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Potential ammonia emissions from penguin guano, ornithogenic soils and seal colony soils in coastal Antarctica: effects of freezing-thawing cycles and selected environmental variables

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Abstract: Very little attention has been paid to quantifying ammonia (NH_3) emissions from Antarctic marine animal excreta. In this paper, penguin guano and ornithogenic soils from four penguin colonies and seal colony soils were collected in coastal Antarctica, and laboratory experiments were conducted to investigate potential NH_3 emissions and effects of environmental factors on NH_3 fluxes. Ammonia fluxes were extremely low from the frozen samples. Significantly enhanced NH_3 emissions were observed following thawing. The mean fluxes were 7.66 ± 4.33 mg NH_3 kg^{-1} h^{-1} from emperor penguin guano, 1.31 ± 0.64 mg NH_3 kg^{-1} h^{-1} from Adélie penguin guano and 0.33 ± 0.39 mg NH_3 kg^{-1} h^{-1} from seal colony soils during the thawing period. Ammonia emissions from penguin guano were higher than those from ornithogenic soils during freezing-thawing cycles (FTCs). The temperature, pH, total nitrogen (TN) and drying-wetting conversion had an important effect on NH_3 fluxes. For the first time, we provide a quantitative relationship between NH_3 flux and temperature, TN and pH. Our results show that marine animal excreta and ornithogenic soils are significant NH_3 emission sources. In coastal Antarctica, FTC-induced NH_3 emissions might account for a large proportion of annual flux from marine animal colonies due to high freezing-thawing frequency.

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Introduction

Ammonia (NH_3) is an important component in the atmosphere that arises from both natural and anthropogenic sources (Bouwman *et al.* 1997, Sutton *et al.* 2000, Blackall *et al.* 2008). It plays a significant role in the nitrogen (N) cycle, having important environmental consequences in many ecosystems (Fangmeier *et al.* 1994, Bouwman *et al.* 2002). Ammonia emissions from anthropogenic sources include domestic animals, synthetic fertilizers, sewage treatment, industry and transport (Bouwman *et al.* 1997, Aneja *et al.* 2000, Blunden & Aneja 2008) and in recent years, NH_3 emissions from large wild animal colonies have been observed (Wilson *et al.* 2004, Theobald *et al.* 2006, Blackall *et al.* 2007, 2008), indicating that they are a significant natural source of atmospheric NH_3. However, the magnitude and location of natural NH_3 sources have received little attention and the estimates that have been made are extremely uncertain (Bouwman *et al.* 1997, Sutton *et al.* 2000, Blackall *et al.* 2007).

In coastal Antarctica, the ice-free areas are colonized by marine animals such as penguins and seals, and vegetation such as mosses, lichens and algae. Marine animal colonies, vegetation and their interactions form a special tundra ecosystem (Tatur *et al.* 1997, Tatur & Myrcha 2002, Sun *et al.* 2004b). Every year a large amount of penguin guano is deposited into terrestrial ecosystems, which leads to the formation of ornithogenic soils (Ugolini 1970, Campbell & Claridge 1987, Tatur 1989, Bockheim & Ugolini 1990, Michel *et al.* 2006, Schaefer *et al.* 2008), which are particularly rich in organic carbon, nitrogen and phosphorus and show large variations in pH (Speir & Cowling 1984, Heine & Speir 1989, Simas *et al.* 2007, 2008, Schaefer *et al.* 2008, Cannone *et al.* 2008). Ornithogenic soils on Antarctic islands have been studied in Admiralty Bay, King George Island (Tatur 1989, Tatur *et al.* 1997, Tscherko *et al.* 2003, Simas *et al.* 2008) and from elsewhere (Simas *et al.* 2007). Continental ornithogenic soils have been studied mostly on and around Ross Island (Speir & Cowling 1984, Speir & Ross 1984, Ramsay & Stannard 1986, Heine & Speir 1989, Porazinska *et al.* 2002) with some research conducted along the northern Victoria Land coast, including Cape Hallett (Hofstee *et al.* 2006) and near Casey Station (Beyer & Bölter 2000). Despite the limited geographical distribution of penguin guano and ornithogenic soils, they are the most important N reservoir in Antarctic terrestrial ecosystems (Simas *et al.* 2007).

The isotopic analyses of ornithogenic soils in the vicinity of penguin colonies also point to the importance of NH_3 volatilization from the guano (Wada *et al.* 1981, Mizutani & Wada 1988). Seabird excretal mass budgets have implied volatilization rates of up to 90% of total excreted nitrogen as NH_3 in penguin colonies (Lindeboom 1984). It was estimated that Antarctic seabirds (with penguins as the dominant group) emit about 129.6 Gg NH_3 yr^{-1}, corresponding to 53.6% of estimated total global seabird

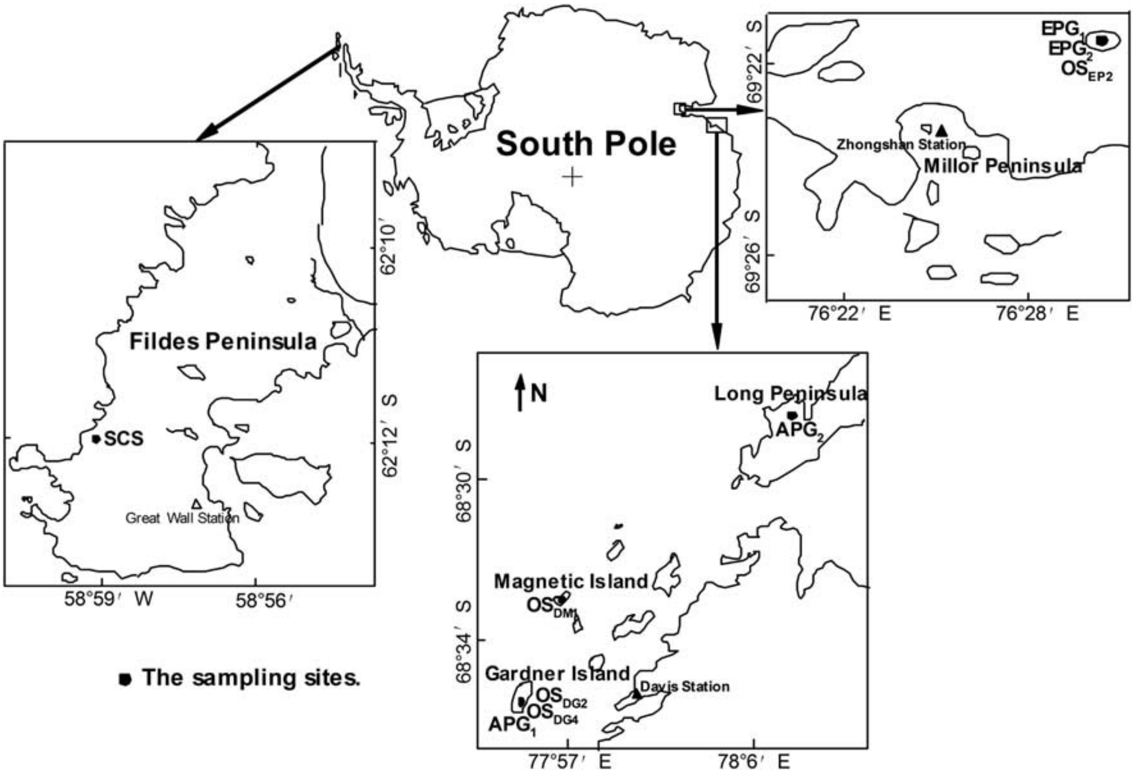

Fig. 1. Sampling sites for penguin guano, ornithogenic soils and seal colony soils in coastal Antarctica. East Antarctica: OS_{DG2} and OS_{DG4} = ornithogenic soil core sites in Adélie penguin colony on Gardner Island, APG_1 and APG_2 = Adélie penguin guano sites on Gardner Island and Long Peninsula, respectively, OS_{DM1} = ornithogenic soil profile site in Adélie penguin colony on Magnetic Island, EPG_1 and EPG_2 = emperor penguin guano sites, OS_{EP2} = ornithogenic soil profile sites in emperor penguin colony. West Antarctica: SCS = seal colony soil sites on Fildes Peninsula.

emissions (Blackall *et al*. 2007). Investigations of other trace gas (e.g. methane, nitrous oxide and phosphine) emissions from marine animal colonies through field observation or laboratory incubation experiments (Sun *et al*. 2002, Zhu *et al*. 2008, 2009), indicate that environmental factors have an important effect on gas emissions.

Field measurements of NH_3 emissions from marine animal colonies are still scarce in coastal Antarctica because of the major experimental difficulties involved. However, laboratory experiments can provide an important step in elucidating the processes involved. In this study, we used penguin guano, ornithogenic soil and soil from a seal colony in laboratory experiments to 1) quantify potential NH_3 emission rates, 2) investigate the effects of freezing-thawing cycles (FTCs), soil chemical properties, temperature, pH and moisture on NH_3 fluxes, and 3) establish the quantitative relationships between NH_3 fluxes and environmental factors.

