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Lichen response to ammonia deposition defines the footprint of a penguin rookery

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Abstract Ammonia volatilized from penguin rookeries is a major nitrogen source in Antarctic coastal terrestrial ecosystems. However, the spatial extent of ammonia dispersion from rookeries and its impacts have not been quantified previously. We measured ammonia concentration in air and lichen ecophysiological response variables proximate to an Adèlie penguin rookery at Cape Hallett, northern Victoria Land. Ammonia emitted from the rookery was ^{15}N-enriched (δ^{15}N value +6.9) and concentrations in air ranged from 36–75 μg m^{-3} at the rookery centre to 0.05 μg m^{-3} at a distance of 15.3 km. δ^{15}N values and rates of phosphomonoesterase (PME) activity in the lichens *Usnea sphacelata* and *Umbilicaria decussata* were strongly negatively related to distance from the rookery and PME activity was positively related to thallus N:P mass ratio. In contrast, the lichen *Xanthomendoza borealis*, which is largely restricted to within an area 0.5 km from the rookery perimeter, had high N, P and ^{15}N concentrations but low PME activity suggesting that nutrient scavenging capacity is suppressed in highly eutrophicated sites. An ammonia dispersion model indicates that ammonia concentrations sufficient to significantly elevate PME activity and δ^{15}N values (≥0.1 μg NH_3 m^{-3}) occurred over c. 40–300 km^2 surrounding the rookery suggesting that penguin rookeries potentially can generate large spatial impact zones. In a general linear model NH_3 concentration and lichen species identity were found to account for 72 % of variation in the putative proportion of lichen thallus N originating from penguin derived NH_3. The results provide evidence of large scale impact of N transfer from a marine to an N-limited terrestrial ecosystem.

Keywords Adèlie penguins · ^{15}N natural abundance · Phosphatase activity · *Umbilicaria decussata* · *Usnea sphacelata* · *Xanthomendoza borealis*

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Introduction

Penguin rookeries and other colonies of marine animals are major sources of nitrogen (N) and

phosphorus (P) input to Antarctic coastal ice-free terrain (Tatur 2002; Riddick et al. 2012). These create hotspots of eutrophication where aerosol and volatilized ammonia (NH_3) generated from marine-derived excreta can enrich surrounding areas through atmospheric dispersion and deposition processes in addition to localized surface run-off. Numerous reports describe how lichen and plant communities are modified by the abundance of excreta generated in penguin rookeries (Beyer et al. 2000; Leishman and Wild 2001; Tatur 2002; Smykla et al. 2007). Active nesting areas are usually devoid of plants and lichens due to a combination of heavy physical disturbance by trampling and the toxic effects of fresh faecal material. However, at the perimeters of rookeries distinct communities frequently develop of algae, cyanobacteria, lichens (e.g. members of the *Teloschistales*) and mosses and, in the maritime Antarctic, vascular plants (Smith 1972, 1988; Smykla et al. 2007), that are tolerant of eutrophicated conditions. This visually evident effect of eutrophication is largely restricted to a zone 100–500 m beyond rookery perimeters. However, volatilized NH_3 can be dispersed to much greater distances.

Wodehouse and Parker (1981) demonstrated an NH_3 concentration ($[NH_3]$) gradient in air along a 200 m transect downwind of an Adélie penguin rookery occupied by c. 6×10^3 breeding pairs of birds on Anvers Island on the Antarctic Peninsula. Similarly, several authors document higher $[NH_4^+]$ values in snow and air sampled at sites near to penguin rookeries than in comparable samples from localities remote from rookeries (Greenfield 1992; Legrand et al. 1998; Park et al. 2007; Nędzarek and Rakusa-Suszczewski 2007) and Crittenden (1998), working in the Windmill Islands, recorded an increase in $[NH_4^+]$ in sequential samples of meltwater from freshly fallen snow during a c. 6 day period of snow melt and suggested that this might have been a result of dry deposition during the melt period of NH_3 from rookeries at a distance of $\geq$2 km. Lindeboom (1984) studied N flow through penguin rookeries on subantarctic Marion Island and reported that the odour of NH_3 was apparent at distances of up to 10 km from the source. Moreover, Erskine et al. (1998) consider that much of the N capital on subantarctic Macquarie Island could have originated from NH_3 volatilized from royal penguin rookeries over periods of thousands of years. Dispersion of NH_3 from rookeries can, therefore, potentially have an influence over large areas surrounding the emission source. However, detailed estimates of NH_3 dispersion from a penguin rookery have not been previously published. While there is a dearth of information on N deposition rates in Antarctica, it is probable that at sites remote from animal colonies such rates [and also those of biological N_2-fixation e.g. Wynn-Williams (1990), Whitton and Potts (2000)] are very low. For example, $[NO_3^-]$ and $[NH_4^+]$ values in falling snow (0.3–16.2 μmol l^{-1}, Maupetit and Delmas 1992) or freshly deposited snow (0.5–7.6 μmol l^{-1}, Crittenden 1998; Mulvaney et al. 1998) in the Antarctic are comparable with, or lower than, values in remote Arctic locations (e.g. Talbot et al. 1992; Walker et al. 2003).

Lichens are the major components of Antarctic vegetation both in terms of biomass and diversity (Longton 1988; Øvstedal and Lewis Smith 2001). Inorganic ions and some simple organic compounds such as amino acids are absorbed efficiently over the thallus surface from precipitation, dry deposits and overland flow. Lichens produce surface bound enzymes capable of hydrolysing peptides and organic phosphates thus releasing accessible N and P from organic deposits (Hogan 2009; Hogan et al. 2010a; Higgins and Crittenden unpublished data). Lichens typically occur in habitats in which available forms of N and P are scarce and many species are highly sensitive to N enrichment. In European settings this sensitivity is reflected in, for example, strong positive correlations between N deposition rates and thallus N concentration (Bruteig 1993; Hyvärinen and Crittenden 1998; Hogan et al. 2010a). In the terricolous heathland lichen *Cladonia portentosa*, N enrichment increases thallus N:P mass ratio, rate of phosphomonoesterase (PME) activity (Hogan et al. 2010a, b) and PO_4^{3-} uptake efficiency (Hogan 2009). These shifts in enzyme and uptake capacities have been interpreted as physiological adjustments driving to maintain cellular N:P stoichiometry under conditions of relative N excess. Hence, while heavy eutrophication in the immediate vicinity of penguin rookeries might induce striking changes in the species composition of lichen communities, more subtle changes in lichen physiology might be used to indicate deposition of smaller but physiologically significant quantities of penguin-derived NH_3 at more remote locations.

In addition, ^{15}N natural abundance in penguin-derived NH_3 might be sufficiently elevated to provide an isotopic signal that is useful in mapping NH_3 capture by lichens in the surrounding terrestrial environment. This suggestion is prompted by (i) the elevated ^{15}N natural abundance documented in penguin biomass and excreta compared to atmospheric N_2 (Mizutani and Wada 1988), a condition that arises from the high trophic position of penguins and the process of trophic enrichment of ^{15}N whereby ^{15}N natural abundance in marine animals increases with increasing trophic status (Rau et al. 1992; Kelly 2000; Michener and Kaufman 2007), and (ii) the very high ^{15}N natural abundance in ornithogenic rookery soils (e.g. Mizutani et al. 1985a, 1986) which is generated by discrimination against ^{15}N–NH_3 during volatilization (Högberg 1997; Frank et al. 2004) but which is likely to yield emissions of ^{15}N-enriched NH_3 despite this isotopic fractionation. The use of ^{15}N natural abundance values in plants to trace N sources has frequently proved problematic due to spatial and chemical heterogeneity of soil N pools and the diversity of N capture strategies and N economies in plants (e.g. variation in rooting depth, mycorrhizal type and infection intensity, internal N recycling efficiency) (Handley and Scrimgeour 1997; Högberg 1997; Hobbie and Högberg 2012). By contrast, environmental circumstances relating to N capture in lichens are potentially far less complex: atmospheric deposition is spatially and chemically more homogeneous and N uptake strategies in lichens are probably considerably less variable than in plants. Lichens in remote background locations are often strongly ^{15}N-depleted (Tozer et al. 2005; Huiskes et al. 2006; Fogel et al. 2008) rendering a local positive ^{15}N signal easier to detect. Hence seeking a relationship between lichen chemistry and a point source of NH_3 emissions is likely to be associated with fewer confounding factors than in plant/soil systems.

Here we report the results of an interdisciplinary study in which NH_3 dispersion is quantified in the vicinity of a major Adélie penguin rookery at Cape Hallett in continental Antarctica and lichen physiological responses are used to determine the area of impact of NH_3 deposition on the terrestrial biota. The results are timely given a growing body of evidence that Antarctic cryptogamic and soil microbial communities are frequently N limited (e.g. Wasley et al. 2006).

Materials and methods

Study site

Cape Hallett (72°19′S, 170°16′E) is situated at the southern end of Moubray Bay, northern Victoria Land, in the western Ross Sea at the northern tip of the Hallett Peninsula (Fig. 1a and Online Resource 1). An Adèlie penguin (*Pygoscelis adeliae*) rookery, estimated in 1998/99 to be occupied by 39,000 breeding pairs (Gordon 2003), is located on Seabee Hook, a recurved spit projecting c. 1,200 m west from the high rock ridge forming the Cape. Seabee Hook is c. 41 ha in total area, generally <5 m above sea level and covered by ornithogenic soils. A description of the vegetation at Cape Hallett is provided by Rudolph (1963) and Brabyn et al. (2006). Ridges, bluffs and gravel beaches around the perimeter of Edisto Inlet support scattered, locally large lichen populations including those of *Buellia frigida*, *Umbilicaria decussata*, and *Usnea sphacelata*. These species do not occur within 0.5 km of the penguin rookery; here putative N-tolerant species occur. These include *Xanthomendoza borealis* and species of *Caloplaca*, *Candelariella*, *Physcia* and *Xanthoria*, lichens that are typical of penguin rookeries and other eutrophicated sites elsewhere in Antarctica (Gremmen et al. 1994; Smith 1988; Øvstedal and Lewis Smith 2001). Several species of bryophyte also occur on gravel terraces and slopes within 0.5 km of the rookery.

