named Wolong Beach between these two scientific stations. Luojiashan Glacier is located about 8 km to southeast of Zhongshan Station. One normal observation site (sampling site 4) for atmospheric phosphine was set up on a hilltop (about 25 m above sea level (asl)) approximately 200 m to the south of Zhongshan station. Other sampling sites were located in the middle of an Empire penguin colony (two locations, about 15 m asl) and salt marsh of Wolong Beach (2 m asl), at the hilltop behind the Russian Progress Station (about 32 m, asl), and on the downwind edges of Tuanjie Lake, Mochou Lake, Nella Bay and Luojiashan Glacier. The air sampling height was about 2 m above the ground. The sampling number at each site was given in Table 1. One observation site of phosphine flux was also established at the Empire penguin colony.

The Chinese Great Wall Station is located on the Fildes Peninsula, western Antarctica. There are a lot of seabirds including skua (*C. maccormicki*), gull (*Larus*

*dominicanus*) and giant petrel (*Macronectes giganteus*) in the eastern coast of this peninsula. A large skua colony is located about 200 m in front of the Great Wall Station. A lot of seals established colonies in the western coast of this peninsula. Ardley Island is located about 500 m to the east of the station. There are several major penguin colonies on this island, and a large amount of seabird guanos are deposited into the tundra soils or lake sediments every year (*2, 3*). The deposition of seabird guanos strongly influences the physical and chemical properties of tundra soils via the effects of microbes, and produces a kind of special soil called ornithogenic soil, which is particularly rich in phosphorus (*2, 3*). Three air sampling sites and observation sites of phosphine fluxes were set up in the middle of gentoo penguin colony on Ardley Island, skua colony and seal colony on Fildes Peninsula. The sampling number at each site was given in Table 1. Fresh penguin guanos and ornithogenic soils or sediments were also sampled for analyses of matrix-bound phosphine (MBP) and laboratory experiments.

Atmospheric air samples at eight sites above the surface of Southern Ocean were also collected on the track of research ship *Xuelong*. To avoid the impacts of anthropogenic factors and research ship self, we collected air samples upwind on the fore. The sampling height was about 2 m from the deck of the fore (about 25 m apart from the oceanic surface). The sampling number at each site was given in Table 1. All the sampling sites are illustrated in Figure S1.

