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Stimulation of gaseous phosphine production from Antarctic seabird guanos and ornithogenic soils

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Abstract

Matrix-bound phosphine (MBP) is a general term used to indicate non-gaseous reduced phosphorus compounds that are transformed into phosphine gas upon reaction with bases or acids. Antarctic seabird guanos and ornithogenic soils were used as materials to compare the different digestion methods for transforming matrix-bound phosphine into phosphine gas. The results demonstrated that more phosphine gas in most of Antarctic environmental materials was formed of matrix-bound phosphine by caustic digestion than by acidic digestion. The comparative study on different digestion methods also revealed that the fraction of MBP converted to gaseous phosphine during the digestion depended on the temperature. The optimal digestion temperature was close to 70°C and the optimal digestion time was about 20 min. Acidic conditions were more favorable for the release of matrix-bound phosphine compared to the neutral conditions. A proper water dilution can increase the production and emission of phosphine from the Antarctic penguin guanos.

Key words: phosphine; matrix-bound phosphine; ornithogenic soil; Antarctica; penguin guano

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Introduction

The gas phosphine (PH_3) is a part of an atmospheric link of the phosphorus cycle on earth. It is also a highly toxic gas that produces acute lethal effects on humans through inhibition of aerobic respiration. Phosphine exists in the environment in two different forms: free gaseous phosphine and matrix-bound phosphine (MBP) (Gassmann and Glindemann, 1993). Gaseous phosphine has been found worldwide in the atmosphere even at the remote locations (Glindemann *et al*., 1996, 2003; Gassmann *et al*., 1996; Liu *et al*., 1999; Zhu *et al*., 2006a, 2007). 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 (Gassmann and Glindemann, 1993; Gassmann, 1994; Yu and Song, 2003; Zhu *et al*., 2006b).

Over the past decade, numerous anthropogenic and environmental emission sources of phosphine have been identified (Gassmann and Glindemann, 1993; Gassmann, 1994; Dévai and Delaune, 1995; Eismann *et al*., 1997; Glindemann *et al*., 1998; Liu *et al*., 1999; Han *et al*., 2000; Zhu *et al*., 2006a). Glindemann *et al*. (2003) identified the following possible source processes that would cause phosphine to accumulate in measurable quantities in the upper troposphere: industry (including inadvertent phosphide and phosphine generation by a combination of high temperature and chemical reduction of phosphate, for example in metallurgy), the biosphere, geochemistry, cosmic phosphide-containing fallout and atmospheric lightning chemistry. These emission could produce enough phosphine to be a trace component throughout the atmosphere influencing the biogeochemical cycles and the atmospheric chemistry of phosphorus. The evidence for the biogenic formation of phosphine has come from laboratory studies using undefined mixed cultures of anaerobic bacteria (Gassmann and Glindemann, 1993), the origin of phosphine in biogas, landfill gas and the troposphere is still under debate.

In recent years, gaseous phosphine and MBP have been investigated in the maritime Antarctic environment (Zhu *et al*., 2006a, 2006b). The results suggested that seabird guano and the ornithogenic soil (formed of seabird guano) may constitute a potentially significant source for local atmospheric phosphine. Earlier field observations showed that sea animal guanos and ornithogenic soils were the important emission sources for methane and nitrous oxide in the maritime Antarctic tundra ecosystems (Sun *et al*., 2002; Zhu *et al*., 2008). In this article, Antarctic seabird guanos and ornithogenic soils are used as research materials in the laboratory to carry out the following subjects: (1) to compare the effects of different digestion methods on gaseous phosphine emissions from MBP in Antarctic seabird guanos and ornithogenic soils; (2) to study the

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effects of digestion temperature and pH on the production of gaseous phosphine; and (3) to simulate the effects of the water dilution on phosphine production and emission from the seabird guanos.

1 Materials and methods

1.1 Study area and sampling description

The sampling sites were mainly selected on the Fildes Peninsula (61°51′–62°15′S, 57°30′–59°00′W), where Chinese Great Wall Station is located, and is next to Ardley Island (62°13′S, 58°56′W) in the western Antarctica. Fildes Peninsula is an ice-free area on King George Island, the largest of South Shetland Islands. There are many seabirds including skua (*Catharacta maccormicki*), gull (*Larus dominicanus*) on the eastern coast. Ardley Island connects with Fildes Peninsula by sandy dam, located to the east of this peninsula. This island is defined as a site of special scientific interest by the Scientific Committee on Antarctic Research (SCAR). It is free of snow and ice during the summer. There are several major penguin rookeries, with an average summer population of about 4000 pairs of breeding gentoo penguins (*Pygoscelis papua*), 1200 pairs of Adélie penguins (*Pygiscelis adeliae*) and a small number of chinstrap penguins (*Pygoscelis antarctica*). Several small and shallow lakes found on the island contain soft sediments impacted by penguin guanos (Sun *et al*., 2000, 2004).