Ammonia sampling

Atmospheric ammonia concentration was measured at 11 sites in the vicinity of Cape Hallett: at the centre of Seabee Hook, at four locations on its perimeter (N, S, W and E), and at six locations on the perimeter of Edisto Inlet up to a distance of 15.3 km from the rookery (Fig. 1a; Table 1). Mean [NH_3] values were determined at each site using Adapted Low-cost Passive High Absorption (ALPHA) samplers (Tang et al. 2001) mounted on wooden poles at 1.5 m above the ground. Samplers were exposed in triplicate at each site for three periods: 26 December 2005–10 January 2006, 11–17 and 17–23 January 2006 and at three sites [3, 5 and 6 (Table 1)] between 8 December 2004 and 24 January 2005. Measurements

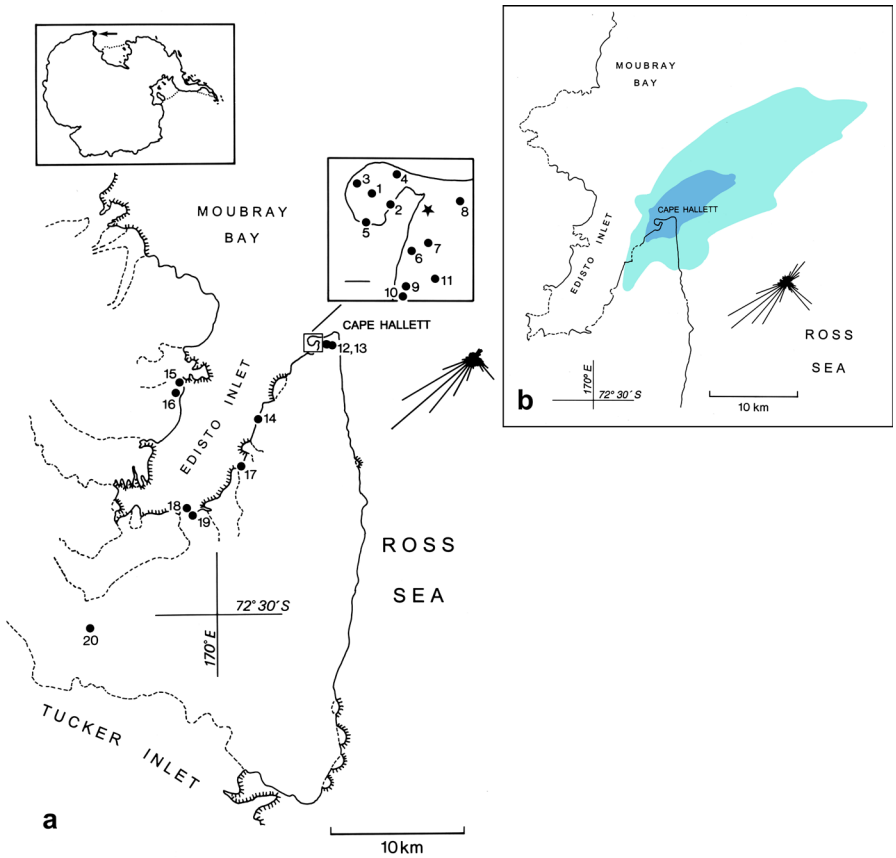

Fig. 1 Geographical detals of study area. **a** Location of sampling sites in the vicinity of Cape Hallett. Site numbering follows that in Table 1 which gives details of sampling undertaken at each location; the wind rose reports the relative frequency of wind directions at 10° intervals during January–May 2006. *Insets* show the location of Cape Hallett on the Antarctic continent and location of sampling sites on and adjacent to Seabee Hook (*scale bar in inset* 250 m); the *asterisk* marks the position of the automatic weather station. *Dashed lines* and *whiskers* indicate location of glaciers. **b** Simulated dispersion of ammonia from the Cape Hallett penguin rookery to concentrations $\geq$0.1 μg m^{-3} using the ADMS model. *Light* and *dark blue* areas indicate dispersion fields based on the high and low emission estimates, respectively (see "Materials and methods" section), and average wind frequencies during the entire measurement period (described by wind rose shown). (Color figure online)

were made at all sites simultaneously. After exposure, the samplers were stored at between 0 and 5 °C until return to the UK for analysis following Tang et al. (2001) to yield mean [NH_3] in air during each sampling period.

Bulk NH_3 collection for isotopic analysis was undertaken at the centre of the rookery by drawing air sequentially through a Teflon pre-filter and a Whatman No 41 filter paper impregnated with citric acid. Air was drawn through the filters using a Capex 1D 12 V DC diaphragm pump (Charles Austin Pumps Ltd, Byfleet, UK) with a capacity of 15 l min^{-1}.

Dispersion modelling

Mean hourly wind speed, wind direction (and standard deviation), air temperature, relative humidity and solar radiation data were recorded by an Automatic Weather Station (Fig. 1a). These data were used to predict mean [NH_3] values resulting from the rookery emissions using three different dispersion models: ADMS (v4.1) (Carruthers et al. 1994; Hill 1998; Dragosits et al. 2002; CERC 2009), LADD (Dragosits et al. 2002) and the Lagrangian stochastic model of Flesch et al. (2004), which is implemented in the WindTrax software (V.2.0.8.3). The rookery was modelled as a

Table 1 Location of sampling sites at Cape Hallett and around Edisto Inlet, the type of sample collected and distance from rookery centre

Site no.[a]	Site name	Co-ordinates	Sample type[b]	Distance from rookery (km)
1	Seabee Hook centre	72°19.15′S, 170°12.84′E	A	0
2	Seabee Hook East	72°19.22′S, 170°13.05′E	A	0.2
3	Seabee Hook West	72°19.11′S, 170°12.47′E	A	0.2
4	Seabee Hook North	72°19.07′S, 170°13.16′E	A	0.3
5	Seabee Hook South	72°19.31′S, 170°12.63′E	A	0.3
6	Hallet 6	72°19.46′S, 170°13.42′E	A, **Xb**	0.7
7	Hallett A	72°19.39′S, 170°13.58′E	Xb	0.7
8	Hallet B	72°19.19′S, 170°14.22′E	**Xb**	0.8
9	Hallett D	72°19.64′S, 170°13.30′E	Xb	0.9
10	Hallet 7	72°19.69′S, 170°13.23′E	A	1
11	Hallett F	72°19.60′S, 170°13.78′E	Us, Ud	1
12	Hallett E1	72°19.28′S, 170°14.85′E	Us, Ud	2
13	Hallett E2	72°19.34′S, 170°15.60′E	**Us**,**Ud**	2.4
14	Salmon Cliff	72°22.39′S, 170°05.33′E	A	7
15	Luther North	72°20.75′S, 169°55.37′E	A, **Us**, **Ud**	10.1
16	Luther	72°21.19′S, 169°54.90′E	Us	10.7
17	Roberts Cliff	72°23.96′S, 170°03.32′E	A	11
18	Redcastle beach	72°25.85′S, 169°56.52′E	A, **Us**	15.3
19	Redcastle Ridge	72°26.00′S, 169°57.00′E	Us	15.8
20	Football Saddle	72°30.56′S, 169°47.47′E	Us, Ud	26.8

[a] See Fig. 1a

[b] *A* ammonia sampling; *Us, Ud* and *Xb* collection of *U. sphacelata, U. decussata* and *X. borealis*, respectively; collections in bold are those used for PME assays

ground–level area source and an arbitrary emission rate was assigned (10 tonnes NH_3 ha^{-1} $year^{-1}$). The simulation assumed a flat terrain; while this is unrealistic for dispersion across land where gradients of up to 75 % are present, it is a realistic assumption for short-range dispersion across the rookery and the sea. The complex terrain option of ADMS 4 was also tested in an attempt to better simulate the dispersion over elevated terrain. However, when using this option, the model makes some assumptions regarding atmospheric turbulence (such as setting limits on the atmospheric stability) that are not appropriate for the flatter regions of the domain, where most of the atmospheric measurements were located. For this reason, it was decided not to use the complex terrain option for the final simulations. Full details of the model parameterisations are given by Theobald et al. (2013). The predicted concentrations at the seven measuring stations closest to the centre of the colony were fitted to the measured values by applying a factor to reduce the geometric variance between predicted and measured concentrations (Chang and Hanna 2004). Since the concentration predictions are proportional to the emission rate used in the model, this factor can be used to estimate the emissions during each period. The factors obtained for the three dispersion models for the 2 measurement periods with the most reliable meteorological data (11–17 and 17–23 January 2006) ranged from 0.03 to 0.08, giving emission estimates between 0.3 and 0.8 tonnes NH_3 ha^{-1} $year^{-1}$ (Theobald et al. 2013). For a rookery occupation of 39,000 breeding pairs distributed over an area of 33.2 ha, these emission estimates are equivalent to an emission of between 0.8 and 1.8 g NH_3–N per breeding pair per day.

Collection of ecological materials

Lichens were collected from 12 locations around the perimeter of Edisto Inlet up to a distance of 26.8 km from the rookery (Table 1; Fig. 1a): *U. sphacelata* from 8 locations, *U. decussata* from 5 locations and *X. borealis* from 4 locations. Lichens were cut from rocks with a scalpel. The terminal 10–20 mm of thallus branches of *U. sphacelata* were selected for analysis whereas in the cases of *U. decussata* and *X. borealis* whole thalli were analyzed. After collection, lichens were stored air-dry in polyethylene vials at ambient temperature while in the field and at 5 °C on return to

the UK. Samples of the surface 5 mm of rookery soil were collected from guano-rich areas between nests. At each location, replicate samples of lichen or soil were taken from spots ≥10 m apart. Samples of Adélie penguin chick leg muscle were dissected from fresh kills by south polar skuas and freeze dried. Powder free latex gloves were worn at all times when handling these materials both in the field and in the laboratory to minimize contamination.

