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Environmental implication of nitrogen isotopic composition in ornithogenic sediments from the Ross Sea region, East Antarctica: $\Delta^{15}N$ as a new proxy for avian influence

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ABSTRACT

We analyzed $\delta^{15}N$ in both acid-treated and untreated sediment profiles from McMurdo Sound of the Ross Sea region, East Antarctica that were influenced by penguin guano. The difference between treated and untreated $\delta^{15}N$ ($\Delta^{15}N$) was significant in three profiles which were heavily impacted by guano, and minor in two profiles with less guano influence. We determined that the total nitrogen in the sediments is primarily derived from penguin guano and algae, and used an N-species test to explain the variation of $\Delta^{15}N$ in two profiles. It was found that post-depositional decomposition and ammonia volatilization, which have important roles in the cold and arid environment of East Antarctica, would render an elevated $\delta^{15}N$ through kinetic isotopic fractionation in the inorganic nitrogen from guano. N-species analysis revealed that the percentage of inorganic nitrogen in total nitrogen, indicative of the degree of guano influence, is the key factor controlling $\Delta^{15}N$ in the sediments. This hypothesis successfully explained the nitrogen isotopic composition in the remaining three sediment profiles. We conclude that the parameter $\Delta^{15}N$, rather than traditionally used untreated $\delta^{15}N$, can be taken as an effective proxy for the strength of avian influence on ornithogenic sediments in East Antarctica.

1. Introduction

Since its first application, isotope analysis has become increasingly important in multiple fields of study. Light element isotopes including hydrogen, carbon, nitrogen and sulfur are now routinely examined in paleoecological research (Peterson and Fry, 1987; Hobson, 1999). Environmental change, whether caused by the evolution of climate, interaction with inhabitant species, or anthropogenic influences, leaves a 'signature' in the isotopic composition of different geochemical carriers (e.g., sediments, algae, guano; Hansson et al., 1997; Rozanski et al., 1997; McDermott, 2004). Nitrogen is one of the most important elements in the circulation of both the biosphere and pedosphere (Kielland, 1994; Kelly, 2000). Various N processes link ecosystems and local environment by substance and energy flow, accompanied with corresponding isotopic fractionations. For example, ^{15}N bioaccumulates up the food chain at about 3.4 ± 1.1‰ per trophic level (Wada et al., 1991) and subsequently is a powerful tool to determine the trophic level of an organism, the origin and possible shifts in its diet over time, and even the migration of the animals (Hesslein et al., 1991; Minami et al., 1995; Marra et al., 1998; Dunton, 2001). In turn, varying $\delta^{15}N$ in migratory animals would affect the nitrogen isotopic composition of the environment in their habitats (Hawke and Newman, 2007; Hawke and Miskelly, 2009; Caut et al., 2012). This methodology has been applied to many different species including plants, organs and tissues of animals, excrement, and marine and lake sediments, revealing numerous mechanisms induced by different environmental drivers (Griffiths et al., 2010; Naito et al., 2010; Robinson et al., 2012; Huang et al., 2013).

Polar regions are remote from anthropogenic influences and have unique ecosystem structures, making them ideal locations for isotope research in ecology (Lee et al., 2009). In the sediments of coastal areas where migrating seabirds have the most impact, continuous and well-preserved historical records of ecological and environmental changes are often stored (Sun et al., 2013). For example, $\delta^{15}N$ in Arctic lacustrine sediments with strong avian influence was closely related to nesting seabird populations due to the deposition of guano which introduced both nutrients and pollutants to the lacustrine ecosystem (Blais et al., 2005; Michelutti et al., 2009b, c). $\delta^{15}N$ in lake and marine sediments from Antarctica was used to study the tropic structure in Antarctic Peninsula and sub-Antarctica (Hansson and Tranvik, 2003; Mincks et al., 2008). Bishop et al. (2003) investigated nitrogen isotope composition in the benthic microbial process under both anoxic and oxic conditions in Lake Hoare of Dry Valleys. Nitrogen and other geochemical indices of ornithogenic (bird-formed) sediments have been studied in Antarctica since the 1960s (Campbell et al., 1966, Sun et al., 2000, 2013). The influence of ornithogenic nitrogen on the local ecosystem as an important nutrient source was explored in various sites around

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Antarctica (Bokhorst et al., 2007). Similar to research in the Arctic, Liu et al. (2006) reported guano controlling $\delta^{15}N$ in penguin-impacted sediment profiles from the Antarctic Peninsula which reflects historical changes in the penguin population. However, due to the high nitrogen content in ornithogenic sediments, post-depositional processes may cause significant change in $\delta^{15}N$ via decomposition of guano and ammonia volatilization (Ugolini, 1972; Speir and Cowling, 1984), as has been documented in East Antarctica (Mizutani et al., 1985; Mizutani and Wada, 1988).

In addition to these investigations on the environmental implications of nitrogen isotopes, how the pretreatment process of sediments may affect the analyses is also of scientific interest (Kennedy et al., 2005; Brodie et al., 2011b). The effect of various treatments, including the type and concentration of acids on different materials such as plants, sediments, and bulk soil has been systematically studied (Lorrain et al., 2003; Schmidt and Gleixner, 2004; Brodie et al., 2011a). Consequently, analyzing $\delta^{15}N$ without acid pretreatment has become the common method for studying sediments, and obviously this analytical method can include all the nitrogen species in the samples (Kennedy et al., 2005). However, these studies seldom consider environmental implications of the pretreatment, which could potentially add new information to these analyses.

Five ornithogenic sediment profiles impacted by Adélie penguins (*Pygoscelis adeliae*) were collected from the Ross Sea region. This region is an important habitat for Adélie penguins and numerous studies have been conducted on penguin remains in ornithogenic soils (e.g., Baroni and Orombelli, 1994; Polito et al., 2002; Emslie et al., 2007; Lorenzini et al., 2010). The sediments collected can provide important information on the paleoenvironment and paleoecology of the region (Hu et al., 2013). Here we conducted $\delta^{15}N$ measurements on both acid-treated and untreated samples to investigate the difference between these two pretreatment methods among the five sediment profiles. The cause for the variation between two of these profiles was determined using N-species analysis. Our results suggested a new proxy for assessing the influence of penguin guano in ornithogenic sediments in the Ross Sea region, and it may potentially apply to other ornithogenic sediments strongly subjected to post-depositional decomposition and ammonia volatilization.

2. Material and methods

Geochemical surveys were conducted in the ice-free areas of the southern Ross Sea region in January 2010. The surveys were carried out primarily on Ross Island and surrounding areas including the east coast of Victoria Land and Beaufort Island (Fig. 1). This region is highly sensitive to climate change as it is located at the conjunction of three different air masses from Victoria Land, the Ross Sea, and the Ross Ice Shelf (Monaghan et al., 2005). The weather here is abrupt and severe: the mean annual temperature is −18 °C; temperatures may reach 8 °C in summer and −50 °C in winter. The average wind speed is 12 knots, but may exceed 100 knots on occasion. Ross Island (~2460 km^2) is of volcanic origin in McMurdo Sound. Most of the island is covered by ice, leaving three ice-free areas where penguins currently breed at Cape Crozier (~18 km^2), Cape Bird (~15 km^2), and Cape Royds (~13 km^2). A large number of Adélie penguins reside in these three areas, forming one of the largest concentrations of this species in Antarctica (>155,000 pairs; Ainley, 2002). Beaufort Island (~18.4 km^2) is 21 km north of Ross Island with Adélie penguins breeding on the ice-free areas on the eastern and southern coasts. Besides the modern penguin colonies, there are also numerous abandoned breeding sites in the ice-free areas mentioned above, allowing the study of penguin paleoecology. Freshwater algae are widely distributed in the ponds and catchments near the penguin colonies (Broady, 1989). A detailed description of sampling sites and sectioning of the five sediment profiles used in this study (designated as MB4, MB6, CL2, BI and CC), as well as collection of background environmental media samples (soil, guano, algae) can be found in Nie et al. (2012).