Samples, including the guanos of skua (*C. maccormicki*) and gull (*L. dominicanus*), were collected on the Fildes Peninsula. The surface 2 cm ornithogenic sediments strongly impacted by penguin guanos were sampled from a lake named Y2 on Ardley Island (Sun *et al*., 2000). One 20 cm-depth ornithogenic soil profile was also collected on this island. The soil samples at depths of 4 and 7 cm were sectioned for the laboratory analyses. In addition, emperor penguin and Adélie penguin guanos were collected in eastern Antarctica. All the samples were sealed, avoided the light and preserved under –20°C.

1.2 Batch experiments

1.2.1 Release of matrix-bound phosphine under different conditions

MBP is defined as the amount of phosphine released from seabird guanos, ornithogenic soils or sediments during an acidic (H_2SO_4) or caustic (NaOH) digestion, which releases adsorbed phosphine, metal-phosphine complexes, and inorganic phosphides (Gassmann and Glindemann, 1993; Zhu *et al*., 2006b). MBP were analyzed because it is likely linked to production, consumption, and emission of free phosphine in the guano, ornithogenic soil or sediment.

To determine whether the amount of phosphine emitted from the various Antarctic matrixes depends upon the digestion temperature, we digested the ornithogenic soils or seabird guanos (about 1 g) with 5 mol/L H_2SO_4 and 5 mol/L NaOH (5 mL), respectively, at different temperatures (40, 50, 60, 70, 80, and 90°C) under an anoxic nitrogen atmosphere. The liberated phosphine was purged with 50 mL pure nitrogen out of the reaction vessel into a 50-mL disposable polypropylene syringe. Gas samples in syringes were directly injected through a drying tube (NaOH as drying agent, No. 101567, Merck, Germany, to remove H_2O, CO_2, and H_2S) into a 6-port valve on the gas chromatography (GC). The phosphine in the N_2 was then enriched in two successive capillary cryo-traps (Al_2O_3/Na_2SO_4, cooled down with liquid nitrogen) and desorbed into the GC column. The gas chromatography (Agilent 4890D, Agilent Inc., USA) was equipped with a capillary column (cross-linked 5% Ph-Me-Silicone, 25 m × 0.2 mm × 0.33 μm film thickness, Hewlett-Packard, USA). A thermo-ionic nitrogen-phosphorus-detector (NPD) was used. The column temperature was 40°C, and the detector temperature was 220°C. The flow-rates of the detector gases were 2 mL/min for H_2, 120 mL/min for air, and 30 mL/min for N_2, as the make-up gas. Phosphine (10 ppmv in N_2, certified) used as authentic reference, was purchased in pressure cylinders (Nanjing Special Gas Plants). Every sample was parallelly measured at least two times, with a maximum deviation of approximately 20% for gas analysis. The determination of MBP concentration was described by Geng *et al*. (2005) and Zhu *et al*. (2006b).

A preliminary experiment was conducted with the Antarctic ornithogenic soils to determine the optimal digestion time for the caustic digestion method. Gas samples were taken after 5, 20, 35, and 50 min.

1.2.2 Effects of pH on the release of matrix-bound phosphine

Batch experiments were performed in 120 mL beaker. Ornithogenic (about 1 g) soils were added into beakers with 60 mL overlying waters. The pH values of overlying waters were adjusted to 1.5, 2, 4, 6, and 10 with concentrated sulfuric acid or sodium hydroxide solutions at the start. Then these samples with the regulated pH values were digested with 5 mol/L NaOH (5 mL) at 70°C under an anoxic nitrogen atmosphere for 5 min. The liberated phosphine collected and the released MBP was determined by the described methods above.

1.2.3 Effects of additional water dilution on phosphine production

A total of 0, 2, 4, 6, 8, and 10 mL clean water together with 5 g Adélie penguin guanos were added into six 150 mL conical flasks, respectively. All flasks were both filled with high-purity nitrogen and sealed with silica gel stopper anaerobically. Then flasks were incubated statically in the dark at 10°C for 24 h. The headspace gas samples were taken after 24 h for the analysis of gaseous phosphine.