Materials and methods

Study areas

Gardner Island (68°34'S, 77°52'E), Magnetic Island (68°32'S, 77°54'E) and Long Peninsula (68°28.37'S, 78°8.82'E) in the Vestfold Hills, East Antarctica (Fig. 1) have a cold, dry and windy climate. Air temperatures are below 0°C for most of the year, summer temperatures rise as high as +13°C and winter temperatures drop to as low as -40°C (Seppelt *et al*. 1988). Gardner Island, Magnetic Island and north Rookery Coast of Long Peninsula have three important Adélie penguin (*Pygoscelis adeliae* (Hombron & Jacquinot)) colonies with 22 180, 17 184 and 6445 estimated numbers of breeding pairs respectively (Whitehead & Johnstone 1990). During CHINARE-22 in 2006, one penguin guano profile (APG_1) and two ornithogenic soil cores (OS_{DG2} and OS_{DG4}) were sampled from Gardner Island, one ornithogenic soil profile (OS_{DM1}) from Magnetic Island, and one penguin guano profile (APG_2) was collected from Long Peninsula.

The emperor penguin colony of Amanda Bay (69°22'S, 76°24'E) has about 10 000 birds (Zhu *et al.* 2009). Two emperor penguin guano samples (EPG_1 and EPG_2) and one ornithogenic soil profile (OS_{EP2}) were collected in this colony.

Fildes Peninsula, West Antarctica (61°51'–62°15'S, 57°30'–59°10'W) lies in the south-west of King George Island, in the maritime Antarctica (Fig. 1). This area has a more oceanic climate with a mean annual temperature *c*. -2.5°C, and a range from -26.6 to 11.7°C. Mean annual precipitation, mainly in the form of snow, is 630 mm,

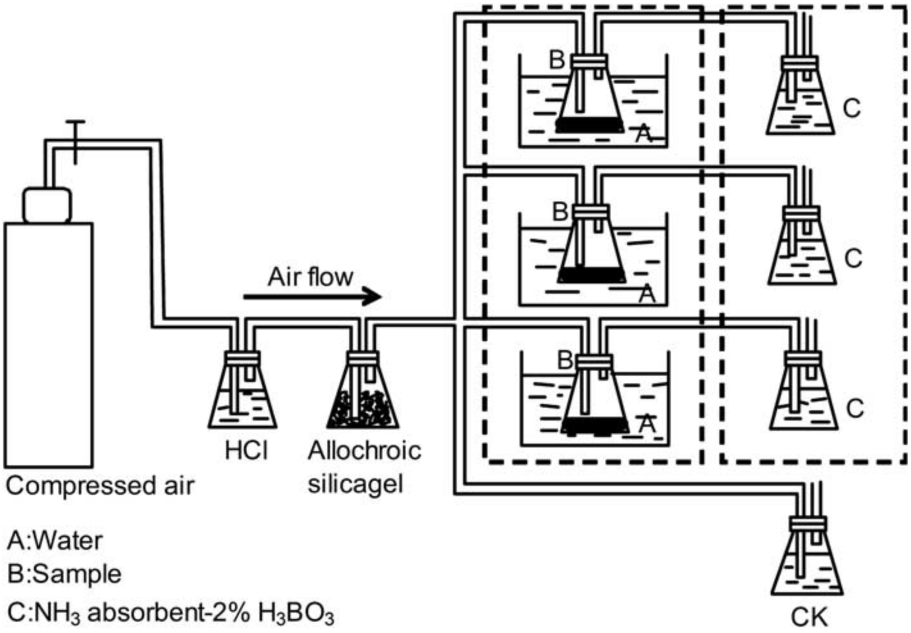

Fig. 2. Flow diagram for the measurements of NH_3 fluxes from penguin guano, ornithogenic soils and seal colony soils.

evenly distributed throughout the year. The western coast of this peninsula has over 10 700 seals each summer, mainly elephant seals (*Mirounga leonine* (L.)) and fur seals (*Arctocephalus gazella* (Peters)). During the moulting and breeding period each summer, their excreta and hairs are deposited into tundra soils or catchments by snowmelt water (Sun *et al*. 2004a). One soil core with seal excreta (SCS) was collected in this colony.

All sites are covered by snow during winter, freezing marine animal excreta and the underlying soils until snowmelt in spring/summer after which freeze-thaw cycles are a frequent occurrence.

Collection and sampling storage

Penguin guano (EPG_1, EPG_2, APG_1 and APG_2) and ornithogenic soil (OS_{DM1} and OS_{EP2}) were collected from different penguin colonies by *in situ* sectioning the accumulative guano or soil layer by layer from top to bottom using a bamboo scoop. The soil cores OS_{DG2} and OS_{DG4} (10 cm inner diameter, 62 cm and 80 cm long, respectively) were sampled by hammering the PVC tubes vertically into the soils and then digging them out (Sun *et al*. 2004a). The soil core SCS (6 cm inner diameter, 30 cm long) was obtained in the same way. These samples were completely sealed, and transported at -10°C to the laboratory in China for the experiments.

Experimental design and NH_3 flux measurements

NH_3 fluxes were determined using a continuous airflow enclosure chamber method (Fig. 2) (Kissel *et al*. 1977, Tian *et al*. 1998, Chadwick 2005, Nyord *et al*. 2008) in four experiments:

Experiment I: effects of freezing-thawing cycles (FTCs) on NH_3 fluxes

Samples EPG_1, APG_1 and SCS were homogeneously mixed and then divided into three parts (about 50 g for each

Table I. Physical and chemical properties of penguin guano, ornithogenic soils and seal colony soils sampled from different sea animal colonies of coastal Antarctica.

Samples	M_C (%)	pH	TOC (%)	TN (%)	NH_4^+-N (μg g^{-1})	C/N
Emperor penguin guano						
EPG_1	323.9	6.8	12.29	2.60	1759.6	4.7
EPG_2	127.8	6.9	6.78	1.33	407.9	2.8
Adélie penguin guano						
APG_1	178.4	7.1	14.65	3.60	1162.2	4.1
APG_2	62.9	7.6	9.94	1.08	2565.2	5.6
Seal colony soil						
SCS	20.0	6.7	0.22	0.05	56.9	4.8
Ornithogenic materials						
OS_{DM1}	32.9	8.2	5.47	1.01	819.3	2.6
OS_{EP2}	37.9	6.3	12.75	0.98	42.7	7.8
OS_{DG2}	-	8.3	4.48	0.34	-	13.2
OS_{DG4}	-	8.3	3.45	0.21	-	16.4