We used the potassium chloride solution extraction–spectrophotometric determination methods provided by the Chinese environmental protection standard in the analysis of N-species including NH_4-N and NO_3-N from the sediment subsamples of MB4 and MB6 profiles. Approximately 4 g of frozen homogeneous samples was weighed and placed into 50 mL centrifuge tubes with 25 mL of potassium chloride solution. The centrifuge tubes were first set on a vibrator at room temperature (20 ± 2 °C) with proper amplitude for 1 h to reach full extraction, and then centrifuged at 3000 rpm. Following this, 5 mL supernatant was transferred to colorimetric tubes for spectrophotometric analysis. For NH_4-N, 20 mL color reagent I (5 mL $Na_2[Fe(CN)_5NO]\cdot H_2O$ (0.8 g/L) and 5 mL C_6H_5OH (70 g/L) mixed with 250 mL deionized water in a beaker, instant use) was added to 1 mL supernatant in colorimetric tubes and fully mixed. After 15 min standing, color reagent II (5.0 g $C_3Cl_2N_3NaO_3H_2O$ dissolved into 1 L $C_6H_5NaO_7\cdot 2H_2O$–NaOH buffer solution) was added and left for at least 4 h (the same process for reagent blank KCl solutions and NH_4Cl solution as calibration curve). NH_4-N was determined by a spectrophotometer at a wavelength of 630 nm with deionized water as a reference (at 15–35 °C). For NO_3-N, a cadmium column (transforming NO_3-N to NO_2-N) needs to be prepared first by washing with NH_4Cl buffer solution II (10 g/L), NH_4Cl buffer solution I (100 g/L) and then NH_4Cl buffer solution II again. 0.2 mL supernatant was prewashed in the column using 10 mL of NH_4Cl buffer solution II, followed by 20 mL NH_4Cl buffer solution II, and was collected in colorimetric tubes. A 0.2 mL color reagent III (20 mL $C_6H_8N_2O_2S$ + 20 mL $C_{12}H_{16}N_2C_{12}$ + 20 mL H_3PO_4) was added to the tubes and fully mixed. After standing 60 to 90 min at room temperature (15–35 °C; the same process for reagent blank KCl solutions and NO_2-N standard

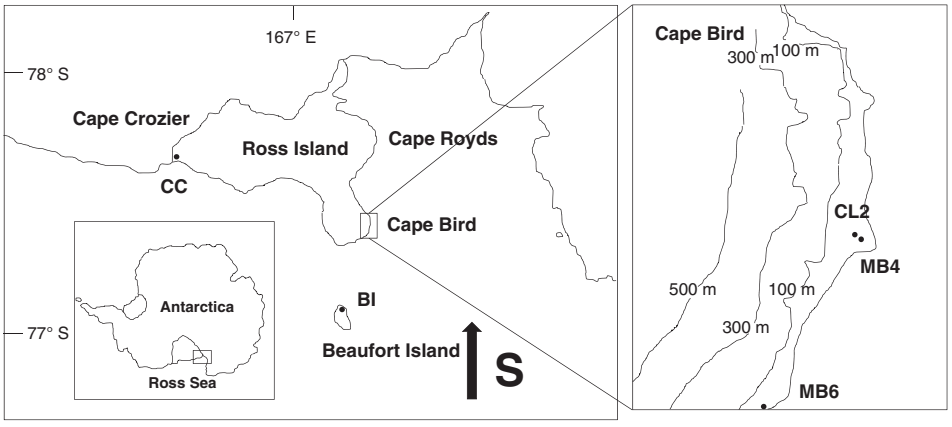

Fig. 1. Sampling sites of the five sediment profiles in the Ross Sea region.

solution as calibration curve), NO_3-N was determined by a spectrophotometer at a wavelength of 543 nm with deionized water as reference. Water content (WC, water weight/dry sample weight) of the bulk sediment samples was calculated by measuring the difference of weight between wet and dry samples (dried in an oven at 120 °C to constant weight). All the NH_4-N and NO_3-N contents are expressed in per 1 g dry weight sample based on the calculation with water content data.

For the measurements of total nitrogen content (TN), total organic carbon (TOC), and Phosphorus (P), sediment subsamples and weathered soil were air-dried, while fresh algae and guano samples were freeze-dried. All the sediment subsamples were homogenized by grinding after the removal of large rock fragments and biological remains through a 74 μm mesh sieve. TN was measured on an element analyzer (Vario EL III) with a relative standard deviation (RSD) <1%. The chemical volumetric method was employed to measure TOC with an RSD less than 0.5%. P in the sediments was determined by inductively-coupled plasma-optical emission spectroscopy (ICP-OES, Perkin Elmer 2100DV) after digestion of HCl–HNO_3–HF–$HClO_4$ and its RSD was within 2% (Liu et al., 2013). Reagent blanks and standard sediment reference materials were included in every batch of samples for quality control (GBW 07415 for TOC; GBW 07401 and 07405 for P; Vario EL III build-in standard reference material for TN). The nitrogen isotope composition of acid-treated (HCl about 1 mol/L) and untreated bulk sediment subsamples in the five profiles was measured using sealed tube combustion method at G.G. Hatch Isotope Laboratories, University of Ottawa (Canada) and the Third Institute of Oceanography, State Oceanic Administration (China). Stable isotope abundances were expressed in δ notation as the deviation from standards in parts per thousand (‰):

$$\delta^{15}N(‰) = \left[\left(R_{sample}/R_{standard}\right) - 1\right] \times 1000$$

where R is the corresponding ratio of $^{15}N/^{14}N$. The $R_{standard}$ values were based on the N_{air}. Samples were weighed into tin capsules and loaded into an elemental analyzer interfaced to an isotope ratio mass spectrometer. Samples were flash combusted at about 1800 °C (Dumas combustion) and the resultant gas products were carried by helium through columns of oxidizing/reducing chemicals optimized for N_2. The gases were separated by a "purge and trap" adsorption column and sent to Isotope Ratio Mass Spectrometer (IRMS, Delta XP Plus Advantage in G.G. Hatch Isotope Laboratory and Delta V Advantage in the Third Institute of Oceanography, manufactured by Thermo, Germany) interface then to IRMS. Standard reference materials (SRMs) used in the labs, including C-55 and acetanilide, were both calibrated to international standards (IAEA-N1, IAEA-N2, USGS-40 and USGS-41 in G.G. Hatch Isotope Laboratories, University of Ottawa; IAEA-N-1 and IAEA-N-2 in Third Institute of Oceanography, State Oceanic Administration of China). Number of replicates, certified values, observed values and standard deviation (STD, <0.2‰ for all SRMs) of $\delta^{15}N$ in SRMs are listed in the Supplementary material. Pearson correlation analysis in this study was carried out using software Origin Pro v8.6.