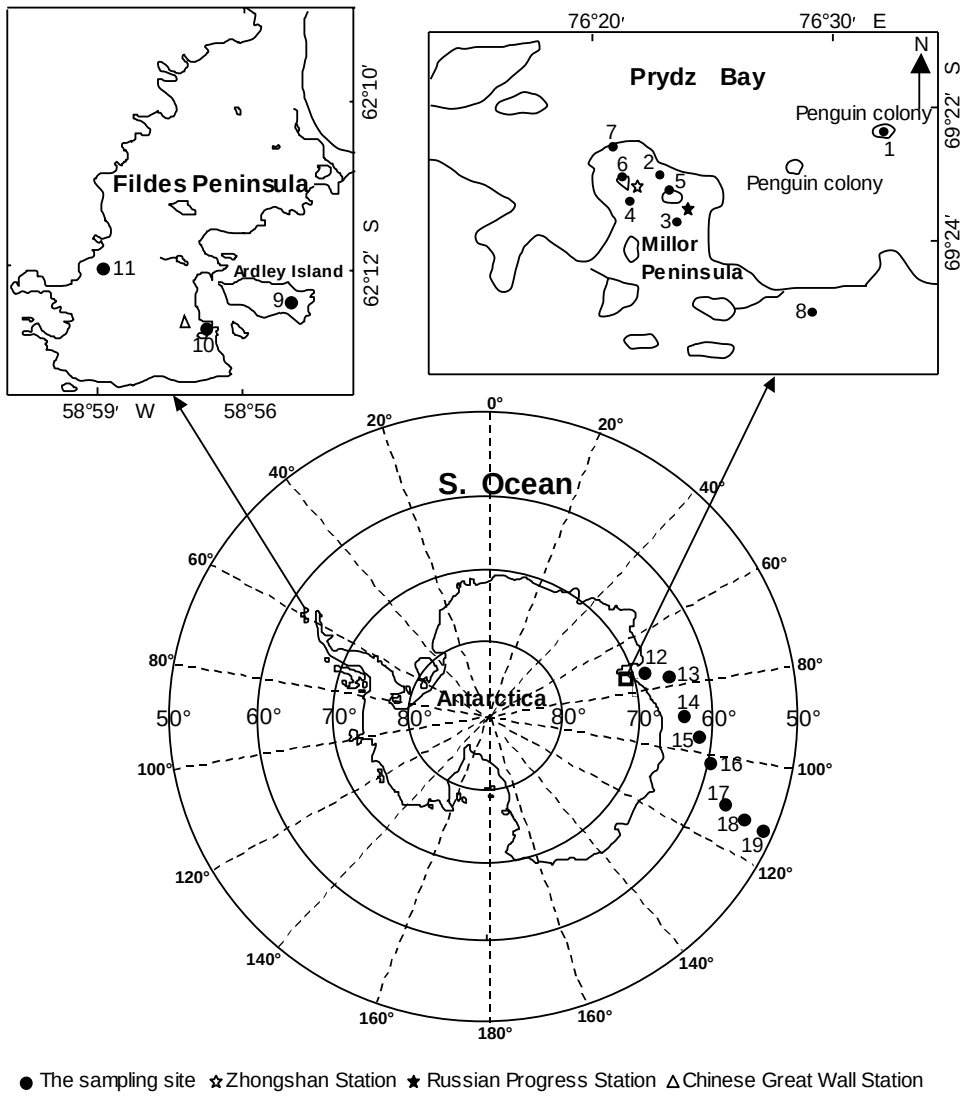


**Figure S1.** Study area and air sampling sites in coastal Antarctica. Eastern Antarctica (1-8): 1. Empire penguin colony; 2. Salt marsh of Wolong Beach; 3. Hilltop behind Russian Progress Station; 4. Hilltop behind Zhongshan Station (normal observation site); 5. Tuanjie lake; 6. Mochou lake; 7. Nella Bay; 8. Luojiashan Glacial. Western Antarctica (9-11): 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. Air sampling sites above the Southern Ocean (12-19): The longitude and latitude for every sampling site are given in Table 1.

## Details of air sampling

The air samples were sucked from the outside through stainless-steel tube installed to the sampler and were stored in 0.5 L Tedlar sampling bags with polypropylene valves (*4*). All the air bags were stored and shipped in a large barrel filled with $N_2$ which produced a phosphine-free storage space. Three control sample bags, which were filled with phosphine-free air before the expedition and shipped in the barrel, did not contain phosphine after the expedition to the laboratory. The barrels with the sample Tedlar bags were frozen and preserved under -20 □ and dark conditions until laboratory analysis.

**TABLE S1. Comparisons between Tedlar gas bag and ordinary gas bag over the transport period.**

| Type | Phosphine standards (ng $m^{-3}$) | Initial time | Determination time | Result (ng. $m^{-3}$) n=3 | CV (%) |
|---|---|---|---|---|---|
| Ordinary gas bag | 151.8 | 2005.11.12 | 2006.4.13 | 77.7±6.0 | -48.8 |
| Ordinary gas bag | 15180 | 2005.11.12 | 2006.4.13 | 1423.2±120.5 | -90.6 |
| Tedlar gas bag | 15180 | 2005.11.12 | 2006.4.13 | 14953.8±289.5 | -1.4 |

Note: Another Tedlar bag was destroyed during the transport.

To test the stability of these air samples, we stored two kinds of phosphine standards (15180 ng $m^{-3}$ and 151.8 ng $m^{-3}$, respectively) in two Tedlar gas sample bags (TPV/L-005) and two aluminium foil compound membrane gas sample bags (ordinary gas bag, LMCL-005), respectively, and found that the concentration did not decline in Tedlar air bags over the transport period while the concentration in ordinary air bags showed a rapid decrease (Table S1). It is concluded that the air samples stored in

Tedlar bags are nearly stable.