Determination of ^{15}N natural abundance and total N and P concentrations

Lichen samples for total P analysis were oven-dried at 80 °C, weighed, digested using the sulphuric acid-hydrogen peroxide procedure (Allen 1989) and then phosphate assayed colorimetrically by the malachite green variant of the methylene blue method (van Veldhoven and Mannaerts 1987). Lichen samples and other materials (penguin muscle, soil and membrane filters) for isotopic analysis were oven-dried at 40 °C, reduced to powder in a ball mill, re-dried at 40 °C and weighed into ultra-clean tin capsules (Elemental Microanalysis Ltd., Oakhampton, UK) using a Cahn C-31 microbalance (Scientific and Medical Products Ltd., Cheadle, UK). ^{15}N natural abundance was determined by continuous-flow elemental analyser-isotope ratio mass spectrometry (ANCA-SL coupled to 20-20 IRMS, Europa Scientific, Crewe, UK). The analytical protocol was adapted from that normally used for plant material (c. 2 % N) to cope with the much lower N content of some of the lichen materials analyzed (c. 0.4 % N). Samples of 20 mg were used and to ensure complete combustion the oxygen pulse was increased by 50 %. Batches of no more than 50 samples were analysed and the CO_2 trap changed after each batch. The combustion ash was also removed more frequently than normal. Working standards containing 100 µg N, freeze dried from a leucine-citric acid mixture (~2 %N), were calibrated for $\delta^{15}N$ against IAEA-N1 and IAEA-N2 (IAEA, Vienna). Precision for the working standards during a run was monitored and was routinely 0.3–0.4 ‰. Pairs of working standards were run with every ten samples. The in-line elemental analyzer also produced measurements of total N in the samples analyzed. Values of the ratio $^{15}N/^{14}N$ (R) are expressed in δ notation in per mil. units (‰) according to the following equation: $\delta^{15}N = [(R_{sample}/R_{standard}) - 1] \times 1{,}000$, where $R_{standard}$ is that of the atmosphere. The proportion of lichen thallus N that originated from penguin-derived NH_3 (F_{NH_3}) was estimated using a two source mixing model (e.g. Fry 2006): $F_{NH_3} = (\delta_{L1} - \delta_{L2})/(\delta_{NH_3} - \delta_{L2})$ where δ_{L1}, δ_{L2} and δ_{NH_3} are, respectively, the $\delta^{15}N$ values in lichen exposed to penguin-derived NH_3, lichen from a background site remote from penguin influence, and penguin derived volatilized NH_3.

Phosphomonoesterase assay

Phosphomonoesterase (PME) activity was assayed in the field using the *p*-nitrophenyl phosphate (*p*NPP) colorimetric method [Bessey et al. (1946) as modified by Hogan et al. (2010a)]. Air dry lichen samples (5–35 mg depending on species) were added to 2.9 ml assay medium comprising citric acid-trisodium citrate buffer made up in melted snow and the assays initiated by the addition of 0.1 ml analogous substrate solution. Samples were then placed in a water-bath at c. 5 °C (measured range 4.8–5.7 °C) for 30 min in the dark after which the reaction was terminated by transferring 2.5 ml assay medium into 0.25 ml terminator solution (1.1 M NaOH, 27.5 mM EDTA, 0.55 M K_2HPO_4) and the absorbance measured at 405 nm using a NanoDrop ND-1000 spectrophotometer (Thermo Scientific, USA). Post assay, thalli were blotted dry, oven dried for 24 h at 80 °C and weighed. Enzyme activity was expressed as µmol substrate hydrolysed g^{-1} dry mass h^{-1} using *p*-nitrophenol to calibrate the assay. No-lichen and no-substrate controls were included. Among the different experiments performed the pH of the bathing solution was varied between 2.5 and 6.9 and the substrate concentration between 0.25 and 8.0 mM.

Adding air dry lichen samples directly to the assay medium will produce a small over-estimation of activity due to water entering the non-free space (symplast) of the thallus. Using Beckett's (1995) estimates of the free-space volume in lichens from xeric habitats (a mean of 32 % of thallus volume), we predict that this over-estimation was probably in the range of 0.2–1.0, 0.2–1.8 and 0.4–1.2 % in *U. sphacelata*, *U. decussata* and *X. borealis*, respectively, being dependent on the mass of lichen sample being assayed. It is widely assumed that the *p*NPP assay detects cell wall-bound PME activity because the hydrolysis product, *p*-nitrophenol, accumulates in the assay medium at a rate that is constant and pH dependent (Bartlett and Lewis 1973).

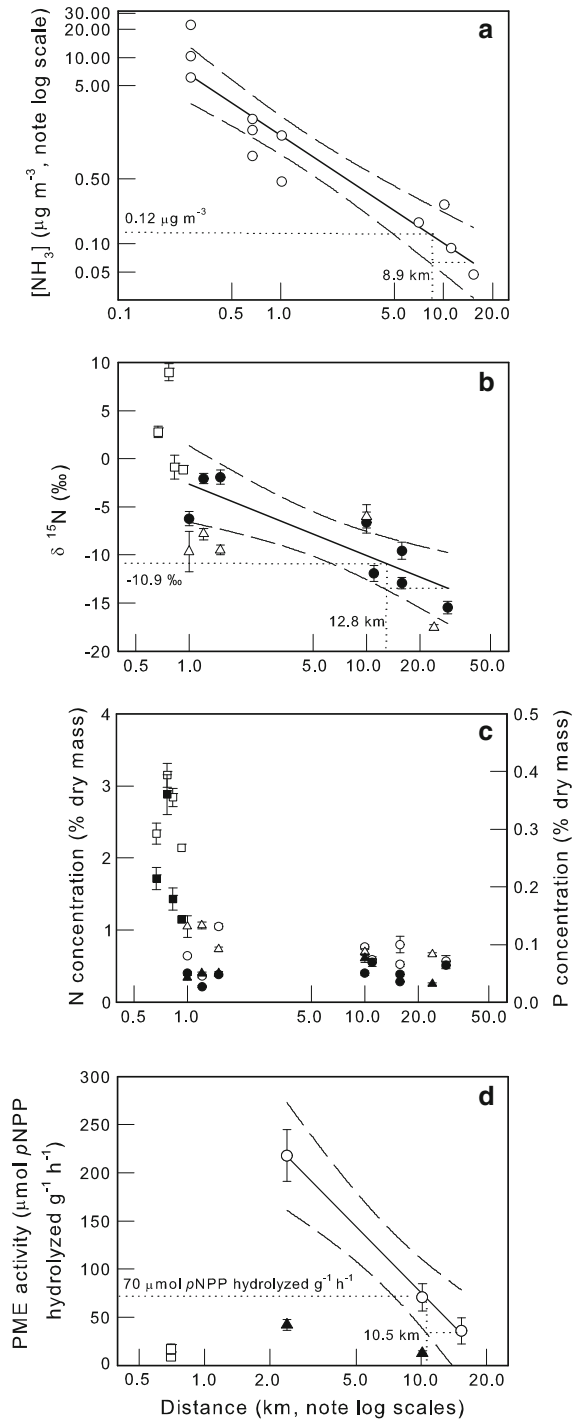

Fig. 2 Relationships between distance from the rookery centre ▶ and **a** NH_3 concentration in air, **b** lichen δ ^{15}N values, **c** total thallus N (*open symbols*) and P (*closed symbols*) concentrations, and **d** lichen PME activity. Lichen species: *U. sphacelata* (*black circle*, *white circle*), *U. decussata* (*white up-pointing triangle*, *black up-pointing triangle*) and *X. borealis* (*black square, white square*). Points are mean values ± 1 SE: **a** $n = 3$; **b**–**d** $n = 1$–19 (note that in **a** SE bars do not exceed the diameter of the points). Where appropriate, regression lines are shown (*solid line*) together with 95 % confidence intervals (*dashed line*): **a**, $r^2 = 0.87$, $P = < 0.001$; **b** *U. sphacelata*, $r^2 = 0.76$, $P = 0.005$ [note that the regression of δ ^{15}N values for all species combined on $\log_{10}$ distance is also significant ($r^2 = 0.57$, $P = < 0.001$)]; **c**, no regression line shown but the log–log relationships for all species combined is significant (N, $r^2 = 0.60$, $P < 0.001$; P, $r^2 = 0.49$, $P = 0.002$); **d**, *U. sphacelata*, $r^2 = 0.996$, $P = 0.042$. 95 % confidence intervals are used to estimate the lowest elevated value of the dependant variable (*dotted lines*) compared to the best estimate of background value, and the distance at which this is predicted to occur

Data analysis

Data for atmospheric variables, lichen chemistry, PME activity and distance from the rookery were subjected to either correlation analysis, linear regression or one-way ANOVA conducted in Sigma Plot 11 (Systat Software Inc.). All data were checked for normality and homogeneity of variances and where test assumptions were not met, either log-transformation or non-parametric correlation analysis were applied.

[NH_3] predicted by the NH_3 dispersion model was tested as a quantitative predictor of F_{NH_3} in a general linear model [GLM in *R* (R Core Team 2014)] using sequential deletion. The residuals were normally distributed (Shapiro–Wilk $W = 0.95$, $P = 0.44$) and so significance was assessed using *F* tests.

Results[1]

Ammonia concentrations and δ^{15}N values

Mean [NH_3] values of up to 75 µg m^{-3} were recorded at the rookery centre while values in the range 6–81 µg m^{-3} were recorded on its perimeter (sites 2–5) where they were weakly but significantly ($P \leq 0.05$) correlated with wind direction (data not shown). Concentrations declined exponentially with distance from the rookery; the lowest concentration recorded was 0.05 µg m^{-3} at 15.3 km and the lowest mean concentration that is significantly greater than this value is 0.12 µg m^{-3} estimated to have occurred

[1] Raw data have been deposited with the Polar Data Centre, British Antarctic Survey, Cambridge, UK. doi: http://doi.org/v27.

at 8.9 km (Fig. 2a). Note that the maximum mean $[NH_3]$ values recorded were insufficient to saturate the passive samplers during a 2 week exposure period (Tang et al. 2004); $[NH_3]$ values >200 μg m^{-3} would be necessary for saturation to be approached (Tang, personal communication). Ammonia captured on filter paper had a mean $\delta^{15}N$ value of +6.94 ± 2.26 ‰ (mean ± SE, $n = 4$). This can be compared with mean values for guano deposits and penguin chick muscle of +20.32 ± 1.33 ($n = 10$) and +8.29 ± 0.08 ‰ ($n = 10$), respectively.