3. Results

Measured $\delta^{15}N$ values of HCl treated ($\delta^{15}N_{at}$) and untreated ($\delta^{15}N_{ut}$) samples in all five sediment profiles were plotted with lithological profiles, WC and basic geochemical parameters including TOC, TN and P (Fig. 2). As with the lithology, WC, TOC, TN and P varied within and among profiles. In MB4, the contents of these four parameters gradually increased from the bottom of the profiles to about 17 cm in depth from the surface, then dropped sharply at the interval of a sand sediment layer between 15 and 5 cm depth, followed by a peak in the surface algae residue layer. Except for the top section that was rich in algal residues, WC in CL2 was low and stable throughout the profile, while TOC, TN and P displayed more fluctuations with peaks between 28 and 20 cm, troughs between 20 and 15 cm, and high levels present in the surface algae residue layer. The sediment layer between 35 and 25 cm in MB6 had high contents of all four proxies, while the remaining bottom part and the upper layer were at low levels. WC, TOC, TN and P in both BI and CC showed an increasing trend from the bottom to the top. In general, we found that the four proxies shared the same distribution patterns. WC data agreed with our field records and lithology, for all profiles were collected in wet environment (on the edge of a pond or catchment with penguin influence) except MB6 (in a dried-out catchment of an active penguin colony), thus explaining the high WC in their top sections. Additionally, the layers with ornithogenic influence and algal residues were generally higher in water content compared with the layers composed of sand and silts.

$\delta^{15}N_{ut}$ in MB4 was stable at about 30‰ with two minor drops at 40–30 cm and 15–10 cm depth from the surface, while $\delta^{15}N_{at}$ in MB4 was almost the same as $\delta^{15}N_{ut}$, except for a much lower trough at the layer between 15 and 10 cm. Both $\delta^{15}N_{ut}$ and $\delta^{15}N_{at}$ shared the same trends with little fluctuation at about 25‰ in CL2. The $\delta^{15}N_{ut}$ in MB6 was relatively stable at about 30‰, while $\delta^{15}N_{at}$ displayed more variations with the bottom layer (below 24 cm) at around 23‰ and the upper layer at around 18‰. A drop could be observed in the surface layer for both $\delta^{15}N_{ut}$ and $\delta^{15}N_{at}$. The $\delta^{15}N_{ut}$ in BI decreased from about 40 to 30‰ from depth to the surface, yet the $\delta^{15}N_{at}$ remained constant at about 30‰. The $\delta^{15}N_{ut}$ and $\delta^{15}N_{at}$ in CC were both stable in the profile at ~30‰ and ~20‰ respectively. Their detailed range, mean values and coefficient of variation (CV) are given in Table 1. The similar mean values of $\delta^{15}N_{at}$ and $\delta^{15}N_{ut}$ in MB4 and CL2 corroborated the little difference between them. By contrast, in the other three profiles (MB6, BI and CC) $\delta^{15}N_{ut}$ was found to have a significantly higher mean value than $\delta^{15}N_{at}$, demonstrating the influence of acid treatment on the nitrogen isotope composition in the ornithogenic sediments. In general, $\delta^{15}N_{at}$ varied the most in profiles MB4 and MB6, while both $\delta^{15}N_{ut}$ and $\delta^{15}N_{at}$ in profile CC were mostly stable throughout. The remaining profiles (BI and CL2) had moderate amplitudes of variation in these measurements (Fig. 2).

TN and $\delta^{15}N$ were analyzed on environmental media samples collected around our sampling area and presented in Fig. 3. Mean TN values in weathered soil, guano and algae were 0.21% (n = 7, STD = 0.094), 13.11% (n = 3, STD = 3.43%) and 1.77% (n = 6, STD = 0.46%) respectively (Fig. 3A). These three constituents of the ornithogenic sediments display distinctive nitrogen contents with that of guano and algae higher than soil by an order of magnitude, identifying them as the main nitrogen source for the bulk sediments. $\delta^{15}N$ in weathered soil, guano and algae was 27.08‰ (n = 3, STD = 3.19), 5.34‰ (n = 3, STD = 0.53‰) and 2.15‰ (n = 6, STD = 2.45‰) respectively (Fig. 3B).

4. Discussion

4.1. Possible cause for the difference between $\delta^{15}N_{at}$ and $\delta^{15}N_{ut}$

Organic matter (OM) sources in the five profiles have been discussed previously (Liu et al., 2013). Weathered soil, guano and algae were the three main constituents of the bulk sediments with the latter two comprising most of TOC. The similar fluctuation patterns of TOC and TN (Fig. 2) were caused by the strong affinity of nitrogen to OM, while the highly correlated TOC and P indicated that guano was mostly responsible for the OM input in the sediments since P is a typical penguin guano bio-element (Sun et al., 2000; Liu et al., 2006; Sun et al., 2013). According to Nie et al. (2012), MB6 and BI were heavily influenced by guano, and algae also thrived in these two profiles due to the high nutrient supply from the seabird droppings. Profile CC was impacted solely by guano. Compared with MB6, CC and BI profiles, MB4 and CL2 were much less influenced by penguin guano, and hence had relatively low algal biomass.

We measured both $\delta^{15}N_{ut}$ and $\delta^{15}N_{at}$ in the profiles to explore any paleoenvironmental information, though conventionally $\delta^{15}N$ of the bulk sediments was analyzed without acid pretreatment to include all

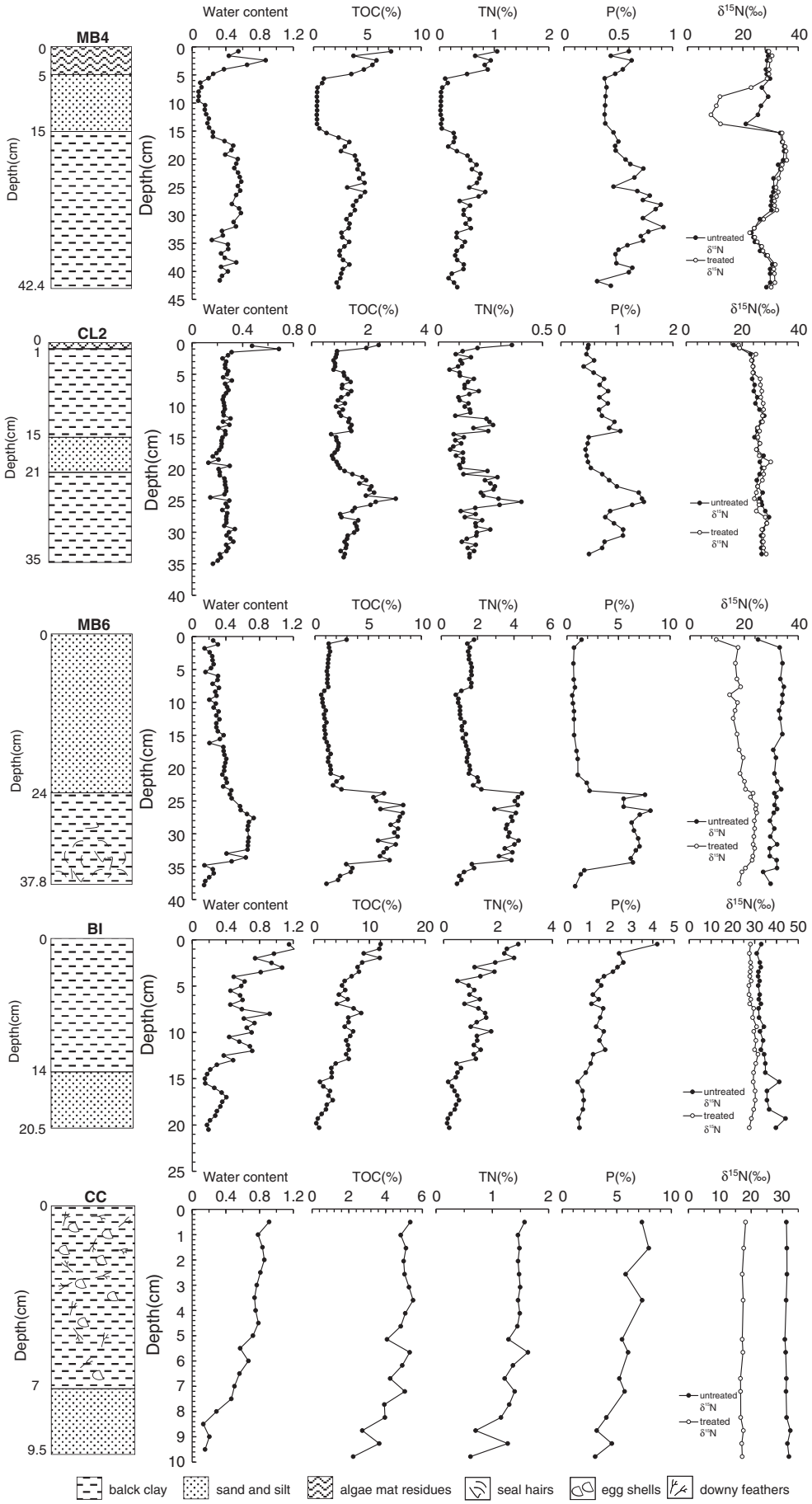

Fig. 2. Plots of water content, TOC, TN, P, and $\delta^{15}N$ with depth in each of the five sediment profiles.