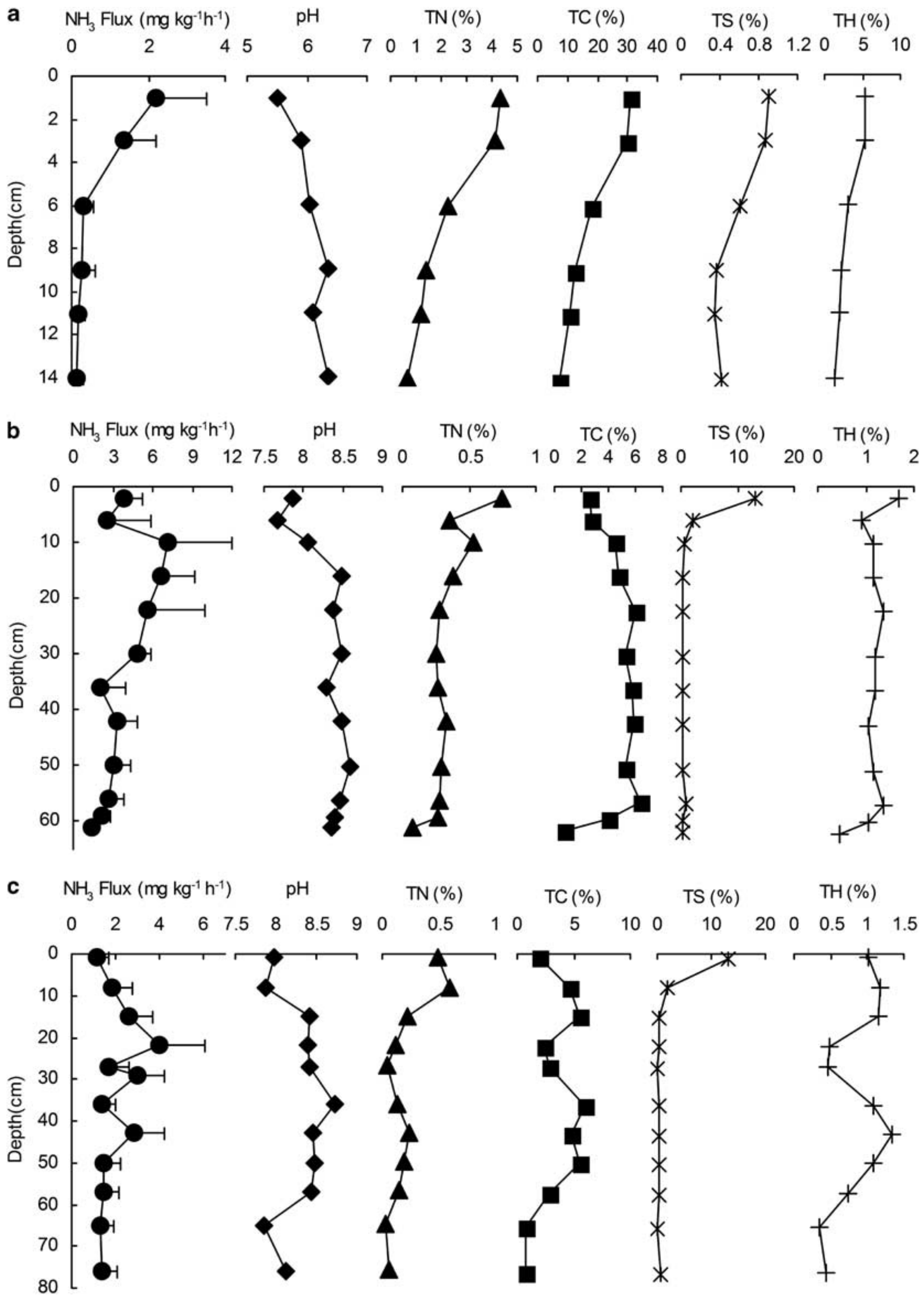

Fig. 3. Variations of mean NH_3 fluxes and chemical properties with soil depths in **a.** OS_{EP2}, **b.** OS_{DG2}, and **c.** OS_{DG4}. The dash lines represent one standard deviation of mean NH_3 flux.

sample), to form the three replicates for freeze-thaw experiments. These were put into glass vessels (250 ml) and frozen for 12 h at -10°C, after which thawing started at 4°C (close to summer mean air temperature at the sampling sites). The thawing period was 8 h during each FTC for each sample. During the FTCs, the headspace gases were continuously removed by the airflow from a steel flask filled with a gas mixture of pure nitrogen and oxygen. Since airflow velocity can influence NH_3 volatilization, the airflow rate was controlled at about 3.0 m s^{-1} (about 14.0 litres

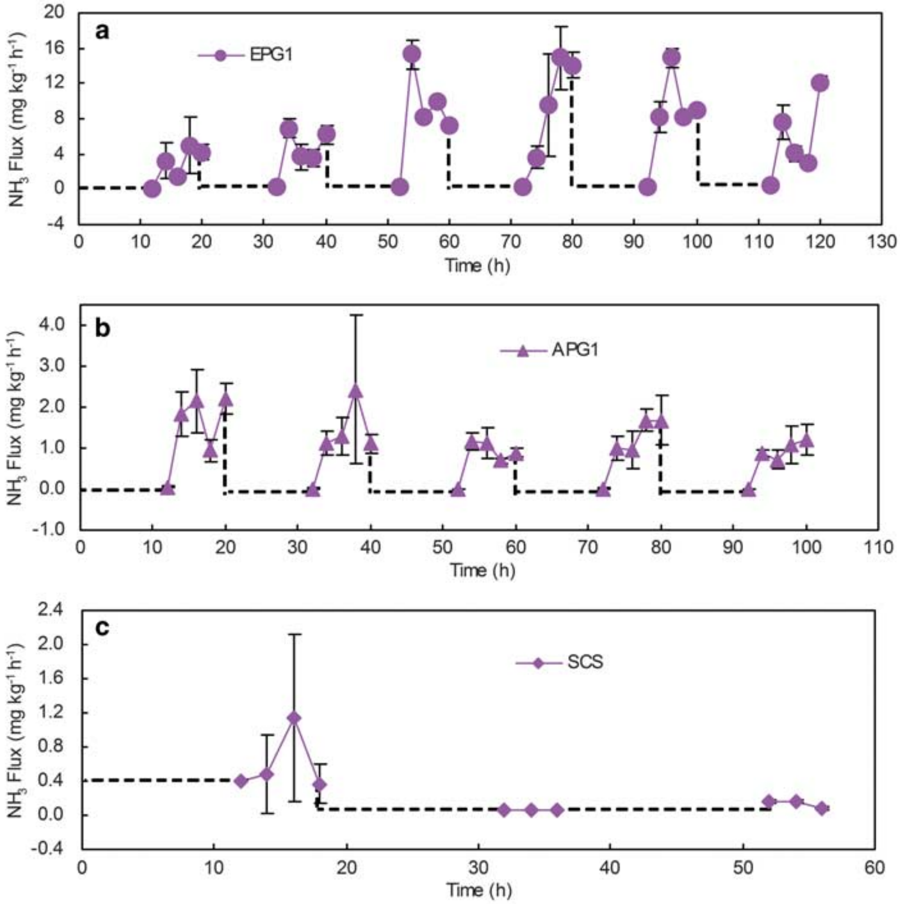

Fig. 4. The NH_3 fluxes from **a.** emperor penguin guano EPG_1, **b.** Adélie penguin guano APG_1, and **c.** seal colony soils SCS during FTCs. The broken and solid lines indicate the freezing and thawing periods, respectively. The error bars represent the standard deviation based on three replicates ($n = 3$).

per minute, close to the average wind velocity at sampling sites). The NH_3 emitted was trapped by 2% H_3BO_3 solution (Fig. 2) and determined every 2 h by 0.01 mol l^{-1} HCl titration using methyl red-bromocresol green as the indicator (Tian *et al*. 1998). The detection limit for this method was 1 mg NH_3 kg^{-1} h^{-1} and if NH_3 emission was lower we used the ionic selection electrode to measure ammonium in the H_3BO_3 solution (Chadwick 2005, Nyord *et al*. 2008). The detection limit for this method was 0.1 mg NH_3 kg^{-1} h^{-1} but it is very slow compared to the titration method. Three replicates were made for each freezing-thawing treatment and the number of FTCs for each sample depended on NH_3 emission rates. Penguin guano EPG_1 and APG_1 showed continuous, high NH_3 emissions, and the fluxes were measured during six and five FTCs, respectively, whereas the fluxes from seal colony soil SCS were measured during only three FTCs due to very low emission rates.

Experiment II: effects of soil depth and chemical properties on potential NH_3 emissions

The soil profiles OS_{EP2}, OS_{DG2} and OS_{DG4} were sectioned at 1 cm intervals. We selected 1 cm, 3 cm, 6 cm, 9 cm, 11 cm, 14 cm soil from OS_{EP2}, 1 cm, 6 cm, 10 cm, 16 cm, 22 cm, 30 cm, 36 cm, 42 cm, 50 cm, 56 cm, 59 cm, 61 cm soil from OS_{DG2} and 1 cm, 8 cm, 15 cm, 22 cm, 27 cm, 29 cm, 36 cm, 43 cm, 50 cm, 57 cm, 65 cm, 76 cm soil from OS_{DG4} to measure potential NH_3 fluxes from different depths of ornithogenic soils using the method described for experiment I.

Experiment III: effects of temperature on NH_3 fluxes

Different depths of the soils were homogeneously mixed from the cores OS_{DG2} and OS_{DG4}, to examine the effects of temperature on mean NH_3 fluxes from ornithogenic soil profiles. Using 50 g samples the experimental temperature started at 4°C, and then increased 2–3°C every hour until close to 30°C. The low limit of 4°C was very close to the local average ground temperature.

Experiment IV: effects of water content on NH_3 fluxes

Penguin guano EPG_2 and APG_2 and soil profiles OS_{DM1} and OS_{EP2} were homogeneously mixed. A total of 0, 10, 15 and 20 ml deionized water were added to 50 g samples and NH_3 fluxes measured each day five or six times.

Calculation of NH_3 emission rates

The NH_3 fluxes (mg NH_3 kg^{-1} h^{-1}) can be calculated according to the following formula:

$$\text{Flux}\,(NH_3) = V_{HCl} \times C_{HCl} \times 17 \times 1000/(M_S \times t).$$

Table II. The mean NH_3 fluxes from penguin guano and ornithogenic soils and calculated specific NH_3-N loss rate (NH_3-N/TN) during the thawing period.