Lichen and soil chemistry

^{15}N natural abundance in lichens was significantly positively related to proximity to the rookery (Fig. 2b). At Football Saddle, 27 km southwest of Seabee Hook, the mean $\delta^{15}N$ values for *U. sphacelata* and *U. decussata* were −15.5 ± 0.7 ($n = 4$) and −17.5 ± 0.3 ‰ ($n = 19$), respectively, increasing to −2.1 ± 0.5 ($n = 9$) and −7.8 ± 0.6 ($n = 11$), respectively, within 1-2 km of the rookery centre. By contrast, $\delta^{15}N$ values for *X. borealis* ranged between −0.9 ± 1.2 ($n = 10$) to +9.0 ± 0.9 ‰ ($n = 9$). Thallus $\delta^{15}N$ signature was strongly related to $[NH_3]$ when data for lichens from the three sites at which both $[NH_3]$ in air and $\delta^{15}N$ in lichens were measured were combined ($r^2 = 0.93$, $n = 4$, $P = 0.008$). Assuming that $\delta^{15}N$ values for *U. sphacelata* and *U. decussata* at 27 km represent the background values for populations uninfluenced by bird-derived NH_3 or excreta and that the effects of other processes that might modify $\delta^{15}N$ signatures are assumed to be negligible (see discussion below), then the two-source mixing model suggests that up to 60 % of thallus N in *U. sphacelata*, and up to 40 % in *U. decussata* could have been derived from NH_3 at sites closer to the rookery. Applying a mean background value of −16.5 ‰ to *X. borealis* suggests that 66–100 % of thallus N could have originated from penguin-derived NH_3. Note that the mixing model assumes that the quantity of thallus N originating from penguin-derived NH_3 is 0 and 100 % when $\delta^{15}N$ values in, e.g. *U. sphacelata*, are −15.5 and +6.9 ‰, respectively. In the general linear model to test the relationship between F_{NH_3} and $[NH_3]$, both modelled $[NH_3]$ (see below) and species identity were significant predictors (Table 2, Fig. 3). Nearly all the differences among species obviously arose because the mean for *Xanthomendoza borealis* was higher than the other two taxa. Modelled $[NH_3]$ and lichen species identity accounted for 72 % of variation in the F_{NH_3} values.

Thallus N and P concentrations were also significantly related to proximity to the rookery when data for the three lichen species were combined (Fig. 2c).

Table 2 General linear model statistics for predictor variables in the model relating F_{NH_3} in *U. sphacelata*, *U. decussata* and *X. borealis* to $[NH_3]$ (as predicted by the dispersion model) and lichen species identity

Independent variables	β ± SE	*F*	(d.f.)	*P*
$[NH_3]$	0.101 ± 0.030	6.91	(1,12)	0.02
Lichen species		4.36	(2,12)	0.04
Mean for *X. borealis*	0.579 ± 0.145			
Differences from the *X. borealis* mean				
U. sphacelata	− 0.341 ± 0.139			
U. decussata	− 0.405 ± 0.139			

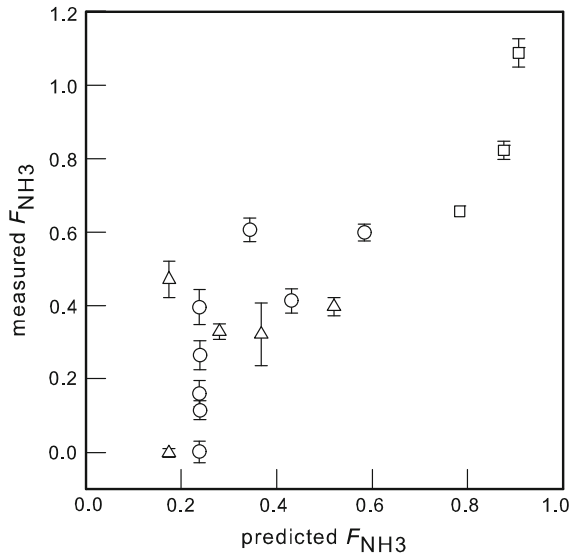

Fig. 3 Relationship between measured F_{NH_3} in the three lichen species studied and values modelled from $[NH_3]$ as a quantitative predictor and species identity as a categorical predictor (Table 2). Plotted *y* values are means ± 1 SE ($n = 1$–19). Lichen species: *U. sphacelata* (*white circle*), *U. decussata* (*white up-pointing triangle*) and *X. borealis* (*white square*) ($R^2 = 0.72$). Data are for 11–17 January 2006. Note that data from Site 8 for *X.* borealis were significant outliers and were omitted from the analysis

Table 3 Bivariate Pearson correlation coefficients (r) between $\delta^{15}N$ values, concentrations of thallus N and P ([N], [P]) and N:P mass ratio in *U. sphacelata* (Us), *U. decussata* (Ud) and *X. borealis* (Xb)

	Thallus [P]	Thallus [N]	N:P	*n*
$\delta^{15}N$ Us	0.421**,†	0.330*,†	−0.064†	55–58
$\delta^{15}N$ Xb	0.895***	0.527**	−0.860***	30
$\delta^{15}N$ Ud	0.776***,†	0.326*,†	−0.329*,†	44–52
[P] Us	–	0.400**	–	55
[P] Xb	–	0.752***	–	30
[P] Ud	–	0.245	–	44

* Correlation significant at the 0.05 level; ** correlation significant at the 0.01 level; *** correlation significant at the 0.001 level

† Spearman's correlation coefficient (non-parametric equivalent of the Pearson's correlation)

However, this relationship is strongly influenced by high concentrations in *X. borealis* (N concentration c. 3–7 times higher, and P concentration c. 5 times, than values in *U. sphacelata* and *U. decussata*) and there were no clear relationships between thallus N and P concentrations and distance from the rookery in any of the three species examined separately. In all species there was marked positive correlation between $\delta^{15}N$ values and P and N concentrations (Table 3; Fig. 4a), and a trend for negative correlation between $\delta^{15}N$ values and N:P mass ratio (Table 3).

The guano rich surface soil sample had a ^{15}N enrichment of +20.3 ± 1.3 ‰, and a total N concentration of 3.4 ± 0.5 %.

Phosphomonoesterase activity

Phosphomonoesterase activity was readily detected in each of the three lichen species assayed. There was a significant effect of assay pH on activity in *X. borealis* with an apparent optimum at pH 6.6 but not in either *U. sphacelata* or *U. decussata* although there was a trend for higher rates at lower pH values (Online Resource 2). Accordingly, subsequent assays were performed at pH 6.6, 2.5 and 3.0 for *X. borealis*, *U. sphacelata* and *U. decussata*, respectively. PME activity was highest in *U. sphacelata* and responded strongly to substrate concentration up to 8 mM; material collected at 10 km from the rookery had K_m and V_{max} values, calculated from a Hanes-Woolf plot, of 2.03 mM and 110 µmol substrate hydrolyzed g^{-1} dry mass h^{-1}. A saturating substrate concentration of 8 mM *p*NPP was used in subsequent assays.

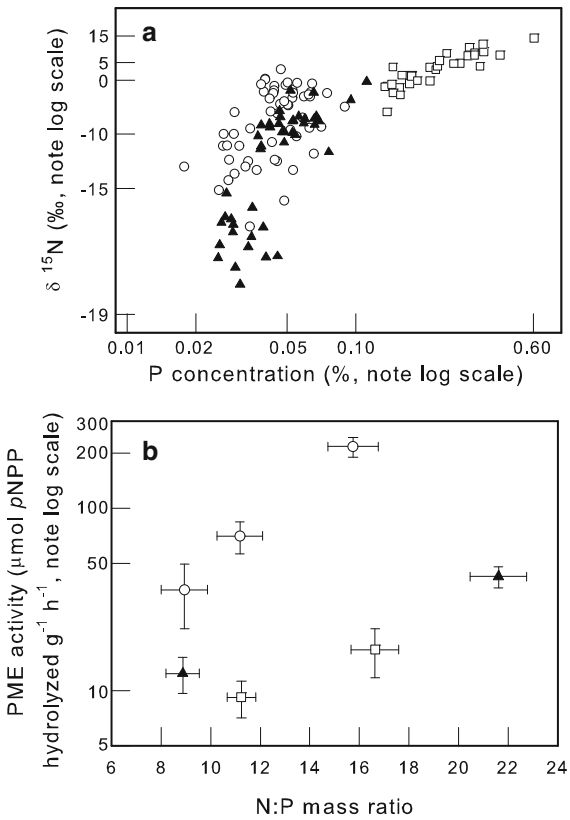

Fig. 4 Relationships in *U. sphacelata* (*white circle*), *U. decussata* (*black up-pointing triangle*) and *X. borealis* (*white square*) between **a** $\delta^{15}N$ value and total P concentration (see Table 3 for statistics), and **b** PME activity and thallus N:P mass ratio [mean values plotted ± 1SE (n = 10–11); note that the probability of obtaining a progressive increase in PME activity with increasing N:P ratio in all cases by chance is 1 in 24]

In *U. sphacelata* there was a strong positive relationship between proximity to the penguin rookery and PME activity (Fig. 2d); enzyme activity at 2 km from the NH_3 source was 5 times higher than that in samples at 15 km. Similarly, activity in *U. decussata* at 2.4 km was 3.4 times higher than that in samples from 10 km. By contrast, activity was low in *X. borealis* at both sites which were <1 km from the rookery centre. PME activity was also positively related to thallus N:P mass ratio (Fig. 4b).

Ammonia dispersion model

The dispersion model was used to predict the area surrounding the emission source in which $[NH_3]$

values were ≥0.1 μg m^{-3} (Fig. 1b). This concentration approximated to that associated with the estimated minimum significant elevation of $\delta^{15}N$ and PME activity in *U. sphacelata*, changes which are used here as evidence of impact. This impacted area was 35 and 270 km^2 for the low and high emission estimates, respectively (see "Dispersion modelling" section above), during the entire measurement period, providing estimates of the dimension of the rookery's potential impact zone. The simulations used the lower range of the dry deposition velocity from Theobald et al. (2013) since this gave the best spatial correlation between the modelled and measured [NH_3]. This suggests that the dry deposition rate to sea ice is lower than might be expected. At Cape Hallett, the influence of NH_3 dispersion on the terrestrial environment is substantially reduced because, due to the prominent south-westerly winds, much of the NH_3 plume falls over the sea (ca 90 % based on the frequency of winds from the 40°–350° sector during the [NH_3] measurement period). It should be noted that although the dispersion models are more uncertain when applied to such locations with complex topography, the model simulations should still provide an estimate of the order of magnitude of the impacted area.