Table 1
Range, mean and CV of $\delta^{15}N$ in untreated and treated subsamples of the five profiles from the Ross Sea region, East Antarctica.

$\delta^{15}N$ (‰)	MB4		MB6		CL2		BI		CC	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Max	34.90	35.83	34.68	24.62	29.56	30.16	44.17	31.55	32.48	18.21
Min	21.07	8.48	25.14	9.66	16.92	18.69	30.97	27.40	30.75	16.58
Mean	29.11	28.25	31.60	20.00	25.57	26.04	34.18	29.01	31.37	17.20
CV (%)	11.62	24.86	6.85	17.96	9.40	8.75	9.39	4.19	1.50	2.75

sedimentary nitrogen species (Kennedy et al., 2005). The $\delta^{15}N_{ut}$ values measured in the five profiles were generally very high (~25 to 34‰ mean) with some subsamples above 40‰ (Fig. 2, Table 1). Our results are consistent with the reports of Mizutani et al. (1986) and Mizutani and Wada (1988) which indicated a $\delta^{15}N$ of 31.8‰ in ornithogenic soil from Cape Bird, and Hage et al. (2007) who showed that $\delta^{15}N$ of ornithogenic organic matter ranged from about 10 to 35‰. However, multiple investigations of ornithogenic soils and sediments indicate that $\delta^{15}N$ in the maritime Antarctic was relatively lower, from about 4 to 18‰ (Liu et al., 2006; Zhu et al., 2009). In the Arctic, $\delta^{15}N$ in the seabird-affected sediments is likely to be closely related to the population of nesting seabirds, for highly enriched ^{15}N in the deposited guano could easily distinguish them from the background sediments (Blais et al., 2005). Thus, the more avian-influenced the sediments are, the more ^{15}N seems likely to be enriched due to the high trophic position of seabirds (Michelutti et al., 2009a). Though heavily influenced by penguin activities, the $\delta^{15}N_{ut}$ curves in the sediment samples here show less fluctuation and have no apparent correlation with the amount of guano input represented by P content (Fig. 2). It is clear that $\delta^{15}N_{ut}$ does not change much compared to the obvious guano influence gradient in the five profiles (Fig. 4), but our ^{15}N analysis with acid-treated (HCl about 1 mol/L) samples yielded some interesting results. $\delta^{15}N_{at}$ in the profile MB4 (except the layer between 7 and 15 cm, will be discussed later) and CL2 with less guano influence was almost the same as $\delta^{15}N_{ut}$, while $\delta^{15}N_{at}$ in the heavily impacted BI, MB6, and CC profiles was apparently lower than $\delta^{15}N_{ut}$, thereby creating a high $\Delta^{15}N$ ($\Delta^{15}N = \delta^{15}N_{ut} - \delta^{15}N_{at}$ Fig. 2). Furthermore, the trends of $\delta^{15}N_{at}$ with depth in the profiles are different from those of $\delta^{15}N_{ut}$, possibly due to the N-containing substance (mostly inorganic nitrogen, like NH_4-N and NO_3-N) washed away in the acid-treatment process.

According to elemental and isotopic analysis on environmental media samples (Fig. 3), though the weathered soil and bedrock are the bulk of the sediments, they contain very little nitrogen. Nitrogen in algae is much more abundant, yet it is still relatively minor compared with guano. The $\delta^{15}N$ of the algae free form guano influence that we collected is 2.15‰ on average, typical for nitrogen-fixing blue green algae (Gu and Alexander, 1993) and consistent with the reported measurements from East Antarctica (Strauch et al., 2011). This signature is likely attributed to its origin from atmospheric N_2 (0‰) through nitrogen fixation process with a fractionation of about −1.5–0.4‰ (Minagawa and Wada, 1986). Algae residues are usually well preserved in the extremely cold environment of East Antarctica, and the nitrogen in their residues existed in stable organic form which was resistant to both depositional processes and HCl treatment (Kennedy et al., 2005). $\delta^{15}N$ in fresh guano (5.34‰) is similar to modern penguin guano at Terra Nova Bay, Victoria Land (Lorenzini et al., 2010). According to Lindeboom (1984), uric acid is the major N-form in penguin guano (~80%) while protein and ammonia are minor components (~20%). Ammonia volatilization, which greatly influences the nitrogen circulation in seabird colonies, is much stronger in high latitude regions such as the Ross Sea region (Mizutani et al., 1991b), suggesting that local climate and post-depositional processes may impose a great influence on penguin guano. Under the extreme conditions in East Antarctica, strong ammonia volatilization tends to occur in ornithogenic soils after the deposition of guano, and the processes of nitrification and denitrification were relatively weak due to the low temperature (Mizota, 2009a; Kazama et al., 2012) and usually considered negligible in respect to isotope analysis (Lindeboom, 1984; Speir and Cowling, 1984; Mizutani and Wada, 1988). Under such circumstances, uric acid would quickly decompose into the inorganic form of NH_4-N, and the ammonia concentrated with lighter ^{14}N through kinetic isotope fractionation (can be as much as −40 to −60‰, Mizutani et al., 1985; Robinson, 2001; Szpak et al., 2012b) escapes the sedimentary system during the volatilization. This process will turn large proportions of guano-N (mainly uric acid) into inorganic nitrogen (IN) and leave the remaining NH_4-N in the sediments with much higher $\delta^{15}N$ as has been observed in our $\delta^{15}N_{ut}$ results (Schmidt et al., 2004). IN was vulnerable to acid treatment and could easily be removed by HCl, leaving low $\delta^{15}N_{at}$ values. Thus, we believe that the percentage of IN in TN (IN/TN) should be the main factor determining the magnitude of $\Delta^{15}N$.

With different amounts of IN containing high $\delta^{15}N$ washed away by the acid treatment, heavily versus lightly guano-impacted profiles should be easily distinguished by $\Delta^{15}N$. Isotopic analysis indicates that $\delta^{15}N$ of weathered soil is 27.08‰, much higher than the background

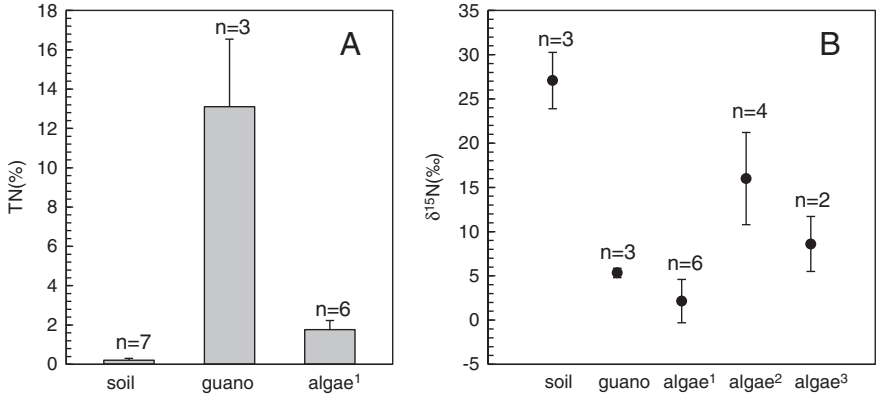

Fig. 3. Measurements of TN (A) and $\delta^{15}N$ (B) of local environmental media (including soil, penguin guano and algae[1] without the effect of penguin guano) collected near sampling sites in the Ross Sea region and comparison of $\delta^{15}N$ with penguin affected algae from references (error bars indicate standard deviation). Algae[2] and algae[3] with the influence of penguin guano are collected from Cape Bird (Mizutani and Wada, 1988) and King George Island (Lee et al., 2009).