Samples	NH_3 flux ($mg\,kg^{-1}\,h^{-1}$)	NH_3-N/TN (‰)
Emperor penguin guano		
EPG1	7.66 ± 4.33	11.7
Adélie penguin guano		
APG1	1.31 ± 0.64	1.2
Soil profile OS_{EP2}		
OS_{EP2}-1	2.52 ± 1.07	1.0
OS_{EP2}-3	1.56 ± 0.72	0.6
OS_{EP2}-6	0.37 ± 0.22	0.3
OS_{EP2}-9	0.33 ± 0.35	0.1
OS_{EP2}-11	0.20 ± 0.20	0.1
OS_{EP2}-14	0.16 ± 0.19	0.1
Soil core OS_{DG2}		
OS_{DG2}-1	4.27 ± 1.96	9.6
OS_{DG2}-6	2.82 ± 1.17	13.4
OS_{DG2}-10	7.79 ± 2.53	24.2
OS_{DG2}-16	7.23 ± 4.61	31.0
OS_{DG2}-22	6.20 ± 1.91	37.8
OS_{DG2}-30	5.39 ± 4.22	35.6
OS_{DG2}-36	2.21 ± 0.83	14.0
OS_{DG2}-42	3.69 ± 1.67	19.0
OS_{DG2}-50	3.37 ± 1.2	20.0
OS_{DG2}-56	2.96 ± 0.94	18.9
OS_{DG2}-59	2.41 ± 0.92	16.2
OS_{DG2}-61	1.52 ± 0.52	37.6
Soil core OS_{DG4}		
OS_{DG4}-1	1.22 ± 0.53	4.4
OS_{DG4}-8	1.98 ± 0.79	5.8
OS_{DG4}-15	2.82 ± 0.86	22.1
OS_{DG4}-22	4.48 ± 1.61	59.9
OS_{DG4}-27	1.87 ± 0.8	80.2
OS_{DG4}-29	3.28 ± 0.88	-
OS_{DG4}-36	1.56 ± 0.43	18.2
OS_{DG4}-43	3.12 ± 1.11	19.2
OS_{DG4}-50	1.57 ± 0.67	12.8
OS_{DG4}-57	1.64 ± 0.51	17.0
OS_{DG4}-65	1.43 ± 0.45	82.4
OS_{DG4}-76	1.55 ± 0.51	38.8

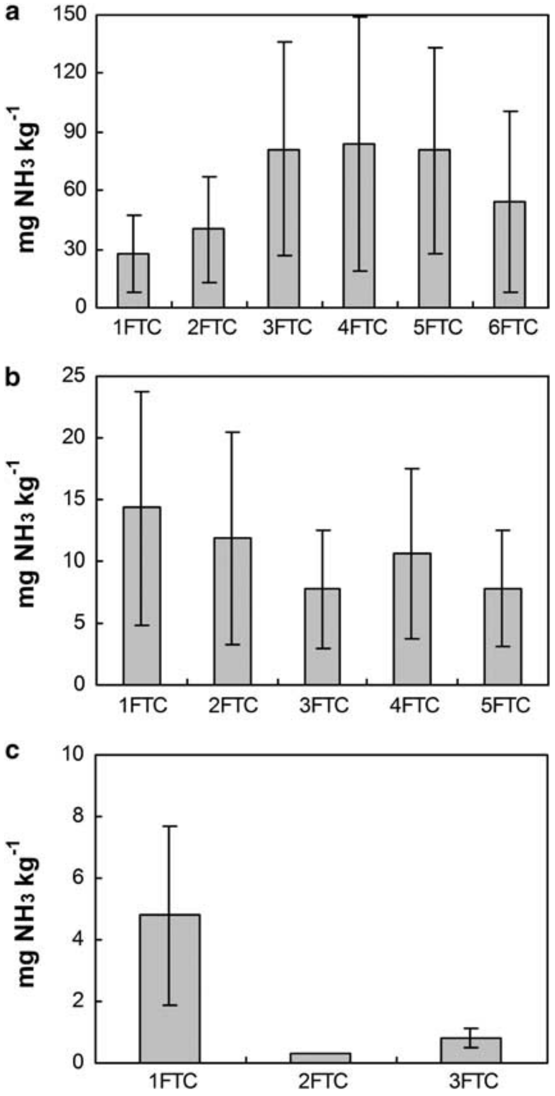

Fig. 5. Cumulative NH_3 emissions from **a.** emperor penguin guano EPG_1, **b.** Adélie penguin guano APG_1, and **c.** seal colony soils SCS during the period from the beginning of each sample thawing, with standard errors.

Where V_{HCl} is the HCl volume (l), C_{HCl} is the HCl concentration ($mol\,l^{-1}$), 17 is the formula weight of NH_3 ($g\,mol^{-1}$), M_S is the sample mass (kg) and t is the time (h). The cumulative flux was calculated by integrating the fluxes over the incubation period of 8 h from the beginning of each thawing. The specific NH_3-N loss rates from penguin guano and ornithogenic soils were obtained through NH_3-N divided by total nitrogen.

Analyses of physical and chemical properties for the samples

All the samples were separated from the profiles or soil cores, and mixed homogeneously. Soil gravimetric moisture content (M_C) was determined by drying the soil at +105°C for 12 h. M_C was calculated as: M_C = (mass before drying-mass after drying)/mass after drying × 100% (Zhu *et al.* 2008). The pH and NH_4^+ was determined by ion selective electrode. Total organic carbon (TOC) content was determined from the dry sample by the potassium dichromate volumetric method (Zhu *et al.* 2008). Total nitrogen (TN), total carbon (TC), total sulphur (TS) and total hydrogen (TH) were analysed by the Elemental Analyzer (Vario, EL).

Statistical analysis

All data were subjected to analysis of Microsoft Excel and SPSS 16.0 for Window XP. We used one-way ANOVA followed by Tukey HSD's multiple comparisons to assess the differences in potential NH_3 fluxes between groups under different treatments. In all analyses where $P < 0.05$, the factor tested and the relationships were considered statistically significant.

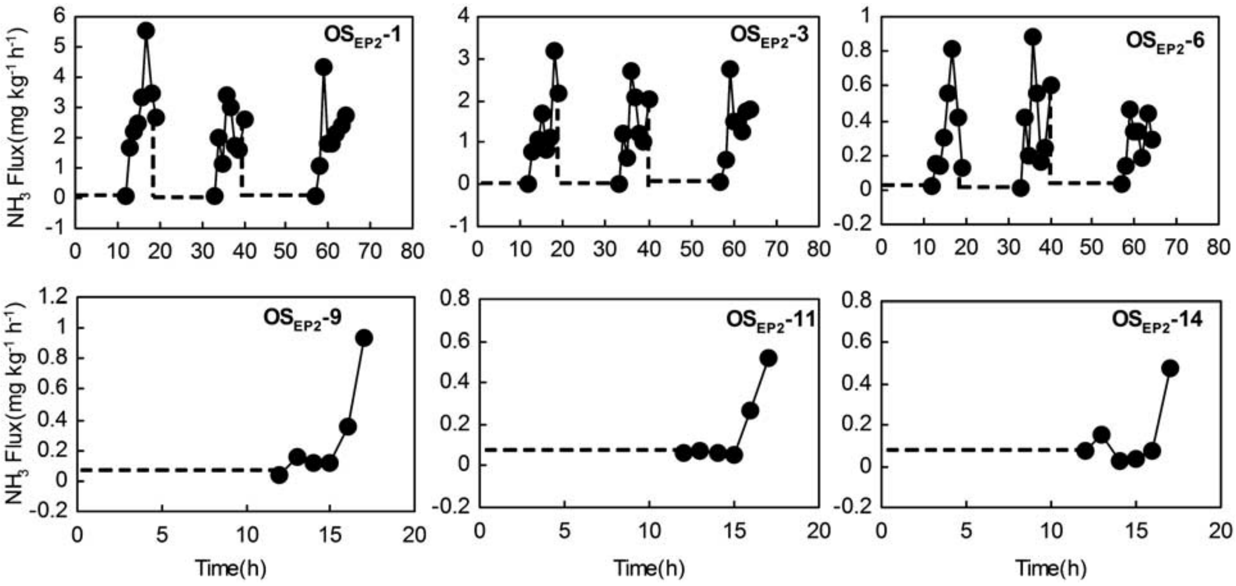

Fig. 6. Potential NH_3 fluxes from different depths of ornithogenic soils for the profile OS_{EP2} during the FTCs. Note: Depths are given by the minus values in the soil sample label given in each subfigure. The broken and solid lines indicate the freezing and thawing periods, respectively.

Results

Physical and chemical properties for all the soil samples are given in Table I and Fig. 3.

Effects of FTCs on NH_3 emissions from penguin guano and seal colony soils

Freezing-thawing cycle induced a rapid increase in NH_3 emission rates from samples EPG_1 and APG_1, and the same pattern was observed during the subsequent FTCs (Fig. 4). However, the emission rates from seal colony soil SCS showed a small increase only at the first FTC, and then the rates were close to zero at the second and third FTCs. The mean NH_3 fluxes from EPG_1, APG_1 and SCS were 6.17 ± 4.90 mg NH_3 kg^{-1} h^{-1}, 1.05 ± 0.70 mg NH_3 kg^{-1} h^{-1} and 0.14 ± 0.17 mg NH_3 kg^{-1} h^{-1} during the FTCs, respectively.