## Measurement of in-situ phosphine fluxes from ornithogenic soils in the field.

The closed-chamber method was used for the measurement of phosphine fluxes from ornothogenic soils in the different sea animal colonies (*5, 6*). Chambers were made of opaque plastics to avoid phosphine photo-degradation. During flux measurements, the boxes were put on the bottom collars inserted into the soil with a cross-sectional area of 0.25 $m^2$ (50×50 cm). The internal height of the chamber is about 20 cm. As illustrated in Figure S1, two parallel plots were employed for flux measurements at each observation site of the Empire penguin colony, gentoo penguin colony, skua colony and seal colony, respectively. A gas sample was taken with 50-ml disposable polypropylene-syringe immediately after the chamber was put on the collar and then continuously transferred into a Tedlar bag through a three-port valve. A second gas sample was taken usually 40 min after the first. Due to lower Antarctic temperature, 40 min was used for phosphine flux measurements, which had an insignificant effect on the microclimate in the chamber according to our previous studies (*7, 8*). Two fluxes were measured at each colony (Table 3).

The fluxes were calculated from the temporal increase of phosphine concentration inside the chambers according to the following equation (*6*):

$$F=\Delta Q/(S\Delta t)=V\Delta c/(S\Delta t)=SH\Delta c/(S\Delta t)= H\Delta c/\Delta t$$

where F is the flux or the emission rate in nanograms per square meter per hour; c is

the $PH_3$ mass concentration in nanograms per cubic meter; t is the sampling duration in hours; H, S and V are, respectively, the effective height, effective cross-sectional area and effective volume of a chamber in meters, square meters and cubic meters; and $\Delta Q$ is the difference of $PH_3$ quantity existing in the chamber with time in nanograms.

## Analysis of free phosphine in air and other gas samples.

Phosphine was analyzed by a HP4890 GC equipped with an NPD (Nitrogen-phosphorus detector) in State Key Laboratory of Pollution Control and Resource Reuse, Nanjing University. Gas samples in syringes were directly injected through a drying tube (NaOH as drying agent, Merck, Germany, No. 101567 to remove $H_2O$, $CO_2$ and $H_2S$) into a 6-port valve on the GC. The phosphine in the $N_2$ was then enriched in two successive capillary cryo-traps (cooled with liquid nitrogen) and desorbed into the GC column. The column temperature was 40 □, and the detector temperature was 220 □. The flow-rates of the detector gases were 2 ml $min^{-1}$ for $H_2$, 120 ml $min^{-1}$ for air and 30 ml $min^{-1}$ for $N_2$, as the make-up gas. Phosphine (10 ppmv in $N_2$, certified) used as authentic reference, was purchased in pressure cylinders from Nanjing Special Gas Plant. Every sample was parallelly measured at least three times. 50 ml gas samples were cryo-trapped to reach a detection limit for 0.1 ng $m^{-3}$ of phosphine. The determination of phosphine concentration was also described by Geng et al (*9*) and Zhu et al (*10*).

## Analysis of phosphorus in the samples.

Total phosphorus (TP) was analyzed by measurement of phosphate in the guanos, ornithogenic soils or sediments after digestion in which the soil samples were put in an oven at 550 □ for 2 h, followed by the extraction with 1 mol L-1 hydrochloric acid for 16-18 h at room temperature, including 2-h vibration (*11*). Phosphate (PO4-P) was measured using the phosphomolybdenum blue method. Inorganic phosphorus (IP) was detected by the same method as total phosphorus just without the procedure of ignition at 550 □ (*11*). Organic phosphorus (OP) was obtained by the difference between TP and IP.

## Frequencies of wind directions during sampling

We also calculated the frequencies of wind directions during each sampling date at the normal observation site 4 using meteorological data collected at Zhongshan Station. As shown by the wind roses in Figure S2, the prevailing wind directions were around northeast during atmospheric sample collection periods.