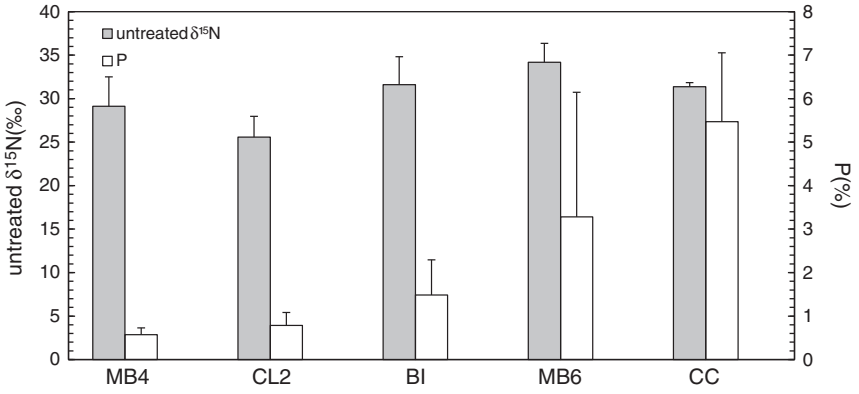

Fig. 4. Measurements of $\delta^{15}N$ in untreated samples from the five sediment profiles in comparison with P, a proxy for the influence of penguin guano on the sediments (error bars indicate standard deviation).

data reported in neighboring Victoria Land (about 0‰, Mizutani et al., 1991a), but on the same level with the ornithogenic profiles (Barrett et al., 2006a). Although the soil samples were collected outside of the active or abandoned colony and were visually free from guano influence, we believe their TN was too low and could possibly be affected by the nitrogen from guano with high $\delta^{15}N$ due to ammonia volatilization. However, considering its low TN content, soil constituents can hardly affect the nitrogen isotopic composition of the bulk sediments. Hence we propose that the high level of $\delta^{15}N_{ut}$ is a result of the strong ammonia volatilization of guano-N in the ornithogenic sediments. This result is supported by the recent studies on the ornithogenic soils from Japan and Fiji, as well as controlled experiment analysis (Mizota and Naikatini, 2007; Mizota, 2009a; Szpak et al., 2012a). As such, the inorganic nitrogen enriched with ^{15}N was washed away during acid treatment, causing distinctive differences between $\delta^{15}N_{ut}$ and $\delta^{15}N_{at}$ in the profiles where guano was abundant and weakening the relation between $\delta^{15}N_{ut}$ and guano input. IN/TN should be the controlling factor for $\Delta^{15}N$, in which IN was directly connected with guano input (Mizota and Naikatini, 2007; Mizota, 2009b) while TN was determined by both guano-N and algae-N.

4.2. Evidence from N-species analysis for the varying $\Delta^{15}N$

To verify the hypothesis mentioned above, an N-species test (mainly NH_4-N and NO_3-N; NO_2-N was found to be lower than the limit of detection and considered negligible in IN composition) was conducted in one heavily guano-impacted profile (MB6) and one less impacted (MB4) for comparison. We found that NH_4-N and NO_3-N were both very low (10^2 μg/g for NH_4-N and several μg/g for NO_3-N) in MB4 (Fig. 5). Assuming IN mainly comprises NH_4-N and NO_3-N, organic nitrogen (ON) was calculated by the following Eq.:

$$IN = NH_4\text{-}N + NO_3\text{-}N$$

$$ON = TN - IN.$$

The NO_3-N curve remains low and stable in the profile with a higher value layer from 30 to 15 cm and an abruptly high point at the surface, while the trend of NH_4-N resembles that of TN, ON and P. Since NH_4-N was the major inorganic N-species in MB4, it is clearly shown by correlation analysis that IN and ON, TN, and P were closely associated ($R \geq 0.5$, Fig. 6). According to TN measured on environmental media, the total nitrogen set in the sediments was attributed to guano-N and algae-N, and IN was mainly the result of uric acid decomposition and ammonia volatilization because algae-N hardly changes during depositional processes (Kennedy et al., 2005). In the otherwise oligotrophic waters of East Antarctica, algal biomass is highly dependent on the nutrient supply from penguin guano (Barrett et al., 2006b; Liu et al., 2007). Thus all four proxies should share the same pattern with depth in the profiles, and the significant correlation between IN (mainly form guano) and P (guano), TN (guano + algae), and ON (guano + algae) would become understandable. $\delta^{15}N$ in ON from guano (though very low in content) after the decomposition of uric acid basically stays on the same level as fresh guano (with a difference about 3‰, Bird et al., 2008), however, utilizing IN from guano alters the nitrogen isotopic composition of the algae in the sediments to a larger extent. According to Robinson (2001), assimilation of IN in plants involves isotope fractionations causing less ^{15}N enriched in algae than IN in the sediments (0–19‰ for NO_3-N and 9–18‰ for NH_4-N). $\delta^{15}N$ of penguin guano-affected algae in Antarctica has been investigated in several studies (algae[2] and algae[3] in Fig. 3B). Generally, the nitrogen isotope composition in the algae influenced by penguin guano is higher than that in unaffected algae we measured, but still lower than the $\delta^{15}N_{ut}$ in the ornithogenic sediments due to the preferential utilization of ^{14}N during nutrient intake process. Mizota (2009b) reported a similar case of seabird guano-affected plants with high $\delta^{15}N$, yet much lower than that of IN in the ornithogenic soils. Thus, ON in the sediments of our study should contain much lower $\delta^{15}N$ than IN, which is also corroborated by our $\Delta^{15}N$ data. As mentioned above, MB4 is much less impacted by seabird droppings compared with MB6, and the low IN/TN (generally below 10%) showed greater algae-N proportion. Thus, the absence of IN after HCl treatment would become negligible to the nitrogen isotopic composition of the bulk sediments due to the buffering effect of ON, which is less enriched in ^{15}N, resulting in minor $\Delta^{15}N$. The layer between 7 and 15 cm was characterized with very low OM, and a sharp decrease of TN from both guano and algae. With the weakening buffering effect from ON, IN/TN was much higher than the rest of the sediments in this layer, and IN loss could easily cause significant $\Delta^{15}N$ during acid treatment (Figs. 2, 5).