Discussion

Numerous reports have described the impacts of penguin rookeries on Antarctic vegetation (e.g. Beyer and Bölter 2002; Smykla et al. 2007). However, this is the first study to determine the spatial extent of NH_3 dispersion from a rookery and its effects on terrestrial biota. At Cape Hallett, lichen species such as *X. borealis* and *Xanthoria elegans*, and the moss *Bryum subrotundifolium* occur within the immediate vicinity of the rookery but are infrequent or absent beyond 1 km from the rookery perimeter. These apparently nitrophilous species demarcate a zone of intense eutrophication. However, the present study shows that the influence of the rookery extends far beyond this zone of marked community change. Our data suggest that NH_3 deposition has modifying effects on lichen chemistry and physiology to a distance up to 10 km inland (upwind according to the predominant wind direction, south south-westwards). Measurements of ^{15}N natural abundance indicate that a major proportion of thallus N could originate from penguin-derived NH_3, the proportion potentially remaining as high as 20 % in *U. sphacelata* at c. 13 km, and F_{NH_3} estimates were strongly related to modelled [NH_3] (Table 2 and Fig. 3). Similarly, PME activity in *U. sphacelata* was significantly elevated to a distance of c. 10 km inland (Fig. 2d). These measurable changes in $\delta^{15}N$ and PME activity were detectable down to an [NH_3] value of c. 0.1 μg m^{-3} and, hence, we selected this concentration to define the boundary of the modelled NH_3 dispersion envelope (Fig. 1b). This model implies that [NH_3] values ≥0.1 μg NH_3 m^{-3} occur over an area of up to 300 km^2 surrounding the emission source. A level of 0.1 μg NH_3 m^{-3} might seem low. For example, the proposed Critical Level of NH_3 for lichen and bryophyte rich vegetation in Europe is 1 μg m^{-3} (Cape et al. 2009). However, the high average wind speeds (e.g. Bargagli 2005) and attendant turbulence over rough terrain in Antarctica will result in comparatively high NH_3 deposition rates to terrestrial surfaces even at low atmospheric concentrations while reference conditions in Antarctica represent an extremely oligotrophic situation allowing comparison to lower [NH_3] levels. The value of 0.1 μg NH_3 m^{-3}, which we consider to be ecologically significant at Cape Hallett, can be compared with 0.005–0.03 μg NH_3 m^{-3} recorded at Antarctic sites remote from animal colonies (Gras 1983) and a mean value of 0.06 NH_3 m^{-3} recorded over the Southern Ocean (Ayers and Gras 1980). It should be noted that ammonia emissions from Adèlie penguin rookeries are likely to be strongly seasonal since they are mostly occupied in the summer months [mid-October to mid-February (Gordon 2003)] and NH_3 volatilization rates in frozen soil are extremely low (Zhu et al. 2011). On the other hand, there is little inter-seasonal or inter-annual variation in the frequencies of wind directions over Cape Hallett (Gordon 2003) so that there is likely to be little temporal change in the NH_3 dispersion pattern. The average tropospheric lifetime for NH_3 is c. 0.9 days but in the pure air of Antarctica with low concentrations of potentially reactant gases (e.g. sulphur dioxide) and aerosols (Adams et al. 1999) the lifetime could be longer.

The $\delta^{15}N$ values presented here for penguin tissues, guano-rich soil, atmospheric NH_3 and lichens compare favourably with those documented in the literature for broadly comparable samples (Table 4). There is a dearth of published data on ^{15}N natural abundance

in atmospheric NH_3. The three positive $\delta^{15}N$ values reported in Table 4 (+2.4 to +6.9 ‰) were for air samples drawn through either H_2SO_4 or acid impregnated filters, whereas the negative $\delta^{15}N$ value (−10.0 ‰) recorded by Erskine et al. (1998) was for NH_3 collected passively relying on diffusion into inverted jars which could have greatly underestimated [^{15}N–NH_3] due to isotopic fractionation during diffusive transfer (Högberg 1997; Tozer et al. 2005). The positive $\delta^{15}N$ values for NH_3 at Cape Hallett likely reflect very high ^{15}N enrichment in the guano/soil matrix resulting from the cumulative effects of discrimination against the heavier isotope during NH_3 volatilization over periods of years and perhaps decades, $\delta^{15}N$ values in the range +33 to +50 having been reported for NH_4^+, NH_3 and NO_3^- in bulk samples of Adelie rookery soils (Mizutani et al. 1985a, 1986; Mizutani and Wada 1988; Zhu et al. 2009). Emission of ^{15}N-depleted N_2O resulting from denitrification, although at rates that are probably at least 2 orders of magnitude lower than those for NH_3 release, will contribute to this process further (Zhu et al. 2008a, b). Isotopic fractionation for NH_3 volatilization is 30–40 ‰ (Mizutani et al. 1985b; Högberg 1997; Frank et al. 2004). Applying this degree of fractionation to soil N with the above levels of ^{15}N enrichment, assuming that these are representative of NH_3 in the soil solution at the soil/air interface, yields $\delta^{15}N$ values for volatilized NH_3 of −7 to +20 encompassing our four measurements in the range +1.2 to +10.9. An alternative approach to understanding this question is as follows. If all N in a unit of excreta were volatilized as NH_3 (plus some N_2O) then the volume weighted average $\delta^{15}N$ value of the emissions would be the same as that of the faeces (in this case c. +8 ‰), fractionation merely creating transient changes in $\delta^{15}N$ values. Since the rookery is >1,000 years old (Gordon Gordon 2003) and has therefore received a long series of annual inputs of excreta ranging from fresh faeces in the current year to those sufficiently old

Table 4 ^{15}N natural abundance values reported in the present work and documented in the literature for Adélie penguin tissues, Adélie guano and rookery soils, volatilized ammonia gas and lichens

Cape Hallett (present work)	Data from other locations
Adélie chick leg muscle +8.3 ‰	+10.3 ± 1.5 ‰ (n = 13), a range of organs (Mizutani and Wada 1988)
	+8.7 (single measurement), leg muscle (Mizutani et al. 1986)
	+12.5 ± 1.6 ‰ (n = 6), breast muscle (Dunton 2001)
	+10.2 ± 0.8 ‰ (n = 8), chick blood (Cherel 2008)
	ca +10.0 ± 1.0 ($n \geq 8$), chick blood (Cherel and Hobson 2007)
	+8.8 to +10.3 ‰ (n = 3–7), chick toenails (Ainley et al. 2003)
	+10.6 ± 0.3 ‰/+ 11.0 ± 0.4 ‰ (n = 20), down/feathers (Vasil et al. 2011)
Adélie guano-rich soil +20.3 (0–5 mm depth)	+13.4 ± 4.2 ‰ (n = 6), guano (Mizutani and Wada 1988)
	+21.9 to +24.5 ‰ (n = 2), guano (0–20 cm depth) (Zhu et al. 2009)
	+31.8 ± 4.2 ‰ (n = 8), rookery soil (0–5 cm depth) (Mizutani and Wada 1988)
	+32.2 ± 3.5 ‰ (n = 6), rookery soil (0–5 cm depth) (Mizutani et al. 1986)
	+28.6 ‰, organic N from rookery soils (Wada et al. 1981)
	+8.0 ± 1.2 ‰ (n = 6), fresh excreta (Lorenzini et al. 2010)
	+8.0 ± 0.4 ‰ (n = 4), fresh excreta (Mizutani and Wada 1988)
Ammonia gas +6.9 ‰	+4.7 ‰ (n = 2), bat cave, Mexico (McFarlane et al. 1995)
	+2.4 ± 0.8 ‰ (n = 6), cape fur seal colony, Namibia (Crittenden et al. unpublished data)
	−10.0 ± 3.1 ‰ (n = 20) royal penguin rookery, Macquarie Island (Erskine et al. 1998)
U. sphacelata −15.5 to −2.0 ‰	−17.8 to +10.4 ‰ *U. decussata* and *Usnea antarctica* (Cocks et al. 1998)
U. decussata −17.5 to −10.0 ‰	−18.2 to +7.5 ‰ *U. decussata* and *Usnea antarctica* (Huiskes et al. 2006)
	−15.3 to −7.8 ‰ *Usnea antarctica* (Lee et al. 2009)
X. borealis −0.9 to + 9.0 ‰	+20.6 ± 0.7 (n = 6), *Caloplaca eudoxa*, Cape fur seal colony, Namibia (Crittenden et al. unpublished data)

for the N capital to be close to exhausted, it is probable that the volatized NH_3 now has a $\delta^{15}N$ signal close to the average value. The low $\delta^{15}N$ values for lichens at remote sites imply that atmospheric supplies of non-biogenic N taken up by lichens are generally highly ^{15}N depleted. This view is consistent with the low $\delta^{15}N$ values for NO_3^- in Antarctic Dry Valley soils [−9 to −26 ‰, Wada et al. (1981)], which Michalski et al. (2005) consider result from ^{15}N-depleted NO_3^- in precipitation, for NO_3^- in Antarctic atmospheric aerosol [−50 to +5, (Wagenbach et al. 1998)] and for NO_3^- in fresh snow on Svalbard [−18 ‰, Heaton et al. (2004)]. The particularly high ^{15}N enrichment in *X. borealis* ($\delta^{15}N = -0.9$ to +9.0 ‰) reflects its preference for eutrophicated habitats close to the rookery perimeter; note that a mean value >+6.9 for *X. borealis* at Site 7 suggests that at such sites deposition of particulate matter, perhaps as aerosol generated by penguin physical activity in a windy environment, is influencing lichen ^{15}N signatures in addition to NH_3. $\delta^{15}N$ values for *X. borealis* can be compared with those for *Caloplaca eudoxa* ($\delta^{15}N = +3.6$ to +20.6) growing on the Namib Desert coast in immediate proximity to a major seal colony (Crittenden et al. unpublished data). Accordingly, our $\delta^{15}N$ measurements at Cape Hallett, together with corroborative data from the literature, are consistent with an N transfer pathway penguins → soil → atmosphere → lichens.

A key assumption in the calculation of F_{NH_3} is that $\delta^{15}N$ values in lichen thalli mirror closely those in atmospheric N sources accessed by the thallus. However, several processes could modify this relationship. First, isotopic fractionation during diffusion of NH_3 through air to the surfaces of both lichens and snow cover will result in discrimination against ^{15}N entering the pool of NH_3/NH_4^+ available for uptake at the thallus surface (Tozer et al. 2005). However, the turbulent nature of air flow in Antarctica will reduce diffusion path lengths over these surfaces and tend to minimise this effect. Second, fractionation in favour of ^{14}N can occur during uptake in both fungi and plants (Högberg 1997, Hobbie and Högberg 2012). This effect is probably insignificant under N-limited conditions; given the high efficiency of inorganic N capture by lichens (Crittenden 1998), it is probable that most NH_3/NH_4^+ molecules in the thallus free space will be taken up. However, it could become significant at eutrophicated sites if N is available in excess of uptake. Third, in mat-forming lichens that produce copious dead basal thallus or "litter" (e.g. species of *Cladonia* subgenus *Cladina*) there are strong gradients in $\delta^{15}N$ values from the growing apices downwards towards the thallus bases; it is thought that these gradients are related to thallus development, age and internal N recycling (Ellis et al. 2003, 2005). The little available evidence suggests that such gradients are less marked in lichens with other growth forms (Ellis et al. 2003). Fourth, lichens lose traces of N in reproductive propagules and organic solutes leached during precipitation (Crittenden 1983, 1998), and further losses could occur due to "pruning" resulting from wind damage, but how these losses influence thallus $\delta^{15}N$ values is unknown. The first two processes will lead to underestimations of F_{NH_3}, the third would contribute to intra and inter species variation in F_{NH_3}, but it is unlikely that any would invalidate the relationship between lichen $\delta^{15}N$ values and distance from the rookery and that between F_{NH_3} and modelled $[NH_3]$.