The mean fluxes from EPG_1, APG_1 and SCS during freezing were close to zero, but they increased significantly during the thawing period (Fig. 4 and Table II). For emperor penguin EPG_1, NH_3 emission rate was 38 times higher during thawing than during freezing whilst for Adélie penguin guano APG_1, the emission rate was 68 times higher. In penguin guano samples, the duration of the FTC-related NH_3 peaks were less than 8 h. For EPG_1, the thawing-related NH_3 emission maximum (17.4 mg NH_3 kg^{-1} h^{-1}) was highest during the fourth FTC (Fig. 4a). However, the emission maximum for APG_1 and SCS did not show similar variations during all the FTCs, and the highest peak for APG_1 (3.71 mg NH_3 kg^{-1} h^{-1}) and SCS (1.14 mg NH_3 kg^{-1} h^{-1}) occurred during the second and first FTC, respectively (Fig. 4b & c).

Cumulative NH_3 emissions from EPG_1 were generally higher than those from APG_1 and SCS. The maximum of cumulative NH_3 emissions occurred during the fourth FTC for EPG_1 (84.1 mg NH_3 kg^{-1}) and during the first FTC for APG_1 (14.3 mg NH_3 kg^{-1}) and SCS (4.8 mg NH_3 kg^{-1}) (Fig. 5). The specific NH_3-N loss rate (NH_3-N/TN) from sample EPG_1 was one order of magnitude higher than that from APG_1 (Table II).

Effects of FTCs on potential NH_3 emissions from ornithogenic soils

Potential NH_3 emissions from different depths of ornithogenic soils were also greatly affected by the FTCs, and in all cases a rapid increase in the emission rates was induced following thawing (Figs 6–8), which was very similar to NH_3 emissions from penguin guano (Fig. 4). The NH_3 fluxes from OS_{EP2} increased about 1–52 times following thawing. For OS_{DG2} and OS_{DG4}, the emissions increased about 40–139 times and 25–86 times, respectively. In all soil depths, the duration of the FTC-related NH_3 peaks were also less than 8 h. For OS_{EP2}, the thawing-related NH_3 emission maximum (5.51 mg NH_3 kg^{-1} h^{-1}) occurred during the first FTC (Fig. 6). For OS_{DG2}, the maximum (12.29 mg NH_3 kg^{-1} h^{-1}) occurred during the first FTC above 30 cm while it occurred during the second or third FTC below 30 cm (Fig. 7). For OS_{DG4}, the maximum (7.63 mg NH_3 kg^{-1} h^{-1}) occurred during the first or third FTC (Fig. 8). However, the emissions during the freezing were extremely low (close to zero) in the three soil profiles.

These ornithogenic soil profiles showed different NH_3 emission rates and patterns with depth. During three FTCs, the mean fluxes from OS_{DG2} (2.72 ± 1.22 mg NH_3 kg^{-1} h^{-1})

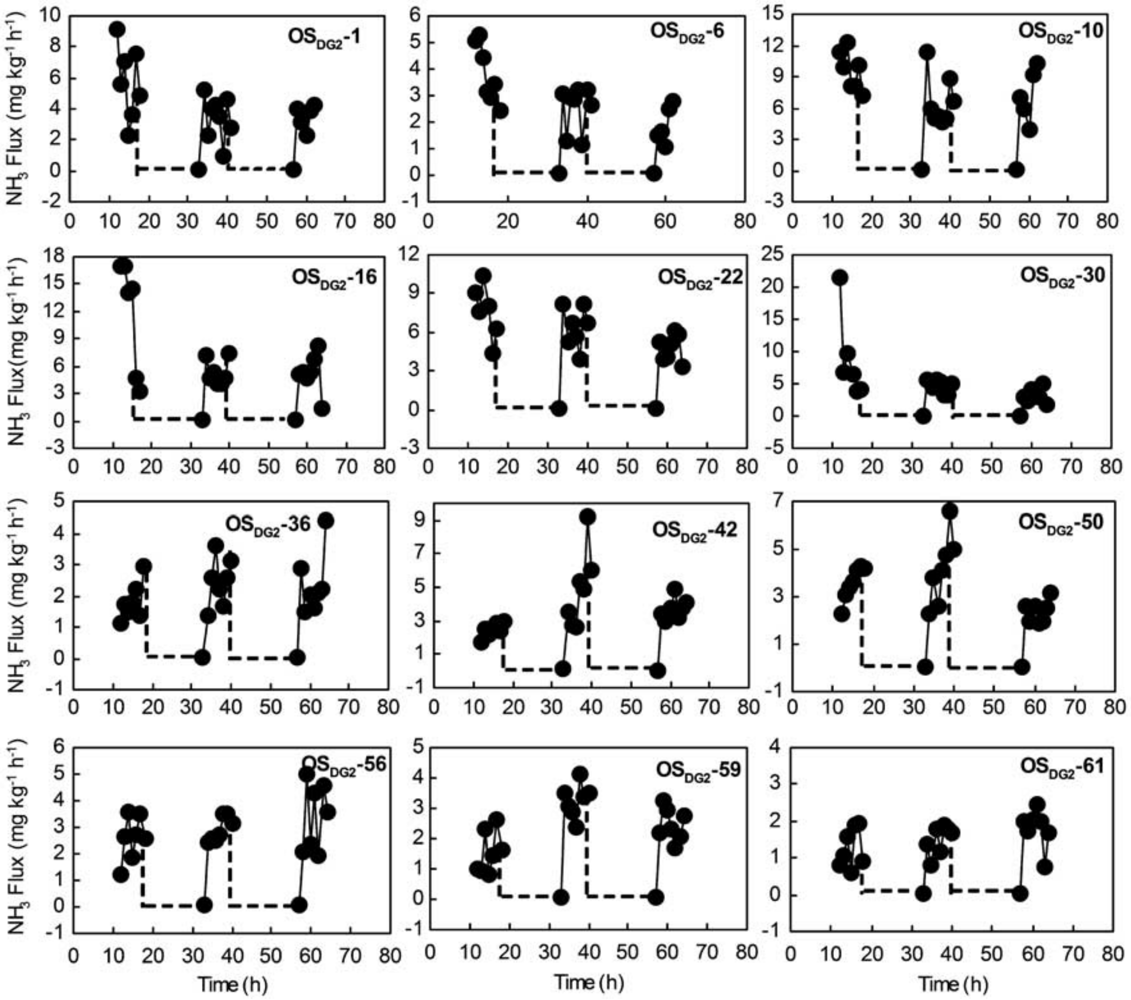

Fig. 7. Potential NH_3 fluxes from different depths of ornithogenic soils for soil core OS_{DG2} during the FTCs. Note: Depths are given by the minus values in the soil sample label given in each subfigure. The broken and solid lines indicate the freezing and thawing periods, respectively.

and OS_{DG4} (1.65 ± 0.57 mg NH_3 kg^{-1} h^{-1}) were one order of magnitude higher than that from OS_{EP2} (0.76 ± 0.85 mg NH_3 kg^{-1} h^{-1}). The NH_3 emissions from surface soils were evidently higher than those from deep soils in all the profiles. For OS_{EP2}, NH_3 fluxes from the soils above the first 3 cm were higher than 1 mg NH_3 kg^{-1} h^{-1} and lower than 0.8 mg NH_3 kg^{-1} h^{-1} below 6 cm (Fig. 8a). For OS_{DG2}, most of fluxes from the soils above the first 30 cm were higher than 4 mg NH_3 kg^{-1} h^{-1} and lower than 4 mg NH_3 kg^{-1} h^{-1} below 30 cm (Fig. 3b). For OS_{DG4}, the fluxes from the soils were lower than 4 mg NH_3 kg^{-1} h^{-1} for all depths (Fig. 3c).

Total cumulative emission of NH_3 during three FTCs is shown in Fig. 9. Three profiles OS_{EP2}, OS_{DG2} and OS_{DG4} showed different cumulative emission amounts and patterns during FTCs. Cumulative NH_3 emissions from surface soils were generally higher than those from deep soils. Additionally, the maximum cumulative NH_3 emissions occurred during the first FTC in the surface soils at OS_{EP2} and OS_{DG2} while profile OS_{DG4} showed a different emission pattern. The highest cumulative emissions were 21.4 mg NH_3 kg^{-1} for OS_{EP2}, 70.4 mg NH_3 kg^{-1} for OS_{DG2} and 36.2 mg NH_3 kg^{-1} for OS_{DG4} during three FTCs. The NH_3-N loss rates (NH_3-N/TN) was markedly larger in OS_{DG2} and OS_{DG4} than in OS_{EP2} (Table II).