## Climatic conditions on Millor Peninsula during the sampling period.

Millor Peninsula is located within the Antarctic Circle. It has the characteristics of a typical polar continental climate. Meteorological data collected at Zhongshan Station from December 23, 2005 to February 17, 2006 indicated that the mean temperature was about –0.1 □. It was clear or cloudy on most days in December and January, and less precipitation occurred in the form of snow in February. This area has a dry climate with an average relative humidity of 57% and a very clean atmosphere with the

average visibility of 31 km (Figure S3). In addition, strong UV radiation is very evident due to the occurrence of Ozone Hole (*12, 13*).

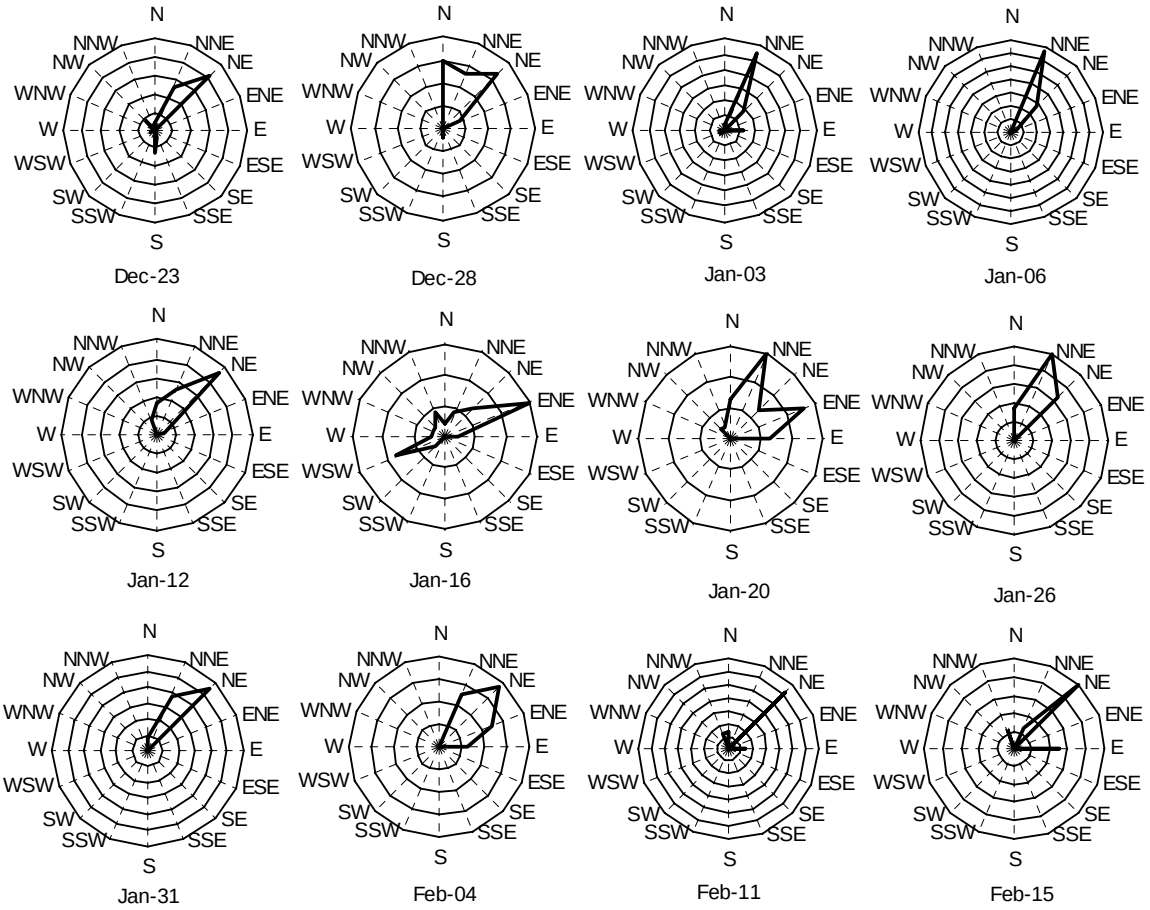


**Figure S2.** Rose figures representing the frequencies of wind direction during atmospheric sampling on Millor Peninsula. The scale (each contour line/circle) is 10%. The prevailing surface wind directions were from northeast.