For MB6, NH_4-N and NO_3-N were present at much higher levels (10^3 μg/g). NO_3-N in MB6 gradually rose from less than 200 to about 3000 μg/g between the bottom and 26 cm depth, then it experienced a weak trough and rose again from 10 cm until an extremely high value at the surface exceeding 10,000 μg/g. NH_4-N was low at about 2000 μg/g below 18 cm, and grew to about 4000 μg/g in the upper layer. More NO_3-N (much higher than background data from Wada et al., 1981) was presented in MB6, indicative of stronger nitrification of NH_4-N. Kinetic isotope fractionation during nitrification would concentrate more ^{14}N in NO_3-N compared with NH_4-N (Mizota, 2009b), but $\delta^{15}N$ in IN was still high as $\Delta^{15}N$ suggested. Unlike MB4, IN in MB6 does not share the same pattern with TN, ON or P. This result seems to contradict our hypothesis that IN in the ornithogenic sediments derives primarily from guano, but in fact, it is the result from the transition of the surrounding environment. Profile MB6 is characterized by the high guano content in its lower depths. We also found the lower sediment

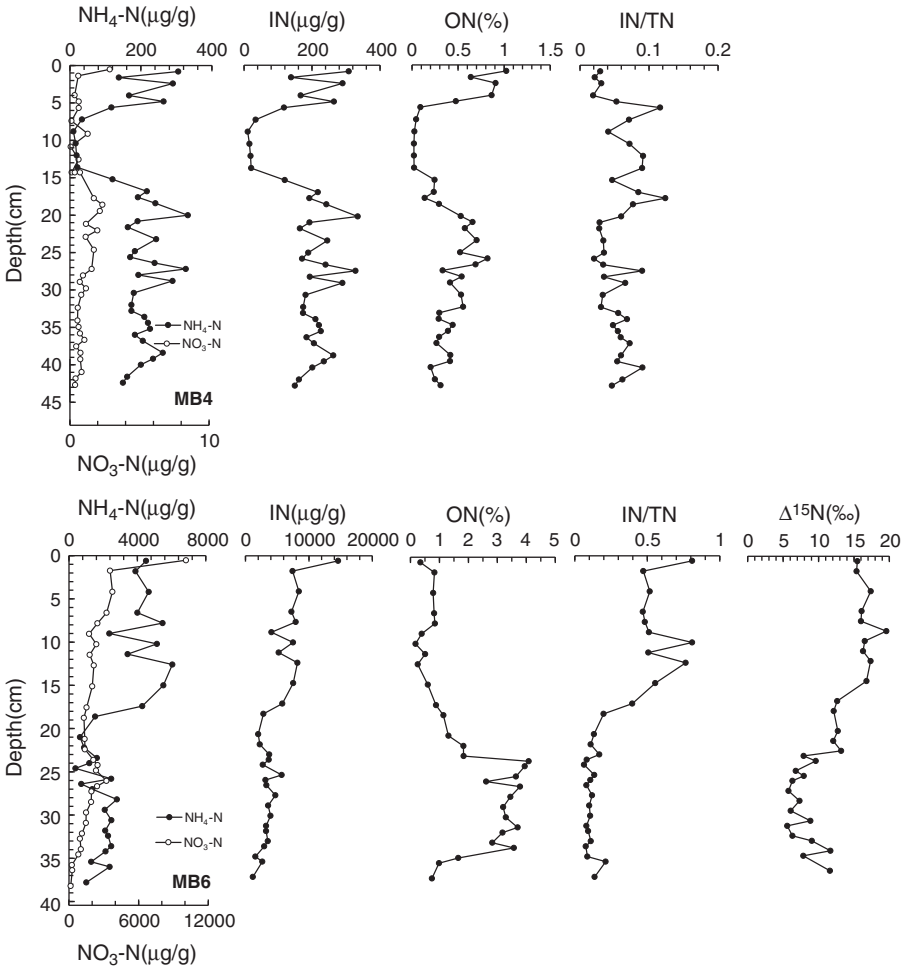

Fig. 5. N-species analysis of MB4 and MB6 sediment profiles.

layer of much higher WC than the upper layer (Fig. 2), which is corroborated with visual observation that the subsamples in the upper layer were apparently deposited in a relatively dry environment. Thus, we suggest that the lower layer represents the time span when the sampling site for MB6 was still filled with water and with a high penguin population density (Hu et al., 2013). Later, with the change of climate and continuous deposition of the sediments, the water in this site disappeared, together with a decreasing nesting penguin population which can be inferred from the TOC, TN and P curves. Moisture is an important factor that controls ammonia volatilization, because higher moisture would bond more ammonia in solution (Blunden and Aneja, 2008; Zhu et al., 2010). Compared with the upper arid layer, the lower layer as a wet depositional environment below 24 cm would reduce the volatilization of NH_3-N from the sediments in the form of ammonia, and in turn affect the breakdown of the deposited guano-N (Speir and Ross, 1984). Thus, though the guano input was greater in the lower layer, IN was relatively scarce instead, leading to the weak correlations between IN and TN, ON, and P. The key parameter IN/TN is generally much higher (can be as high as 50% in the upper layer) in MB6 due to the intense guano influence compared with MB4, and closely related with $\Delta^{15}N$ ($R = 0.82$; Fig. 7). This result was due to more IN in TN washed away by acid pretreatment, leading to larger $\Delta^{15}N$ in the profile. Interestingly, $\Delta^{15}N$ in MB6 was found to be inversely correlated with ON ($R = -0.86$; Fig. 7). As mentioned above, $\Delta^{15}N$ was determined not only by IN from guano, but also by TN with algae-N as an important component. We assumed that in the lower half of MB6 where guano was abundant, algae growth increased as well due to the sufficient nutrient supply (Schmitz et al., 2010). More algal biomass enhances

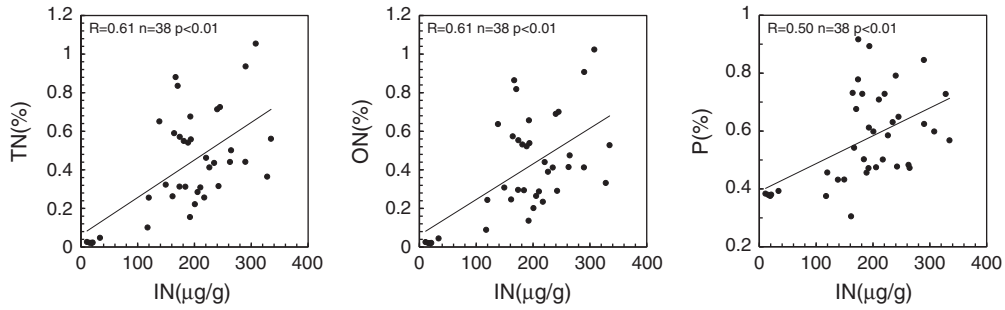

Fig. 6. Pearson correlation analysis showing the property of inorganic nitrogen in MB4.

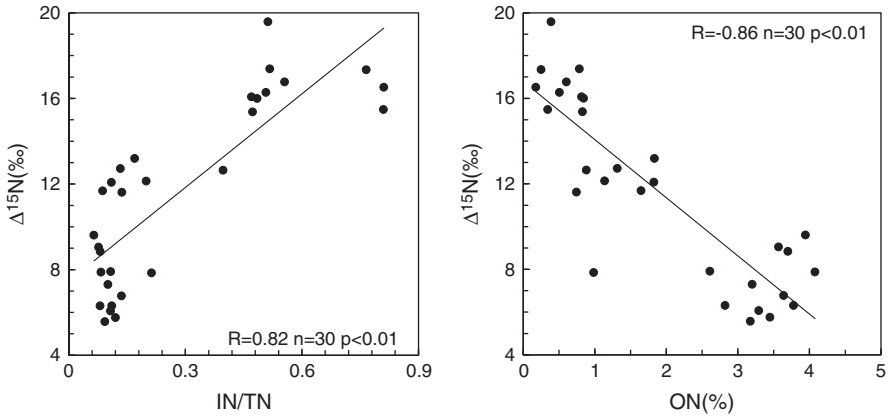

Fig. 7. Pearson correlation analysis of $\Delta^{15}N$–IN/TN and $\Delta^{15}N$–ON in MB6.