NH_3 fluxes and environmental variables

There was no difference in TN and TC contents in soil profiles OS_{DG2} and OS_{DG4}, and they were higher in the profile OS_{EP2} than in OS_{DG2} and OS_{DG4}. However, NH_3 emissions from OS_{EP2} were significantly lower than those from OS_{DG2} and OS_{DG4} (Fig. 3). Additionally, NH_3 fluxes, TN, TC and TH showed consistent variability with depth in profiles OS_{EP2}, OS_{DG2} and OS_{DG4} (Fig. 3). There was a relatively low correlation between NH_3 fluxes and TC contents in OS_{DG2} and OS_{DG4} (Fig. 10a). However, NH_3

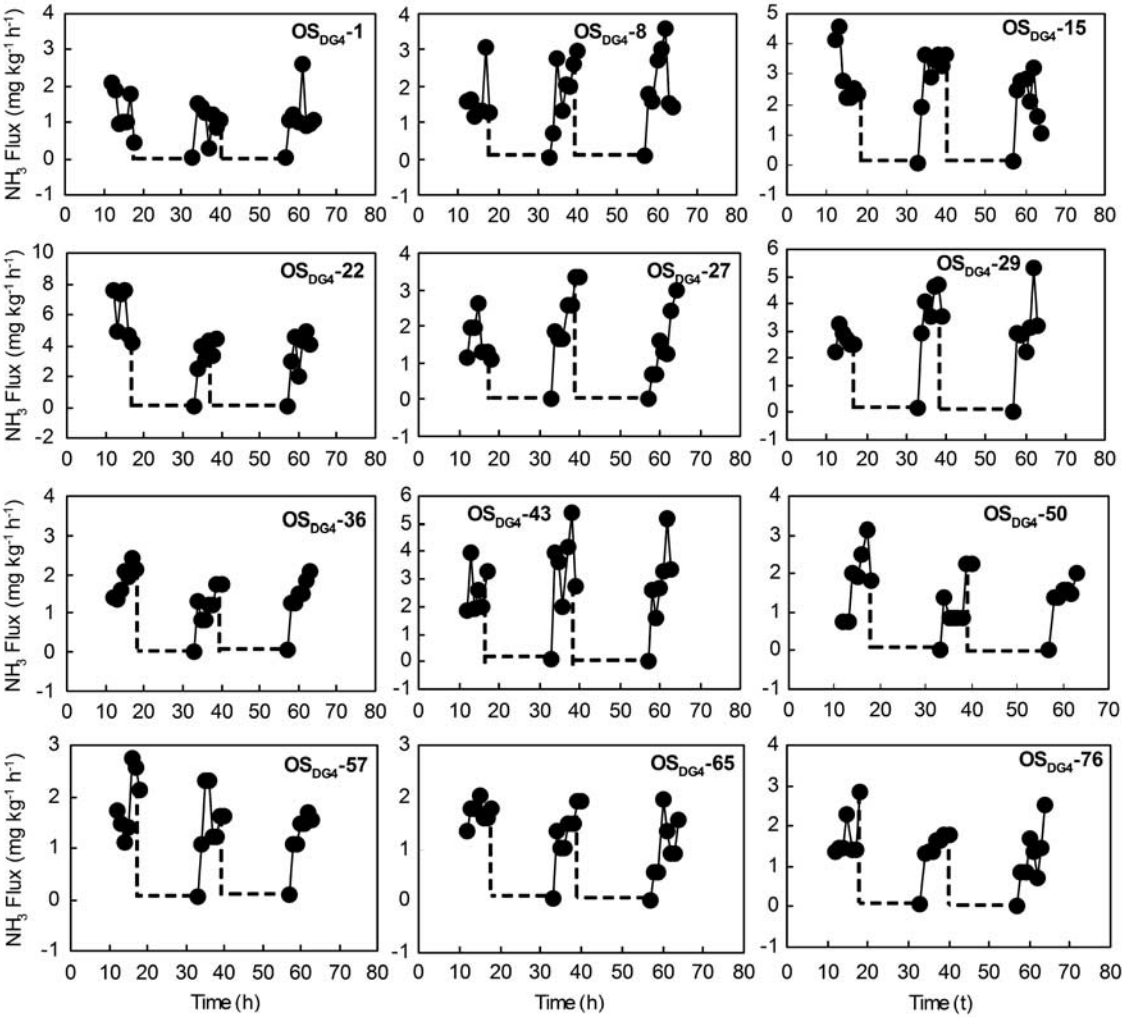

Fig. 8. Potential NH_3 fluxes from different depths of ornithogenic soils for soil core OS_{DG4} during the FTCs. Note: Depths are given by the minus values in the soil sample label given in each subfigure. The broken and solid lines indicate the freezing and thawing periods, respectively.

fluxes showed a significant linear correlation with TN (for OS_{DG2} and OS_{DG4}, $flux_{NH3} = 10.22TN+0.69$, $P < 0.001$; for OS_{EP2}, $flux_{NH3} = 0.51TN-0.44$, $P = 0.008$) in these three profiles (Fig. 10b), indicating that TN content was one of important factors affecting the magnitude of NH_3 emission.

The pH was within the range of 5.5–6.3 for OS_{EP2} and within the range of 7.8–8.6 for OS_{DG2} and OS_{DG4} (Fig. 3). Overall, NH_3 fluxes from the three profiles showed a significant exponential correlation with pH (Fig. 10c). According to pH values, NH_3 fluxes could be categorized into two groups: the first group represented NH_3 fluxes from OS_{EP2} which had relatively lower fluxes at $pH < 6.5$. The second group represented NH_3 fluxes from OS_{DG2} and OS_{DG4} which had relatively higher fluxes at $pH > 7.5$ (Fig. 10c). Therefore NH_3 volatilizes more easily from ornithogenic soils at $pH > 7.5$, suggesting that pH played a role in the potential for NH_3 volatilization. The relationship between NH_3 fluxes and controlled temperatures was also examined from soil cores OS_{DG2} and OS_{DG4} over a wide range of temperature (4–30°C). NH_3 fluxes from OS_{DG2} and OS_{DG4} showed an exponential increase with the temperatures (Fig. 11).

As illustrated in Fig. 12, NH_3 emissions from samples EPG_2 and APG_2 were higher than those from soil profiles OS_{EP2} and OS_{DM1} under different moisture treatments. When 10 ml, 15 ml and 20 ml water was added, significantly or slightly enhanced NH_3 emissions occurred in APG_2, OS_{EP2} and OS_{DM1} during the five-day incubation period. However, decreased NH_3 emissions occurred in EPG_2 during the initial three days, which may be due to particularly high water content (the ratio of the lost water amount and dry soil weight x 100% = 127.8%) in emperor penguin guano (Table I). In addition, NH_3 emissions from APG_2, OS_{EP2} and OS_{DM1} showed an insignificant difference between treatments of 10 ml, 15 ml and 20 ml water addition (Table III).