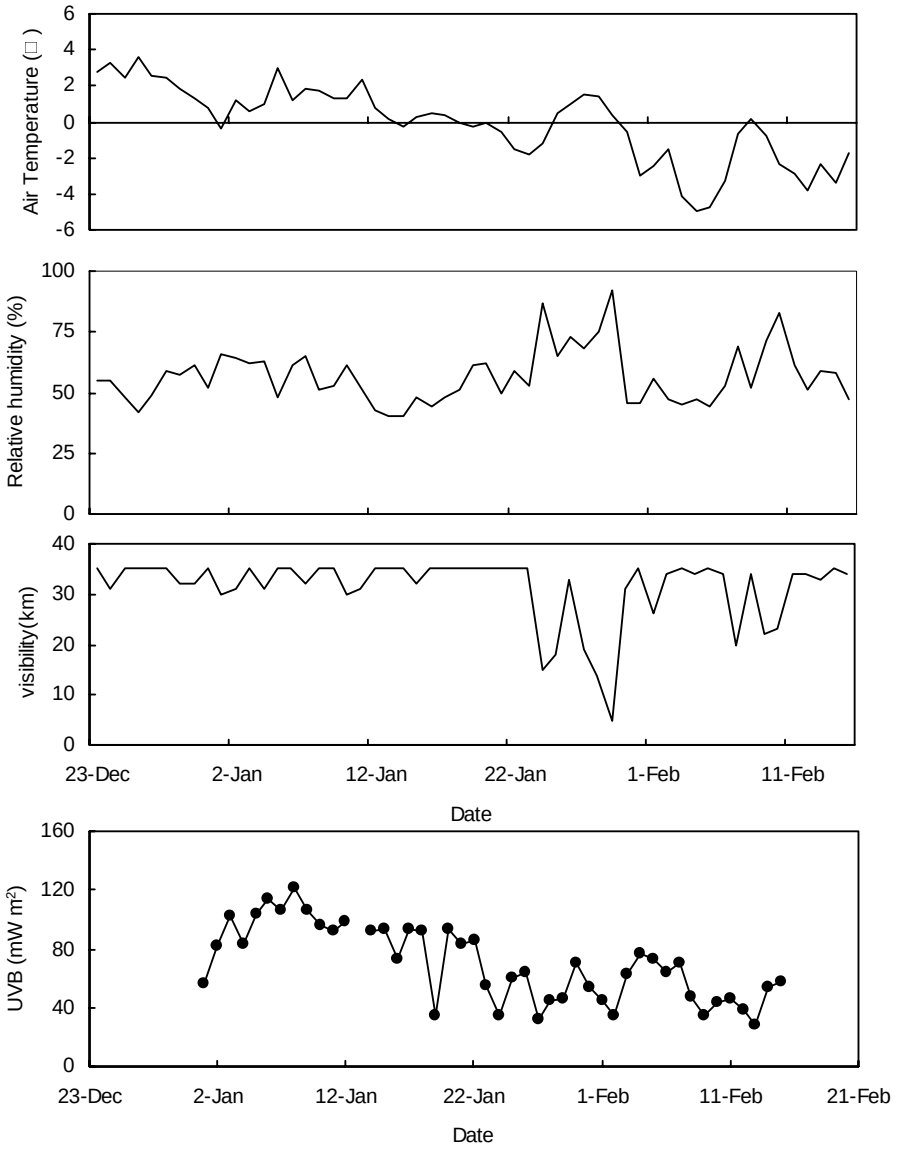


**Figure S3.** The variations of daily average air temperature, relative humidity, visibility and ultraviolet-B (UVB) dose rate during the sampling period on Millor Peninsula, eastern Antarctica.

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