ON deposition in the sediments by adding organic nitrogen of lower $\delta^{15}N$. With no apparent increase of IN in the lower layer, algae-N would significantly decrease the isotopic impact of IN loss, and subsequently display strong buffering effects to avoid large $\Delta^{15}N$ from acid pretreatment. Under such circumstances, the upper layer with relatively low guano input would in turn be of higher IN/TN and $\Delta^{15}N$, and result in the inverse correlation between $\Delta^{15}N$ and ON.

With the evidence from MB4 and MB6, we suggest in CL2 where guano influence was similarly weak as in MB4, IN/TN should be low due to the little difference between $\delta^{15}N_{ut}$ and $\delta^{15}N_{at}$. BI, on the other hand, was similar to MB6: compared with the lower layer where guano input was scarce, rich algal biomass caused by sufficient nutrient supply from guano would lead to the decrease of IN/TN and $\Delta^{15}N$ in the upper layer, though IN may still be increasing. In profile CC which typically receives influence from guano alone, IN/TN was expected to be high (owing to the post-depositional processes), as we detected a significant $\Delta^{15}N$. Due to the relatively stable guano input and the absence of algal influence on TN, the curves of $\delta^{15}N_{ut}$ and $\delta^{15}N_{at}$ display parallel trends against depth in the profile.

4.3. Environmental implication of $\Delta^{15}N$

Our hypothesis on the difference of $\Delta^{15}N$ among profiles was supported by the comparison of N-species: IN was influenced by guano input in the sediments, and IN/TN was the key factor controlling the magnitude of $\Delta^{15}N$. Due to the high guano content in the profiles, MB6, BI and CC were found to have high $\Delta^{15}N$, while in MB4 and CL2 where guano influence was much weaker, $\Delta^{15}N$ was hardly detectable. Average values of $\Delta^{15}N$ in all the profiles were plotted with P and IN/TN in MB4 and MB6 for comparison (Fig. 8). Unlike $\delta^{15}N_{ut}$ (Fig. 4), $\Delta^{15}N$ clearly indicates the different gradients of guano influence among the profiles, and IN/TN of MB4 and MB6 are consistent with $\Delta^{15}N$. The relationship between $\Delta^{15}N$ and P (Fig. 8) does not contradict the data in MB6 (Fig. 7) because the histogram was a general comparison among profiles to a greater extent. $\Delta^{15}N$ as a parameter controlled by IN/TN (with IN directly from guano), is certainly connected with P in the mass. We propose that in the ornithogenic sediment profiles of East Antarctica where ammonia volatilization process was strong due to the extreme climate there, $\Delta^{15}N$ rather than $\delta^{15}N_{ut}$, can be an effective proxy to indicate the degree of guano input, and hence penguin influence. Actually, we believe this parameter would be applicable to ornithogenic sediments/soils from various locations as long as guano or other animal excrement is the bulk nitrogen source (the ideal situation is as in profile CC; sediments with more complex nitrogen composition, like MB6, need more specific discussion), and the ammonia volatilization remains the dominant nitrogen process in the deposition environment. This conclusion was based on the fact that nitrogen composition in fresh bird guano was generally similar with uric acid as the main component, and the strong ammonia volatilization of the decomposed uric acid, which can cause relatively high NH_4-N content in the bulk sediments, is the key factor for the occurrence of high $\delta^{15}N_{ut}$ and detectable $\Delta^{15}N$. At present, $\delta^{13}C$ and $\delta^{15}N$ have become routine analyses for geological carriers like ornithogenic sediments. Since acid treatment is mandatory for $\delta^{13}C$ test, $\delta^{15}N_{at}$ could be measured quite conveniently using the same processed samples, obtaining $\Delta^{15}N$ and giving a quick glance for the degree of guano influence. We believe in its potential and expect wider application of the parameter in other regions.

5. Summary and conclusion

The differences between $\delta^{15}N$ measured in both acid-treated and untreated sediments in five sediment profiles of Ross Sea region were

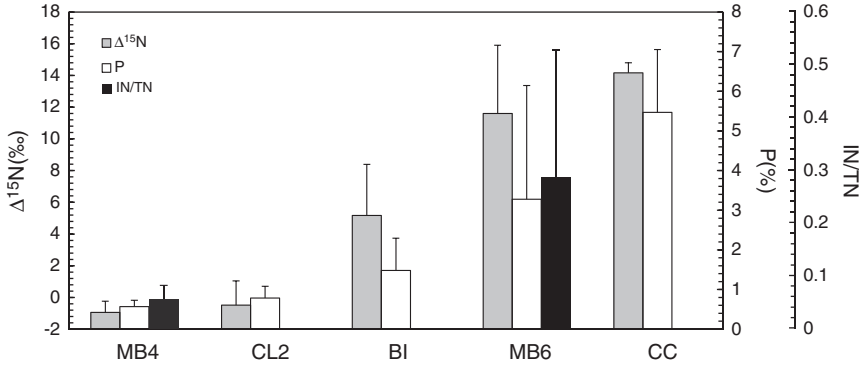

Fig. 8. The $\Delta^{15}N$ in comparison with P and IN/TN (only in MB4 and MB6) as a proxy for the influence of penguin guano on the sediments in the five profiles from the Ross Sea region (error bars indicate standard deviation).

explained based on the elemental/isotopic analysis of environmental media and N-species test in MB4 and MB6. We confirmed that IN/TN is the controlling factor for the calculated $\Delta^{15}N$ in the sediments influenced by penguin guano, and discussed the distribution pattern of IN/TN in MB6 versus depth, considering the input of algae-N in TN and the possible effect from changes in ambient environment on post depositional processes. Our results suggest that in East Antarctica, guano decomposition and ammonia volatilization strongly alter the isotopic composition of sedimentary nitrogen, so that $\delta^{15}N_{ut}$ can no longer sufficiently serve its role in paleoenvironmental studies, since there is no close relationship between $\delta^{15}N_{ut}$ and the P content, indicative of guano input into the ornithogenic sediments. By contrast, $\Delta^{15}N$ is not only a phenomena caused by different pretreatment methods, but also an effective proxy with clear environmental implications to indicate the degree of influence by penguins and their guano on ornithogenic sediments. Considering the fact that ammonia volatilization obviously occurred in the sediments and soils influenced by animal excrements, this new proxy may have the potential to be applied to these geological carriers from other regions, which are subject to intense post-depositional decomposition and ammonia volatilization. In order to confirm this finding, future research should be directed towards applying $\Delta^{15}N$'s implication under similar post-depositional process to the Ross Sea region.