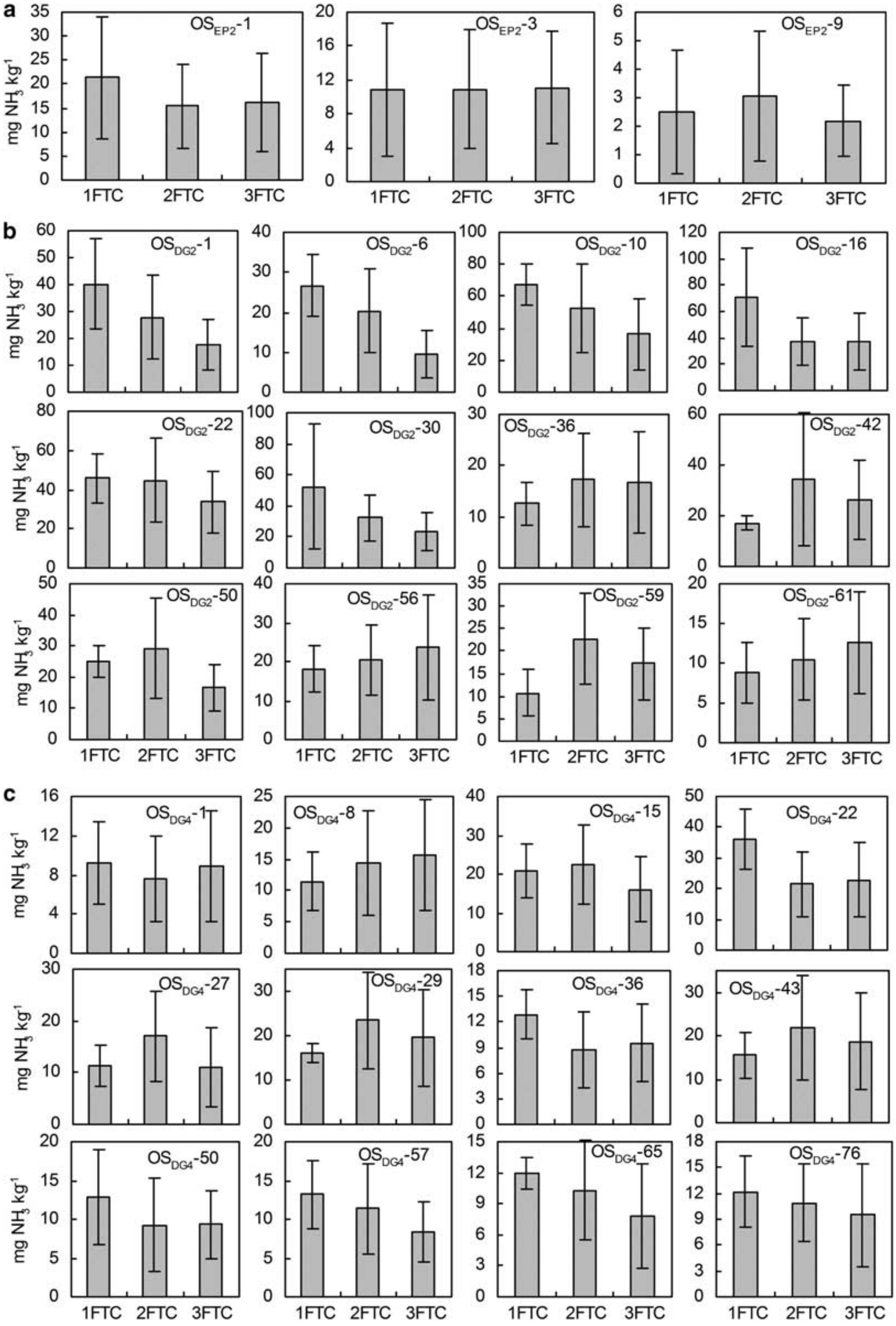

Fig. 9. Cumulative NH_3 emissions from different depths of ornithogenic soils for profiles **a.** OS_{EP2}, **b.** OS_{DG2}, and **c.** OS_{DG4} during the period from the beginning of each sample thawing, with standard errors. Note: Depths are given by the minus values in the soil sample label given in each subfigure.

Discussion

Effects of FTCs on NH_3 emissions

In all the experimental samples, enhanced NH_3 emissions following thawing have been observed (Fig. 4 and Figs 6–8). High NH_3 emissions during the thawing period were probably controlled by two processes:

1) the microbial decomposition of uric acid to ammonium, and the rate of ammonification (Blackall *et al.* 2008).

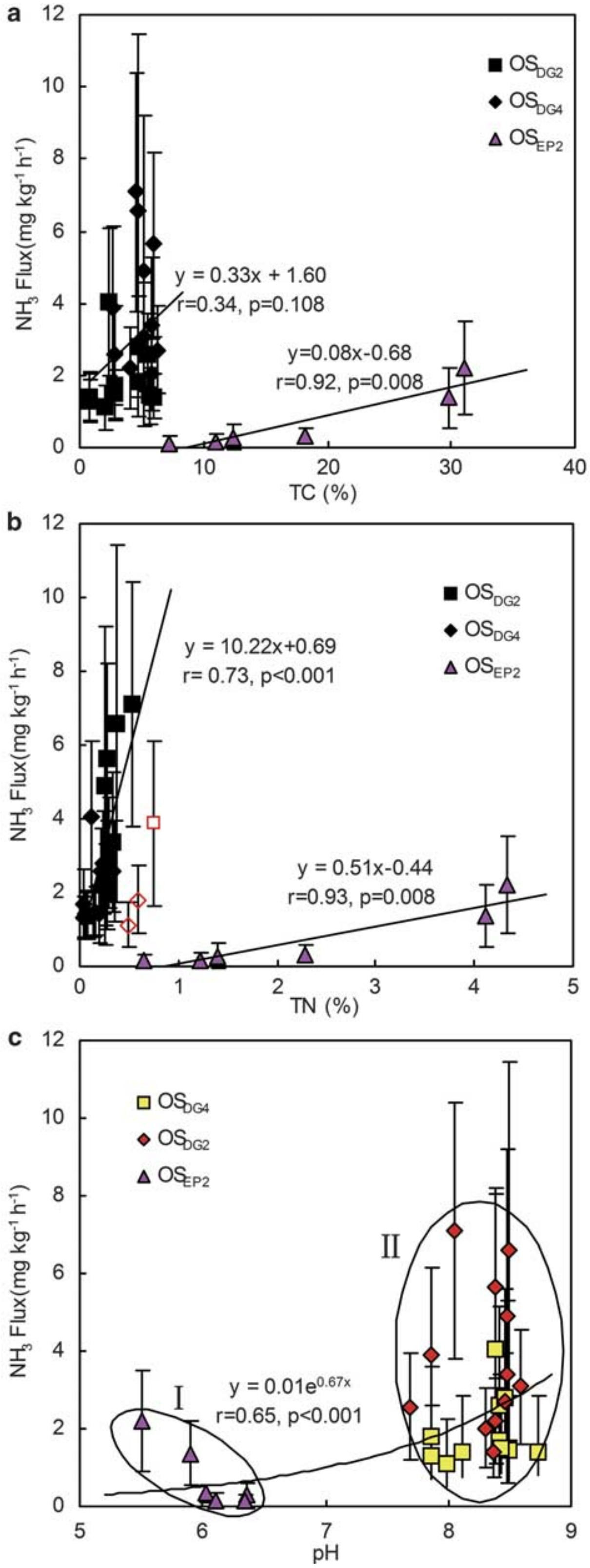

Fig. 10. Correlation between NH_3 fluxes from ornithogenic soils **a.** OS_{EP2}, OS_{DG2} and OS_{DG4} and TC, **b.** TN, and **c.** pH. Vertical lines represent one standard deviation of mean NH_3 flux. Note: Three outlier data exempts from the correlation in b.

Significantly elevated microbial respiration has been found in penguin guano, ornithogenic soils and seal colony soils during FTCs due to the high levels of nutrients from excreta (Zhu *et al.* 2009). In the boreal regions of the Northern Hemisphere, the activity of all heterotrophic microbes increased during tundra soil FTCs (Schimel & Clein 1996). In this study, microbial decomposition rates of uric acid in penguin guano or ornithogenic soils might be greatly increased during FTCs, leading to an increase in the rate of ammonification, and thus increased NH_3 emissions, indicating that freeze-thaw increased the availability of substrates for heterotrophic microbes (Premié & Christensen 2001, Teepe *et al.* 2001). Recent studies have shown that increased N_2O and CH_4 fluxes from soils or marine animal excreta that occurred during FTCs (Teepe *et al.* 2001, Koponen *et al.* 2006, Zhu *et al.* 2009) were very similar to NH_3 emissions in this present study,

2) There was some NH_3 production and emission in frozen penguin guano and ornithogenic soils although the fluxes were very low (Fig. 4 & Figs 6–8). Therefore part of NH_3 released during the thawing period might have originated from the NH_3 stored in frozen guano or soils.

Effects of TOC and TN contents on NH_3 emissions

Ammonia fluxes from ornithogenic soils showed a positive correlation with TN and TC (Fig. 10a & b). Previous studies have found that the accumulated flux of NH_3 is linearly related to the amount of TN in the slurry (Sommer 1997, Aneja *et al.* 2000, 2001). Our study agrees with this. Penguin guano and ornithogenic soils both have particularly high nitrogen contents (Table I) with uric acid as the dominant nitrogen species (Lindeboom 1984). Uric acid degrades through allantoin and urea to ammonium in summer when soils thaw (Boyd & Boyd 1963, Legrand *et al.* 1998). Ammonium, as an end product of the breakdown, can be partly lost to the atmosphere as ammonia (Legrand *et al.* 1998). The NH_4^+-N contents in fresh penguin guano are significantly higher than those in the aged penguin guano or ornithogenic soils (Table I), so NH_3 emissions from fresh penguin guano or surface sediments were higher than those from the aged guano or deep soils (Figs 3, 4, 6, 7). At present, seabird excretal mass budgets have assumed volatilization rates of up to 90% of total excreted nitrogen as NH_3 although direct measurements of NH_3 emissions in Antarctica are not available (Lindeboom 1984). Legrand *et al.* (1998) estimated NH_3 emissions from the total breeding population of five million Adélie penguins around the Antarctic continent as a maximum of 250 t NH_3-N during the summer. Our results provide a more quantitative relationship between NH_3 flux from ornithogenic Antarctic soils and TN than those reported in the literature (Fig. 10b).