The inferred positive correlation between $[NH_3]$ and PME activity in *U. sphacelata* and *U. decussata* (comparing Fig. 2a, d) is corroborated by data for *C. portentosa* in mainland Britain (Hogan et al. 2010a). PME capacity in this heathland lichen was higher at the most N-polluted heathlands (annual wet inorganic N deposition of 33 kg ha^{-1}) by a factor of 2.3 compared with rates at background sites (4.1 kg N ha^{-1} $year^{-1}$). In reciprocal transplants, activity increased or decreased to that of native lichen in the new environment within 6–12 months Hogan (2009) and, furthermore, the relationship between N deposition and PME activity was reproduced in a field manipulation experiment involving N- and P-enrichment treatments, thus demonstrating causality Hogan et al. (2010b). These findings for *C. portentosa* provide strong evidence to suggest that higher PME activity in *U. sphacelata* and *U. decussata* near to the penguin rookery is caused by greater N availability. Up-regulation of PME activity in response to N enrichment has been observed in a wide range of plant-soil systems [see Hogan et al. (2010a) for a discussion], a frequent explanation for which is that fertilization with N releases plants and microorganisms from N-limitation but in turn induces P-limitation. In *C. portentosa*, this link between PME capacity and the

relative availability of N and P was also evident in striking positive relationships between PME capacity and thallus N:P mass ratio. Evidence for such a relationship between N:P mass ratio and PME capacity was also found in lichens at Cape Hallett (Fig. 4b).

Given the trend in *U. sphacelata* and *U. decussata* for increasing PME activity with greater proximity to the rookery, why was activity in *X. borealis* so low (Figs. 2d, 3b)? *X. borealis* is an ornithocoprophilous lichen growing near the rookery perimeter and exposed to aerosol and NH_3 deposition rates that are probably toxic to *U. sphacelata* and *U. decussata*. Its total thallus N and P concentrations are up to 5 times higher than those in *U. sphacelata* and *U. decussata*, up to 100 % of its N capital could have been penguin-derived and it is probably N and P saturated. We suggest that moderated nutrient uptake rates and PME activities are likely to be advantageous traits in lichens growing in such a heavily eutrophicated habitat. Interestingly, similar differences in PME capacity have been found between eutrophication tolerant and intolerant epiphytic lichens in the British Isles (Lewis 2012).

Not all relationships between the measured variables and distance from the rookery were unambiguous. Despite evidence that a significant fraction of thallus N might be derived from volatilized NH_3, total thallus N concentration was only weakly related to proximity to the rookery. An obvious explanation is that increased N uptake promotes lichen growth rate resulting in growth dilution of thallus N. An alternative explanation is that there might be significant additional local sources of bird-derived nutrient enrichment e.g. from south polar skuas, at some sites distant from the rookery. The strong relationship between $\delta^{15}N$ and [P] values is consistent with this suggestion. However, bird colonies were not evident at lichen collection sites >1 km from the rookery and the link between $\delta^{15}N$ and [P] could equally be due to long distance dispersal of penguin-derived P in the form of P-laden aerosol and/or phosphine (Zhu et al. 2006), and/or up-regulation of PME activity in N-enriched lichens. South polar skuas nest in the vicinity of the penguin rookery and snow petrels have been occasionally sighted; note that Cocks et al. (1998) showed that $\delta^{15}N$ values in lichens are markedly elevated within 10 m of major snow petrel colonies. However, according to Gordon (2003) populations of both species in the study area are small (c. 100 skuas and one small colony of snow petrels on the West coast of Edisto Inlet) while sightings of other species such as giant petrel and Wilson's storm petrel are infrequent. The effect of these birds, if any, is likely to have been a contributory factor to variability of lichen data, due to highly dispersed in-flight defecation, rather than a major confounding factor.

A high capacity for surface PME activity in an Antarctic lichen assayed at c. 5 °C is perhaps surprising. It is widely assumed that extracellular phosphatases promote the release of inorganic phosphate from organic P in the environment (usually soil) and, hence P uptake. The sources of organic P available to *U. sphacelata* and *U. decussata* in the unpolluted aerial environment might not be immediately obvious. However, Yoshioka et al. (2009) analyzed rainfall in Matsue, Japan, and found that the volume weighted concentration ratio of total P to soluble reactive P was on average 5:1 raising the possibility of a significant organic-P component. Hence, extracellular PME might increase the efficiency of P capture from trace organic solutes in precipitation. It is also possible that high surface enzyme activities in lichens are adaptations for exploiting infrequent, spatially unpredictable but highly eutrophicating events associated with deposition of animal excreta in otherwise oligotrophic areas. At Cape Hallett this would be excreta from bird species such as skuas and snow petrels flying at some distance from their nesting and roosting sites (Tomassen et al. 2005; Bokhorst et al. 2007).

There is uncertainty concerning the extent to which nutrients might limit production among Antarctic terrestrial microbial and cryptogamic communities. Earlier opinion, and one still reflected in some more recent literature, is that nutrients are generally not limiting (e.g. Longton 1988; Beyer et al. 2000; Robinson et al. 2003; Wasley et al. 2006; Block et al. 2009). However, there is a growing body of evidence deriving from nutrient amendment experiments suggesting that Antarctic soil bacterial and fungal communities are frequently N-limited (Davey and Rothery 1992; Dennis et al. 2013 and references therein]. Wasley et al. (2006) reported that addition of nutrients to lichen and bryophyte communities in the Windmill Islands, continental Antarctica, resulted in increased photosynthetic electron transport rate and total chlorophyll and thallus N concentrations in crustose lichens, *Usnea* spp and bryophytes and this was interpreted as indicating nutrient limitation in

these communities [cf. Crittenden et al. (1994)]. The present work at Cape Hallett provides additional physiological evidence that Antarctic lichens respond strongly to the relative availabilities of N and P. Current warming trends in the Antarctic could result in a greater availability of both colonisable surfaces and water in seasonal ice-free terrain (Convey 2011) and there is speculation that expansion of existing lichen populations and possibly new local introductions might occur in the future (Frenot et al. 2005; Green et al. 2011; Chown et al. 2012). At the same time it is estimated that warming will lead to significantly increased NH_3 emission from penguin and other seabird colonies (Sutton et al. 2013). Combining these two effects, it seems possible that NH_3 dispersion fields centred on penguin rookeries and other large animal colonies where potential N-limitation is ameliorated (cf. Vidal et al. 2003; Casanovas et al. 2013, Haussmann et al. 2013) might be amongst those sites in which such changes are most likely to occur. Further afield there are many locations in the Arctic at which NH_3 emitted from large seabird colonies is likely to influence otherwise N-limited terrestrial ecosystems (Wainright et al. 1998; Riddick et al. 2012; Zwolicki et al. 2013). However, Riddick et al. (2012) estimate that between 61 and 84 % of global NH_3 emissions from seabirds occurs in Antarctica and islands in the Southern Ocean, most being attributable to penguins; these authors consider principal penguin rookeries to be the largest biogenic point sources of NH_3 globally. Accordingly, NH_3 impacts in the vicinity of penguin rookeries in particular merit further study.

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References

Adams PJ, Seinfield JH, Koch DM (1999) Global concentrations of tropospheric sulphate, nitrate and ammonium aerosol simulated in a general circulation model. J Geophys Res 104:13791–13823

Ainely DG, Ballard G, Barton KJ, Karl BJ, Rau GH, Ribic CA, Wilson PR (2003) Spatial and temporal variation of diet within a presumed metapopulation of Adélie penguins. Condor 105:95–106

Allen SE (ed) (1989) Chemical analysis of ecological materials, 2nd edn. Blackwell Scientific Publications, Oxford

Ayers GP, Gras JL (1980) Ammonia gas concentrations over the Southern Ocean. Nature 284:539–540

Bargagli R (2005) Antarctic ecosystems. Environmental contamination, climate change, and human impact. Springer, Berlin

Bartlett EM, Lewis DH (1973) Surface phosphatase activity of mycorrhizal roots of beech. Soil Biol Biochem 5:249–257

Beckett RP (1995) Some aspects of the water relations of lichens from habitats of contrasting water status studied using thermocouple psychrometry. Ann Bot-Lond 76:211–217

Bessey OA, Lowry OH, Brock MJ (1946) A method for the rapid determination of alkaline phosphatases with five cubic millimeters of serum. J Biol Chem 164:321–329

Beyer L, Bölter M (eds) (2002) Geoecology of Antarctic ice-free coastal landscapes. Springer, Berlin

Beyer L, Bölter M, Seppelt RD (2000) Nutrient and thermal regime, microbial biomass, and vegetation of Antarctic soils in the Windmill Islands region of East Antarctica (Wilkes Land). Arct Antarct Alp Res 32:30–39. doi:10.2307/1552407

Block W, Lewis Smith RI, Kennedy AD (2009) Strategies of survival and resource exploitation in the Antarctic fellfield ecosystem. Biol Rev 84:449–484. doi:10.1111/j.1469-185X.2009.00084.x

Bokhorst S, Huiskes A, Convey P, Aerts R (2007) External nutrient inputs into terrestrial ecosystems of the Falkland Islands and the Maritime Antarctic region. Polar Biol 30:1315–1321. doi:10.1007/s00300-007-292-0

Brabyn L, Beard C, Seppelt RD, Rudolph ED, Türk R, Green TGA (2006) Quantified vegetation change over 42 years at Cape Hallett, East Antarctica. Antarct Sci 18:561–572. doi:10.1017/S0954102006000605

Bruteig IE (1993) The epiphytic lichen *Hypogymnia physodes* as a biomonitor of atmospheric nitrogen and sulphur deposition in Norway. Environ Monit Assess 26:27–47

Cape JN, van der Eerden L, Fangmeier A, Ayres J, Bareham S, Bobbink R, Branquinho C, Crittenden P, Cruz C, Dias T et al (2009) Critical Levels for ammonia. In: Sutton MA, Reis S, Baker SMH (eds) Atmospheric ammonia. Detecting emission changes and environmental impacts. Results of an Expert Workshop under the Convention on Long-range Transboundary Air Pollution. Springer Science + Business Media BV, Dordrecht, pp 375–382