1.3 Phosphorus fractionation of the Antarctic ornithogenic soils

Total phosphorus (TP) was analyzed by measurement of phosphate in the sediment after digestion in which the sediment samples (dried at room temperature) were put in oven at 550°C for 2 h, followed by the extraction with 1 mol/L hydrochloric acid for 16–18 h at room temperature, including 2-h vibration (Aspila *et al*., 1976). Phosphate (PO_4^{3-}-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°C (Aspila *et al*., 1976). Organic phosphorus (OP) was obtained by the difference between TP and IP. All reagents in the experiment were analytical reagent grade.

2 Results and discussion

2.1 Matrix-bound phosphine determined by different methods

The data obtained during the experiments are presented in Table 1 for comparison of the different digestion methods to measure MBP in the ornithogenic soils, gull guano, emperor penguin guano, and skua guano. The MBP content in the ornithogenic soil (GN-1-7 and GN-1-4) or sediment (Y2-1-2), measured after digestion with NaOH, was generally higher than that with H_2SO_4. These results are in accordance with the measurements of the sludge and pig manure reported by Roels *et al*. (2005). The previously observed pattern, with higher value for MBP after digestion with NaOH, was further confirmed in the Antarctic environmental materials. However, the MBP content in gull guano measured after digestion with NaOH, was much lower than that with H_2SO_4, which may be related with the phosphine gas leakage during the digestion with NaOH. The true reason needs further research. Of all three sea animal guanos (including gull, emperor penguin, and Skua guano), the lowest MBP content of 0.30 ng/kg dw was obtained in emperor penguin guano after digestion with H_2SO_4.

Table 1 shows that the concentrations of TP and OP are very high with the range of 0.97%–5.48% and 0.36%–0.69%, respectively, in Antarctic seabird guanos and the ornithogenic soils or sediments. The MBP detected in this study (Table 1), and in other matrixes of the Antarctic biosphere (Zhu *et al*., 2006b), indicated that seabird guanos and the ornithogenic soils or sediments may produce phosphine via the effects of microorganisms under cold Antarctic conditions. Therefore, it is possible that the high TP content is a source of MBP and atmospheric phosphine. In addition, it is notable phenomenon that the MBP content in the ornithogenic soil (GN-1-4), measured after digestion with NaOH or H_2SO_4, is considerably high while TP content is the lowest compared with the other Antarctic matrixes. It is likely that more MBP in the ornithogenic soil GN-1-4 was formed and emitted into the atmosphere, which may lead to the lowest TP content. The measured MBP is the stationary state concentration between PH_3 production, consumption, and release from the ornithogenic soils.

2.2 Effects of digestion temperature and time on the release of MBP

Figure 1 convincingly shows that during digestion of Antarctic seabird guanos or ornithogenic soils, the release of MBP follows a single-peaked trend with increasing digestion temperature. When the digestion temperature increased from 50 to 70°C, the release amount of MBP linearly increased, then rapidly decreased. Under the acidic digestion, the release amount of MBP in the ornithogenic soil (GN-1-4) increased from 0.51 to 2.06 ng/kg dw, and then dropped to 1.54 ng/kg dw at 80°C (Fig. 1a). In contrast, the release amount of MBP under the caustic digestion increased from 2.72 to 30.33 ng/kg dw, and then fell down to 3.61 ng/kg dw at 80°C (Fig. 1b), suggesting that MBP concentration obtained by caustic digestion method was significantly higher than that by acidic digestion. Similarly, the release amount of MBP in the ornithogenic soil (GN-1-7) increased from 0.07 to 0.57 ng/kg dw, then dropped to 0.15 ng/kg dw at 90°C (Fig. 1c). The release amount of MBP in Antarctic Skua guano increased from 0.29 to 0.96 ng/kg dw, then decreased to 0.67 ng/kg dw at 80°C (Fig. 1d). As illustrated in Fig. 1, the release amount of MBP reached the maximum when digestion temperature is in the range of 65–75°C. Therefore, the optimal digestion temperature is close to 70°C for the determination of MBP content.

An experiment using the ornithogenic soils as materials was conducted to determine the optimal digestion time for the caustic (NaOH) digestion method (Fig. 2). After 20 min, the maximum of cumulative phosphine emission was recorded, indicating that the optimal digestion time for NaOH digestion may be approximately 20 min.