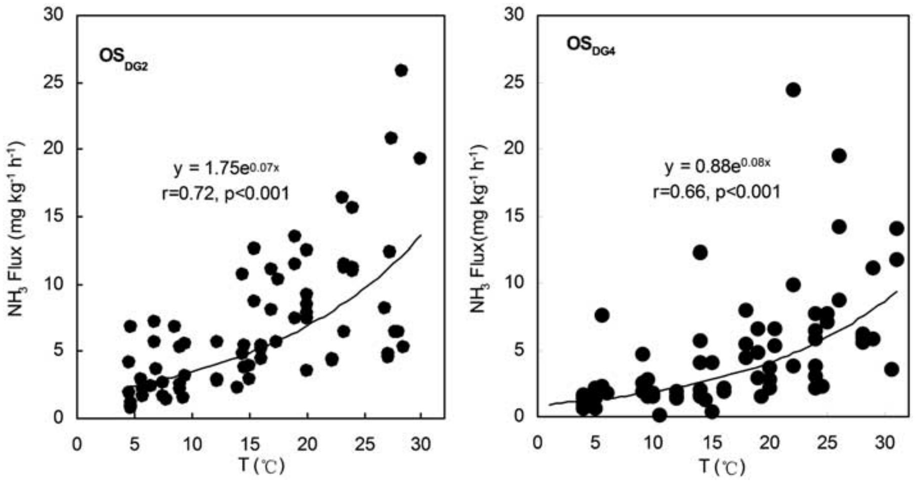

Fig. 11. Correlation between NH_3 fluxes from ornithogenic soils OS_{DG2} and OS_{DG4} and temperatures.

Ammonia emissions from surface soils were lower for profiles OS_{DG2} and OS_{DG4} due to the effects of high TS content (primarily as SO_4^{2-}) and low pH values, although TN contents of surface soils were much higher than those of deep soils (Fig. 3b & c). High SO_4^{2-} can reduce the NH_4^+ production, and thus resulted in less NH_3 emissions through the following equation (Duplessis & Kroontje 1964):

$$(NH_4)_2SO_4 \Leftrightarrow 2NH_4^+ + SO_4^{2-}$$

Effects of pH on NH_3 emissions

In this study, a variation in pH coincided with the variation in NH_3 emission rates except for profile OS_{EP2} (Fig. 3), and a significant exponential correlation between NH_3 flux and pH was found (Fig. 10c). Several published modelling studies (Aneja *et al*. 2000, 2001, Roelle & Aneja 2002) corroborate this positive relationship between NH_3 flux and pH. It is known that NH_3 volatilization from soil solution is affected by the equilibrium between NH_3 and NH_4^+ ions in the aqueous phase. Hence, more NH_3 could be released with the increase in soil pH (OH^- increases) according to the equilibrium reaction (Duplessis & Kroontje 1964, Aneja *et al*. 2001):

$$NH_4^+ + OH^- \Leftrightarrow NH_4OH \Leftrightarrow NH_3 \uparrow + H_2O$$

Changes in pH had the most significant effect on the abiotically induced NH_3 emissions (Dewes 1996). The alkaline nature of occupied ornithogenic Antarctic soils reported by Speir & Cowling (1984), with pH around 8, permits such a loss of NH_3 to the atmosphere (Legrand *et al*. 1998). In this study, ornithogenic soils showed higher NH_3 emissions when pH was

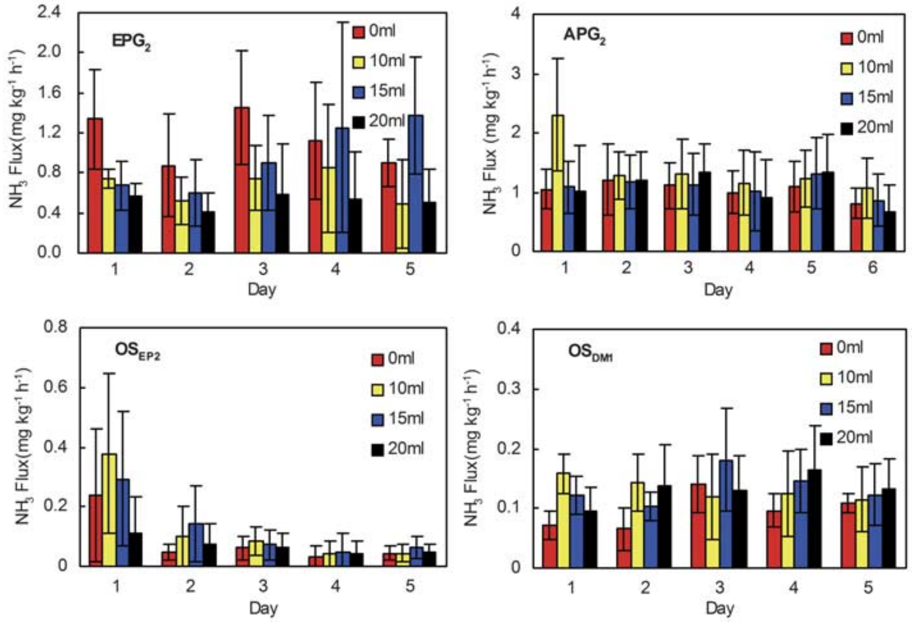

Fig. 12. Effects of water addition on NH_3 fluxes from penguin guano and ornithogenic soils APG_2, EPG_2, OS_{DM1} and OS_{EP2}.

Table III. Comparisons between the NH_3 fluxes from penguin guano and ornithogenic soils under different water treatments.

Water addition	NH_3 flux ($mg\,kg^{-1}\,h^{-1}$)			
	APG_2	EPG_2	OS_{DM1}	OS_{EP2}
0 ml	1.06a	1.15a	0.093a	0.085a
10 ml	1.40b	0.68bc	0.138b	0.130a
15 ml	1.11ab	0.95ab	0.139b	0.124a
20 ml	1.10a	0.53c	0.130ab	0.068a

Note: The different letter indicates statistically significant difference while the same letter indicates no significant difference.

in the range of 7.5 to 9.0 (Fig. 10c). For the first time, our results also give a quantitative relationship between NH_3 fluxes and pH in ornithogenic Antarctic soils.

Effects of temperature on NH_3 emissions

The relationship between NH_3 fluxes and temperature was examined over a wide range (4–30°C). A strong exponential correlation was obtained between NH_3 emission and temperature from ornithogenic soils (Fig. 11). Several previous studies on animal waste have also found temperature to be a major factor in controlling the release of NH_3 into the atmosphere (Dewes 1996, Sommer 1997, Aneja *et al*. 2000, Blunden & Aneja 2008). The temperature dependence of NH_3 emission may be explained by the fact that changes in temperature can directly influence chemical and biological processes (especially the biological breakdown of uric acid) occurring simultaneously in the penguin guano or ornithogenic soils (Legrand *et al*. 1998, Roelle & Aneja 2002). High incubation temperatures stimulated the microbial breakdown of the easily mineralized organic substrates from animal waste, especially at the very beginning of decomposition (Dewes 1996, Aneja *et al*. 2001). Additionally, the liquid phase mass transfer coefficients of NH_3 in water are exponential functions of temperature in the range 5 to 30°C (Ibusuki & Aneja 1984, Dasgupta & Dong 1986). In coastal Antarctica, the microbial decomposition of uric acid in penguin guano or ornithogenic soils might be accelerated due to the enhanced summertime temperature, which can lead to higher NH_3 emissions into the local atmosphere. The results of this study provide a good quantitative relationship between NH_3 flux from ornithogenic Antarctic soils and temperature.

Effects of moisture on NH_3 emissions

In this study, penguin guano APG_2 and ornithogenic materials OS_{EP2} and OS_{DM1} had particularly low water contents (32.9–62.9%) (Table I) and significantly enhanced NH_3 emissions occurred in these samples during the initial two day incubation following water addition (Fig. 12). Previous experiments have showed a large transient NH_3 pulse following water addition to dry soils, presumably driven by an increase in soil NH_4^+ concentrations and stimulation of microbial activity following soil wetting (McCalley & Sparks 2008). However, NH_3 emissions reduced from EPG_2 during the initial three days following water addition, which may be due to particularly high water content (127.8%) (Table I). Similarly, some studies showed that increasing the water content, e.g. precipitation events, may reduce NH_3 volatilization since more ammonia is tightly bound in solution (Whitehead & Raistrick 1991, Blunden & Aneja 2008). This study area has a cold and dry climate, and moisture is one of major limiting factors affecting the uric acid biological breakdown of Antarctic ornithogenic soils in summer due to high bacterial biomass (Speir & Ross 1984). Therefore soil moisture conditions can have an important effect on NH_3 emissions from penguin guano or ornithogenic soils.

Conclusion

In our laboratory experiments Antarctic penguin guano and ornithogenic soils showed potential high NH_3 emissions, suggesting that sea animal colonies are a strong emission source of atmospheric NH_3. Freezing-thawing cycle induced enhanced NH_3 emissions from penguin guano and ornithogenic soils, confirming that FTC is an important factor influencing summer NH_3 emissions from marine animal colonies in coastal Antarctica. In addition, temperature, TN content and pH are significant variables influencing NH_3 flux. Our results provide a quantitative relationship between NH_3 flux and TN, pH and temperature from ornithogenic Antarctic soils.

In coastal Antarctica, the number of marine animal colonies is large. The cycles of freezing and thawing in such sites are high throughout the summer, during which NH_3 emissions may account for a large proportion of N annual flux from animal colonies on land. Field studies are now needed to investigate *in situ* NH_3 emissions and associated environmental factors to validate our conclusions.

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