Carruthers DJ, Holroyd RJ, Hunt JCR, Weng W-S, Robins AG, Apsley DD, Thompson DJ, Smith FB (1994) UK-ADMS: a new approach to modelling dispersion in the earth's atmospheric boundary layer. J Wind Eng Ind Aerod 52:139–153. doi:10.1016/0167-6105(94)90044-2

Casanovas P, Lynch HJ, Fagan WF (2013) Multi-scale patterns of moss and lichen richness on the Antarctic Peninsula. Ecography 36:209–219. doi:10.1111/j.1600-0587.2012.07549.x

CERC (2009) ADMS 4 technical specification. http://www.cerc.co.uk

Chang JC, Hanna SR (2004) Air quality model performance evaluation. Meteorol Atmos Phys 87:167–196. doi:10.1007/s00703-003-0070-7

Cherel Y (2008) Isotopic niches of emperor and Adélie penguins in Adélie Land, Antarctica. Mar Biol 154:813–821. doi:10.1007/s00227-008-0974-3

Cherel Y, Hobson KA (2007) Geographical variation in carbon stable isotope signatures of marine predators: a tool to investigate their foraging areas in the Southern Ocean. Mar Ecol-Prog Ser 84:9–18

Chown SL, Huiskes AHL, Gremmen NJM, Lee JE, Terauds A, Crosbie K, Frenot Y, Hughes KA, Imura S, Kiefer K, Lebouvier M et al (2012) Continent-wide risk assessment for the establishment of nonindigenous species in Antarctica. Proc Natl Acad Sci USA 109:4938–4943. doi:10.1073/pnas.1119787109

Cocks MP, Balfour DA, Stock WD (1998) On the uptake of ornithogenic products by plants on the inland mountains of Dronning Maud Land, Antarctica, using stable isotopes. Polar Biol 29:107–111

Convey P (2011) Antarctic terrestrial biodiversity in a changing world. Polar Biol 34:1629–1641. doi:10.1007/s00300-011-1068-0

Crittenden PD (1983) The role of lichens in the nitrogen economy of subarctic woodlands: nitrogen loss from the nitrogen-fixing lichen *Stereocaulon paschale* during rainfall. In: Lee JA, McNeill S, Rorison IH (eds) Nitrogen as an ecological factor. Blackwell Scientific Publications, Oxford, pp 43–68

Crittenden PD (1998) Nutrient exchange in an Antarctic macrolichen during summer snowfall-snow melt events. New Phytol 139:697–707. doi:10.1046/j.1469-8137.1998.00236.x

Crittenden PD, Kałucka I, Oliver E (1994) Does nitrogen supply limit the growth of lichens? Cryptogam Bot 4:143–155

Davey MC, Rothery P (1992) Factors causing the limitation of growth of terrestrial algae in maritime Antarctica during late summer. Polar Biol 12:595–601

Dennis PG, Newsham KK, Rushton SP, Ord VJ, O'Donnell AG, Hopkins DW (2013) Warming constrains bacterial community responses to nutrient inputs in a southern, but not northern, maritime Antarctic soil. Soil Biol Biochem 57:248–255. doi:10.1016/j.soilbio.2012.07.009

Dragosits U, Theobald MR, Place CJ, Lord E, Webb J, Hill J, ApSimon HM, Sutton MA (2002) Ammonia emission, deposition and impact assessment at the field scale: a case study of sub-grid spatial variability. Environ Pollut 117:147–158. doi:10.1016/S0269-7491(01)00147-6

Dunton KH (2001) $\delta^{15}N$ and $\delta^{13}C$ measurements of Antarctic Peninsula fauna: trophic relationships and assimilation of benthic seaweeds. Am Zool 41:99–112. doi:10.1668/0003-1569(2001)041[0099:NACMOA]2.0.CO;2

Ellis CJ, Crittenden PD, Scrimgeour CM, Ashcroft C (2003) The natural abundance of ^{15}N in mat-forming lichens. Oecologia 136:115–123. doi:10.1007/s00442-003-1201-z

Ellis CJ, Crittenden PD, Scrimgeour CM, Ashcroft C (2005) Translocation of ^{15}N indicates nitrogen recycling in the mat-forming lichen *Cladonia portentosa*. New Phytol 168:423–434. doi:10.1111/j.1469-8137-2005.01524.x

Erskine PD, Bergstrom DM, Schmidt S, Stewart GR, Tweedie CE, Shaw JD (1998) Subantarctic Macquarie Island—a model ecosystem for studying animal-derived nitrogen sources using ^{15}N natural abundance. Oecologia 117:187–193. doi:10.1007/s004420050647

Flesch TK, Wilson JD, Harper LA, Crenna BP, Sharpe RR (2004) Deducing ground-to-air emissions from observed trace gas concentrations: a field trial. J Appl Meteorol 43:487–502. doi:10.1175/1520-0450(2004)043<0487:DGEFOT>2.0.CO;2

Fogel ML, Wooller ML, Cheeseman J, Smallwood BJ, Roberts Q, Romero I, Meyers MJ (2008) Unusually negative nitrogen isotopic compositions (δ15 N) of mangroves and lichens in an oligotrophic, microbially-influenced ecosystem. Biogeosciences 5:1693–1704. doi:10.5194/bg-5-1693-2008

Frank DA, Evans RD, Tracy BF (2004) The role of ammonia volatilization in controlling the natural abundance of a grazed grassland. Biogeochemistry 68:169–178. doi:10.1023/B:BIOG.0000025736.19381.91

Frenot Y, Chown SL, Whinam J, Selkirk PM, Convey P, Skotnicki M, Bergstrom DM (2005) Biological invasions in the Antarctic: extent, impacts and implications. Biol Rev 80:45–72. doi:10.1017/S1464793104006542

Fry B (2006) Stable isotope ecology. Springer, New York

Gordon S (2003) Site description and literature review of Cape Hallett and surrounding areas. Antarctica New Zealand, Christchurch

Gras JL (1983) Ammonia and ammonium concentrations in the Antarctic atmosphere. Atmos Environ 17:815–818

Green TGA, Sancho LG, Pintado A, Schroeter B (2011) Functional and spatial pressures on terrestrial vegetation in Antarctica forced by global warming. Polar Biol 34:1643–1656. doi:10.1007/s00300-011-1058-2

Greenfield LG (1992) Precipitation nitrogen at maritime Signy Island and continental Cape Bird, Antarctica. Polar Biol 11:649–653

Gremmen NJM, Huiskes AHL, Francke JW (1994) Epilithic macrolichen vegetation of the Argentine Islands, Antarctic Peninsula. Antarct Sci 6:463–471

Handley LL, Scrimgeour CM (1997) Terrestrial plant ecology and ^{15}N natural abundance: the present limits to

interpretation for uncultivated systems with original data from a Scottish old field. Adv Ecol Res 27:135–212

Haussmann NS, Rudolph EM, Kalwij JM, McIntyre T (2013) Fur seal populations facilitate establishment of exotic vascular plants. Biol Conserv 162:33–40. doi:10.1016/j.biocon.2013.03.024

Heaton THE, Wynn P, Tye AM (2004) Low $^{15}N/^{14}N$ ratios for nitrate in snow in the High Arctic (79°). Atmos Environ 38:5611–5621. doi:10.1016/j.atmosenv.2004.06.028

Hill JH (1998) Applications of computational modelling to ammonia dispersion from agricultural sources. PhD thesis, Imperial College London, University of London

Hobbie EA, Högberg P (2012) Nitrogen isotopes link mycorrhizal fungi and plants to nitrogen dynamics. New Phytol 196:367–382. doi:10.1111/j.1469-8137.2012.04300.x

Hogan EJ (2009) Nitrogen–phosphorus relationships in lichens. PhD thesis, University of Nottingham

Hogan EJ, Minnullina G, Smith RI, Crittenden PD (2010a) Effects of nitrogen enrichment on phosphatase activity and nitrogen:phosphorus relationships in *Cladonia portentosa*. New Phytol 186:911–925. doi:10.1111/j.1469-8137.2010.03222.x

Hogan EJ, Minnullina G, Sheppard LJ, Leith ID, Crittenden PD (2010b) Response of phosphomonoesterase activity in the lichen *Cladonia portentosa* to nitrogen and phosphorus enrichment in a field manipulation experiment. New Phytol 186:926–933. doi:10.1111/j.1469-8137.2010.03221.x

Högberg P (1997) ^{15}N natural abundance in soil–plant systems. New Phytol 137:179–203. doi:10.1046/j.1469-8137.1997.00808.x

Huiskes AHL, Boschker HTS, Lud D, Moerdijk-Poortvliet TCW (2006) Stable isotope ratios as a tool for assessing changes in carbon and nutrient sources in Antarctic terrestrial ecosystems. Plant Ecol 182:79–86. doi:10.1007/s11258-005-9032-0

Hyvärinen M, Crittenden PD (1998) Relationships between atmospheric nitrogen inputs and the vertical nitrogen and phosphorus concentration gradients in the lichen *Cladonia portentosa*. New Phytol 140:519–530. doi:10.1046/j.1469-8137.1998.00292.x

Kelly JF (2000) Stable isotopes of carbon and nitrogen in the study of avian and mammalian trophic ecology. Can J Zool 78:1–27

Lee YI, Lim HS, Yoon HI (2009) Carbon and nitrogen isotope composition of vegetation on King George Island, maritime Antarctic. Polar Biol 32:1607–1615. doi:10.1007/s00300-009-0659-5

Legrand M, Ducroz F, Wagenbach D, Mulvaney R, Hall J (1998) Ammonium in coastal Antarctic aerosol and snow: role of polar ocean and penguin emissions. J Geophys Res 103:11043–11056. doi:10.1029/97JD01976

Leishman MR, Wild C (2001) Vegetation abundance and diversity in relation to soil nutrients and soil water content in Vestfold Hills, East Antarctica. Antarct Sci 13:126–134

Lewis JEJ (2012) Bio-monitoring for atmospheric nitrogen pollution using epiphytic lichens and bryophytes. PhD thesis, University of Nottingham

Lindeboom HJ (1984) The nitrogen pathway in a penguin rookery. Ecology 65:269–277

Longton RE (1988) The biology of polar bryophytes and lichens. Cambridge University Press, Cambridge

Lorenzini S, Baroni C, Fallick AE, Baneshi I, Salvatore MC, Zanchetta G, Dallai L (2010) Stable isotopes reveal Holocene changes in the diet of Adélie penguins in Northern Victoria Land (Ross Sea, Antarctica). Oecologia 164:911–919. doi:10.1007/s00442-010-1790-2