2.3 Effects of pH on MBP release

As shown in Fig. 3, the severely acidic conditions may be more favorable for the release of MBP from the

Table 1 Comparison of measured matrix-bound phosphine content in the Antarctic various matrixes using different methods, and total phosphorus (TP), organic phosphorus (OP) and inorganic phosphorus (IP)

Matrix type	Sampling amount (g)	Digestion temperature (°C)	Digestion liquid	MBP (ng/kg dw)	TP (%)	OP (%)	IP (%)
Ornithogenic soil (GN-1-7)	0.930	75	H_2SO_4	1.64	1.26	0.49	0.77
	0.980	75	NaOH	5.71			
Ornithogenic soil (GN-1-4)	0.990	70	H_2SO_4	2.06	0.97	0.45	0.52
	0.930	70	NaOH	30.33			
Ornithogenic sediment (Y2-1-2)	0.991	70	H_2SO_4	0.44	3.05	0.69	2.36
	0.980	70	NaOH	0.53			
Gull guano	1.070	70	H_2SO_4	2.23	5.48	0.59	4.88
	0.830	75	NaOH	0.35			
Emperor penguin guano	1.130	70	H_2SO_4	0.30	1.65	0.36	1.29
Skua guano	0.920	70	NaOH	0.96	2.99	0.41	2.58

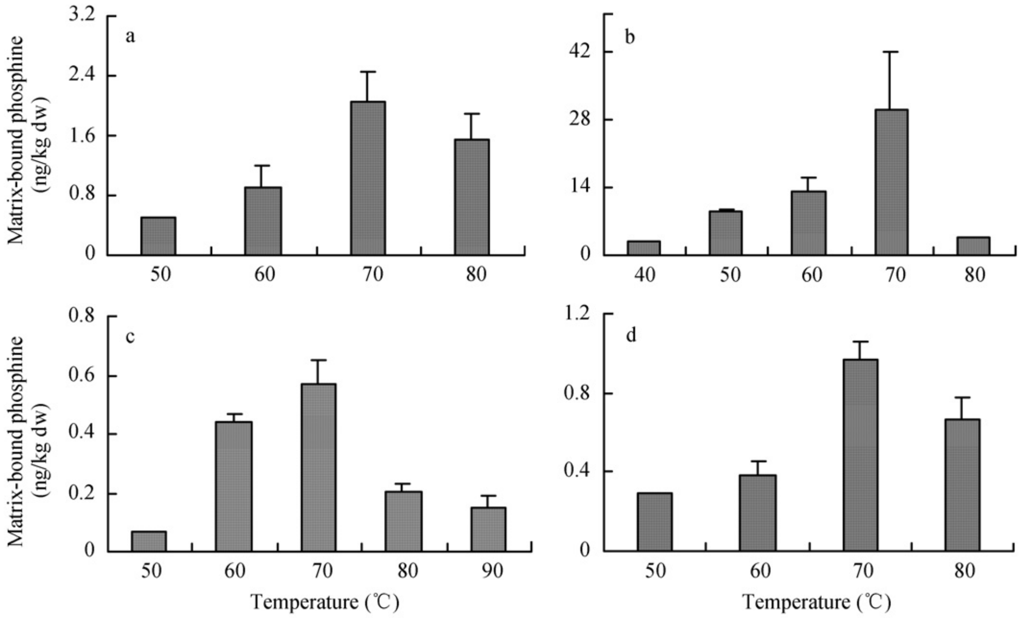

Fig. 1 Relationship between the digestion temperature and release amount of MBP. (a) GN-1-4, H_2SO_4; (b) GN-1-4, NaOH; (c) GN-1-7, NaOH; (d) Skua guano, NaOH.

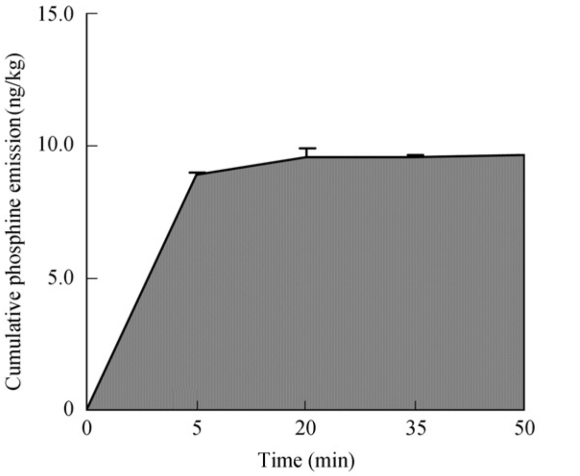

Fig. 2 Correlation between the cumulative phosphine emission from the ornithogenic soils and the digestion time.

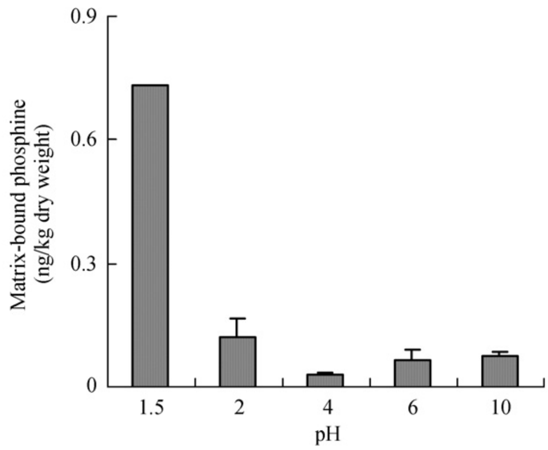

Fig. 3 Correlation between the release amount of MBP from the ornithogenic soil and pH.

ornithogenic soils. When the pH increased from 1.5 to 4, the release amount of MBP abruptly decreased from 0.73 ng/kg dw to a minimum of 0.03 ng/kg dw; when the pH increased from 4 to 10, the emission of gaseous phosphine slightly increased, which is in accordance with the results reported by Geng *et al*. (2005). However, this result is different from the conclusion of Han *et al*. (2002), who claimed that neutral conditions (pH 6.74) produced the highest gaseous phosphine and the level in acidic soil (pH 4.85) was the lowest. They believe that a large amount of biogas production affected the concentrations of MBP in various matrixes, but this needs more evidences to verify. In this article, the MBP concentration did not significantly increase under the alkaline conditions, which may be related to the comparatively weak alkaline (pH $\leqslant$ 10) level. Another possible reason was that the MBP was released out, and was not collected for the determination during the pH mediation. This may lead to the low MBP. However, there is the need of further study to support the hypothesis.

2.4 Effects of water dilution on phosphine production

The net phosphine production was determined after 24 h of incubation when different amount of water was added into Adélie penguin guanos (Fig. 4). Surprisingly, phosphine production rates significantly increased with the addition of water. When 2 mL water was added into the penguin guanos, phosphine production rates rapidly reached the highest value of 38.29 ng/kg dw. The lowest PH_3 production rate of 18.49 ng/kg dw was observed when 10 mL water was added into Adélie penguin guanos, suggesting that too much water can decrease the production of PH_3 from Adélie penguin guanos. Zhu *et al*. (2006a) also found that the dilution of the ornithogenic soils with additional water caused an increase of phosphine production after 72 h of incubation. Therefore, it could be concluded that phosphine production rates will significantly increase

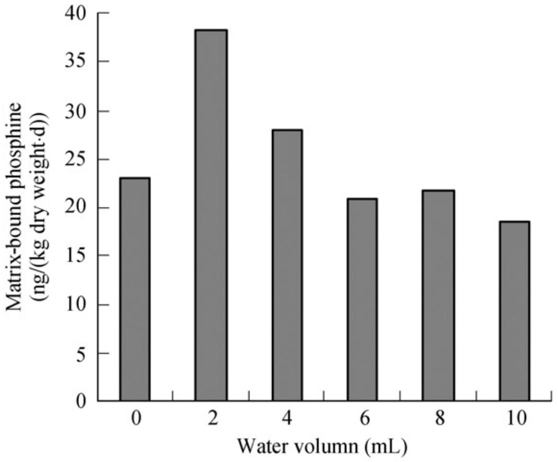

Fig. 4 Effects of water dilution on phosphine production in the Adélie penguin guanos.

when fresh penguin guanos are diluted by the suitable amount of ice or snowmelt water in the Antarctica coast.

3 Conclusions

A study was carried out to compare the effects of different digestion methods on the transformation of matrix-bound phosphine in the Antarctic seabird guanos and ornithogenic soils into phosphine gas. The results indicated that more phosphine gas was formed of matrix-bound phosphine by caustic digestion than that by acidic digestion in most of Antarctic samples. The comparative study on different digestion methods also revealed that the fraction of MBP converted to gaseous phosphine during the digestion depended on the temperature, and the optimal digestion temperature was close to 70°C for the determination of MBP content. Acidic conditions were more favorable for the release of MBP compared to the neutral conditions. The proper water dilution can increase the production and emission of phosphine from the Antarctic penguin guanos.

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