Maupetit F, Delmas RJ (1992) Chemical composition of falling snow at Dumont D'Urville, Antarctica. J Atmos Chem 14:31–42

McFarlane DA, Keeler RC, Mizutani H (1995) Ammonia volatilization in a Mexican bat cave ecosystem. Biogeochemistry 30:1–8. doi:10.1007/BF02181037

Michalski G, Bockheim JG, Kendall C, Thiemens M (2005) Isotopic composition of Antarctic Dry Valley nitrate: implications for NO_y sources and cycling in Antarctica. Geophys Res Lett 32:L13817. doi:10.1029/2004GL022121

Michener RH, Kaufman L (2007) Stable isotopes as tracers in marine food webs: an update. In: Michener RH, Lajtha K (eds) Stable isotopes in ecology and environmental science, 2nd edn. Blackwell, Malden, pp 238–282

Mizutani M, Wada E (1988) Nitrogen and carbon isotope ratios in seabird rookeries and their ecological implications. Ecology 69:340–349

Mizutani H, Kabaya Y, Wada E (1985a) Ammonia volatilization and high $^{15}N/^{14}N$ ratio in a penguin rookery in Antarctica. Geochem J 19:323–327

Mizutani H, Kabaya Y, Wada E (1985b) High performance liquid chromatographic isolation of uric acid from soil for isotopic determination. J Chromatogr 331:371–381

Mizutani H, Hasegawa H, Wada E (1986) High nitrogen isotope ratio for soils of seabird rookeries. Biogeochemistry 2:221–247

Mulvaney R, Wagenbach D, Wolff EW (1998) Postdepositional change in snowpack nitrate from observation of year-round near surface snow in coastal Antarctica. J Geophys Res 103:11021–11031

Nędzarek A, Rakusa-Suszczewski S (2007) Nutrients and conductivity in precipitation in the coast of King George Island (Antarctica) in relation to wind speed and penguin colony distance. Pol J Ecol 55:705–716

Øvstedal DO, Lewis Smith RI (2001) Lichens of Antarctica and South Georgia. A guide to their identification and ecology. Cambridge University Press, Cambridge

Park J-H, Day TA, Strauss S, Ruhland CT (2007) Biogeochemical pools and fluxes of carbon and nitrogen in a maritime tundra near penguin colonies along the Antarctic Peninsula. Polar Biol 30:199–207. doi:10.1007/s00300-006-0173-y

R Core Team (2014) R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org

Rau GH, Ainley DG, Bengtson JL, Torres JJ, Hopkins TL (1992) $^{15}N/^{14}N$ and $^{13}C/^{12}C$ in Weddell Sea birds, seals, and fish: implications for diet and trophic structure. Mar Ecol-Prog Ser 84:1–8

Riddick SN, Dragosits U, Blackall TD, Daunt F, Wanless S, Sutton M (2012) The global distribution of ammonia emissions from seabird colonies. Atmos Environ 55:319–327. doi:10.1016/j.atmosenv.2012.02.052

Robinson SA, Wasley J, Tobin AK (2003) Living at the edge—plants and global change in continental and maritime

Antarctica. Glob Change Biol 9:1681–1717. doi:10.1046/j.1529-8817.2003.00693.x

Rudolph ED (1963) Vegetation of Hallett Station area, Victoria Land, Antarctica. Ecology 44:585–586

Smith RIL (1972) Vegetation of the South Orkney Islands with particular reference to Signy Island. Brit Antarct Surv Sci Reps 68:1–124

Smith RIL (1988) Classification and ordination of cryptogamic communities in Wilkes Land, Continental Antarctica. Vegetatio 76:155–166

Smykla J, Wołek J, Barcikowski A (2007) Zonation of vegetation related to penguin rookeries on King George Island, Maritime Antarctic. Arct Antarct Alp Res 39:143–151. doi:10.1657/1523-0430(2007)39[143:ZOVRTP]2.0.CO;2

Sutton MA, Reiset S, Riddick SN, Dragosits U, Nemitz E, Theobald MR, Tang YS, Braban CF, Vieno M, Doreet AJ et al (2013) Toward a climate-dependent paradigm of ammonia emission and deposition. Philos Trans R Soc B 368:20130166. doi:10.1098/rstb.2013.0166

Talbot RW, Vijgen AS, Harriss RC (1992) Soluble species in the Arctic summer troposphere: acid gases, aerosols, and precipitation. J Geophys Res 97:16531–16543

Tang YS, Cape JN, Sutton MA (2001) Development and types of passive samplers for monitoring atmospheric NO_2 and NH_3 concentrations. ScientificWorldJournal 1:513–529. doi:10.1100/tsw.2001.82

Tang YS, van Dijk N, Love L, Dragosits U, Vjeno M, Smith RI, Rippey B, Sutton MA (2004) Ammonia monitoring in Northern Ireland. Final report to SNIFFER (Scotland and Northern Ireland Forum for Environmental Research) Project UKPIR04 230/804, June 2004

Tatur A (2002) Ornithogenic ecosystems in the Maritime Antarctic—formation, development and disintegration. In: Beyer L, Bölter M (eds) Geoecology of Antarctic ice-free coastal landscapes. Springer, Berlin, pp 161–184

Theobald MR, Crittenden PD, Tang YS, Sutton MA (2013) The application of inverse-dispersion and gradient methods to estimate ammonia emissions from a penguin colony. Atmos Environ 81:320–329. doi:10.1016/j.atmosenv.2013.09.009

Tomassen HBM, Smolders AJP, Lamers LPM, Roelofs JGM (2005) How bird droppings can affect the vegetation composition of ombrotrophic bogs. Can J Bot 83:1046–1056. doi:10.1139/B05-051

Tozer WC, Hackell D, Miers DB, Silvester WB (2005) Extreme isotopic depletion of nitrogen in New Zealand lithophytes and epiphytes; the result of diffusive uptake of atmospheric ammonia? Oecologia 144:628–635. doi:10.1007/s00442-005-0098-0

van Veldhoven PP, Mannaerts GP (1987) Inorganic and organic phosphate measurements in the nanomolar range. Anal Biochem 161:45–48

Vasil CA, Polito MJ, Patterson WP, Emslie SD (2011) Wanted dead or alive? Isotopic analysis ($\delta^{13}C$ and $\delta^{15}N$) of *Pygoscelis* penguin chick tissues supports opportunistic sampling. Rapid Commun Mass Spectrom 26:487–493. doi:10.1002/rcm.5340

Vidal E, Jouventin P, Frenot Y (2003) Contribution of alien and indigenous species to plant-community assemblages near penguin rookeries at Crozet archipelago. Polar Biol 26:432–437. doi:10.1007/s00300-003-0500-5

Wada E, Shibata R, Torii T (1981) ^{15}N abundance in Antarctica: origin of soil nitrogen and ecological implications. Nature 292:327–329

Wagenbach D, Legrand M, Fischer H, Pichlmayer F, Wolff EW (1998) Atmospheric near-surface nitrate at coastal Antarctic sites. J Geophys Res 103:11007–11020. doi:10.1029/97JD03364

Wainright SC, Haney JC, Kerr C, Golovkin AN, Flint MV (1998) Utilization of nitrogen derived from seabird guano by terrestrial and marine plants at St. Paul, Pribilof Islands, Bering Sea, Alaska. Mar Biol 131:63–71. doi:10.1007/s002270050297

Walker TR, Crittenden PD, Young SD (2003) Regional variation in the chemical composition of winter snow pack and terricolous lichens in relation to sources of acid emissions in the USA river basin, northeast European Russia. Environ Pollut 125:401–412. doi:10.1016/S0269-7491(03)00080-0

Wasley J, Robinson SA, Lovelock CE, Popp M (2006) Climate change manipulations show Antarctic flora is more strongly affected by elevated nutrients than water. Glob Change Biol 12:1800–1812. doi:10.1111/j.1365-2486.2006.01209.x

Whitton BA, Potts M (2000) The ecology of cyanobacteria. Their diversity in time and space. Kluwer, Dordrecht

Wodehouse EB, Parker BC (1981) Atmospheric ammonia nitrogen: a potential source of nitrogen eutrophication of freshwater Antarctic ecosystems. In: Parker BC (ed) Terrestrial biology III (Antarctic Research Series 30). American Geophysical Union, Washington DC, pp 155–167

Wynn-Williams DD (1990) Ecological aspects of Antarctic microbiology. Adv Microbiol Ecol 11:71–146

Yoshioka K, Kamiya H, Kano Y, Saki Y, Yamamuro M, Ishitobi Y (2009) The relationship between seasonal variations of total-nitrogen and total-phosphorus in rainfall and air mass advection paths in Matsue, Japan. Atmos Environ 43:3496–3501. doi:10.1016/j.atmosenv.2009.04.027

Zhu R, Kong D, Sun L, Geng J, Wang X, Glindemann D (2006) Troposhperic phosphine and its sources in coastal Antarctica. Environ Sci Technol 40:7656–7661

Zhu R, Liu Y, Li X, Sun J, Xu H, Sun L (2008a) Nitrous oxide emissions from sea animal colonies in the maritime Antarctic. Geophys Res Lett 35:L09807. doi:10.1029/2007GL032541

Zhu R, Liu Y, Li X, Sun J, Xu H, Sun L (2008b) Stable isotope natural abundance of nitrous oxide emitted from Antarctic tundra soils: effects of sea animal excrement depositions. Rapid Commun Mass Spectrom 22:3570–3578. doi:10.1002/rcm.3762

Zhu R, Liu Y, Ma E, Sun J, Xu H, Sun L (2009) Nutrient compositions and potential greenhouse gas production in penguin guano, ornithogenic soils and seal colony soils in coastal Antarctica. Antarct Sci 21:427–438. doi:10.1017/S0954102009990204

Zhu R, Sun J, Liu Y, Gong Z, Sun L (2011) Potential ammonia emissions from penguin guano, ornithogenic soils and seal colony soils in coastal Antarctica: effects of freeze-thawing cycles and selected environmental variables. Antarct Sci 23:78–92. doi:10.1017/S0954102010000623

Zwolicki A, Zmudczyńska-Skarbek KM, Iliszko L, Stempniewicz L (2013) Guano deposition and nutrient enrichment in the vicinity of planktivorous and piscivorous seabird colonies in Spitsbergen. Polar Biol 36:363–372. doi:10.1007/s00300-012-1265-5