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References

Ainley, D.G., 2002. The Adélie Penguin: Bellwether of Climate Change. Columbia University Press.
Baroni, C., Orombelli, G., 1994. Abandoned penguin colonies as Holocene paleoclimatic indicators in Antarctica. Geology 22, 23–26.
Barrett, J.E., Virginia, R.A., Hopkins, D.W., Aislabie, J., Bargagli, R., Bockheim, J.G., Campbell, I.B., Lyons, W.B., Moorhead, D.L., Nkem, J.N., 2006a. Co-variation in soil biodiversity and biogeochemistry in northern and southern Victoria Land, Antarctica. Antarct. Sci. 18 (04), 535–548.
Barrett, J.E., Virginia, R.A., Hopkins, D.W., Aislabie, J., Bargagli, R., Bockheim, J.G., Campbell, I.B., Lyons, W.B., Moorhead, D.L., Nkem, J.N., 2006b. Terrestrial ecosystem processes of Victoria Land, Antarctica. Soil Biol. Biochem. 38 (10), 3019–3034.
Bird, M.I., Tait, E., Wurster, C.M., Furness, R.W., 2008. Stable carbon and nitrogen isotope analysis of avian uric acid. Rapid Commun. Mass Spectrom. 22 (21), 3393–3400.
Bishop, J.L., Anglen, B.L., Pratt, L.M., Edwards, H.G.M., Des Marais, D.J., Doran, P.T., 2003. A spectroscopy and isotope study of sediments from the Antarctic Dry Valleys as analogues for potential paleolakes on Mars. Int. J. Astrobiol. 2 (4), 273–287.
Blais, J.M., Kimpe, L.E., McMahon, D., Keatley, B.E., Mallory, M.L., Douglas, M.S.V., Smol, J.P., 2005. Arctic seabirds transport marine-derived contaminants. Science 309 (5733), 445-445.
Blunden, J., Aneja, V.P., 2008. Characterizing ammonia and hydrogen sulfide emissions from a swine waste treatment lagoon in North Carolina. Atmos. Environ. 42 (14), 3277–3290.
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 (10), 1315–1321.
Broady, P.A., 1989. Broadscale patterns in the distribution of aquatic and terrestrial vegetation at three ice-free regions on Ross Island, Antarctica. Hydrobiologia 172 (1), 77–95.
Brodie, C.R., Casford, J.S.L., Lloyd, J.M., Leng, M.J., Heaton, T.H.E., Kendrick, C.P., Zong, Y., 2011a. Evidence for bias in C/N, $\delta^{13}C$ and $\delta^{15}N$ values of bulk organic matter, and on environmental interpretation, from a lake sedimentary sequence by pre-analysis acid treatment methods. Quat. Sci. Rev. 30, 3076–3087.
Brodie, C.R., Heaton, T.H., Leng, M.J., Kendrick, C.P., Casford, J.S.L., Lloyd, J.M., 2011b. Evidence for the biasing by pre-analysis acid preparation methods on $\delta^{15}N$ composition of terrestrial and aquatic organic materials. Rapid Commun. Mass Spectrom. 25, 1089–1099.
Campbell, I.B., Claridge, G.G.C., Bureau, S., 1966. A sequence of soils from a penguin rookery, Inexpressible Island, Antarctica. N. Z. J. Sci. 9, 361–372.
Caut, S., Angulo, E., Pisanu, B., Ruffino, L., Faulquier, L., Lorvelec, O., Chapuis, J.L., Pascal, M., Vidal, E., Courchamp, F., 2012. Seabird modulations of isotopic nitrogen on islands. PloS ONE 7 (6), e39125.
Dunton, K.H., 2001. $\delta^{15}N$ and $\delta^{13}C$ measurements of Antarctic Peninsula fauna: trophic relationships and assimilation of benthic seaweeds. Am. Zool. 41 (1), 99–112.
Emslie, S.D., Coats, L., Licht, K., 2007. A 45,000 yr record of Adélie penguins and climate change in the Ross Sea, Antarctica. Geology 35 (1), 61–64.
Griffiths, K., Michelutti, N., Blais, J.M., Kimpe, L.E., Smol, J.P., 2010. Comparing nitrogen isotopic signals between bulk sediments and invertebrate remains in High Arctic seabird-influenced ponds. J. Paleolimnol. 44 (2), 405–412.
Gu, B., Alexander, V., 1993. Estimation of N_2 fixation based on differences in the natural abundance of ^{15}N among freshwater N_2-fixing and non-N_2-fixing algae. Oecologia 96 (1), 43–48.
Hage, M.M., Uhle, M.E., Macko, S., 2007. Biomarker and stable isotope characterization of coastal pond-derived organic matter, McMurdo dry valleys, Antarctica. Astrobiology 7 (4), 645–661.
Hansson, L.A., Tranvik, L.J., 2003. Food webs in sub-Antarctic lakes: a stable isotope approach. Polar Biol. 26 (12), 783–788.
Hansson, S., Hobbie, J.E., Elmgren, R., Larsson, U., Fry, B., Johansson, S., 1997. The stable nitrogen isotope ratio as a marker of food-web interactions and fish migration. Ecology 78 (7), 2249–2257.
Hawke, D.J., Newman, J., 2007. Carbon-13 and nitrogen-15 enrichment in coastal forest foliage from nutrient-poor and seabird-enriched sites in southern New Zealand. N. Z. J. Bot. 45 (2), 309–315.
Hawke, D.J., Miskelly, C.M., 2009. ^{13}C and ^{15}N enrichment in snipe (*Coenocorypha spp.*) from islands across the New Zealand biogeographic region. J. R. Soc. New Zealand 39 (1), 35–42.
Hesslein, R.H., Capel, M.J., Fox, D.E., Hallard, K.A., 1991. Stable isotopes of sulfur, carbon, and nitrogen as indicators of trophic level and fish migration in the lower Mackenzie River basin, Canada. Can. J. Fish. Aquat. Sci. 48 (11), 2258–2265.
Hobson, K.A., 1999. Tracing origins and migration of wildlife using stable isotopes: a review. Oecologia 120 (3), 314–326.
Hu, Q., Sun, L., Xie, Z., Emslie, S.D., Liu, X., 2013. Increase in Penguin Populations During the Little Ice Age in the Ross Sea. Scientific reports 3.
Huang, T., Sun, L., Long, N., Wang, Y., Huang, W., 2013. Penguin tissue as a proxy for relative krill abundance in East Antarctica during the Holocene. Scientific reports 3.
Kazama, K., Murano, H., Tsuzuki, K., Fujii, H., Niizuma, Y., Mizota, C., 2012. Input of seabird-derived nitrogen into rice-paddy fields near a breeding/roosting colony of the Great Cormorant (*Phalacrocorax carbo*), and its effects on wild grass. Appl. Geochem. 28, 128–134.
Kelly, J.F., 2000. Stable isotopes of carbon and nitrogen in the study of avian and mammalian trophic ecology. Can. J. Zool. 78 (1), 1–27.
Kennedy, P., Kennedy, H., Papadimitriou, S., 2005. The effect of acidification on the determination of organic carbon, total nitrogen and their stable isotopic composition in algae and marine sediment. Rapid Commun. Mass Spectrom. 19 (8), 1063–1068.
Kielland, K., 1994. Amino acid absorption by arctic plants: implications for plant nutrition and nitrogen cycling. Ecology 75 (8), 2373–2383.
Lee, Y.I., Lim, H.S., Yoon, H.I., 2009. Carbon and nitrogen isotope composition of vegetation on King George Island, maritime Antarctic. Polar Biol. 32 (11), 1607–1615.
Lindeboom, H.J., 1984. The nitrogen pathway in a penguin rookery. Ecology 269–277.
Liu, X., Nie, Y., Sun, L., Emslie, S.D., 2013. Eco-environmental implications of elemental and carbon isotope distributions in ornithogenic sediments from the Ross Sea region, Antarctica. Geochim. Cosmochim. Acta 117, 99–114.
Liu, X., Sun, L., Xie, Z., Yin, X., Zhu, R., Wang, Y., 2007. A preliminary record of the historical seabird population in the Larsemann Hills, East Antarctica, from geochemical analyses of Mochou Lake sediments. Boreas 36 (2), 182–197.
Liu, X.D., Li, H.C., Sun, L.G., Yin, X.B., Zhao, S.P., Wang, Y.H., 2006. $\delta^{13}C$ and $\delta^{15}N$ in the ornithogenic sediments from the Antarctic maritime as palaeoecological proxies during the past 2000 yr. Earth Planet. Sci. Lett. 243 (3), 424–438.
Lorenzini, S., Baroni, C., Fallick, A.E., Baneschi, I., Salvatore, M.C., 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 (4), 911–919.
Lorrain, A., Savoye, N., Chauvaud, L., Paulet, Y.M., Naulet, N., 2003. Decarbonation and preservation method for the analysis of organic C and N contents and stable isotope ratios of low-carbonated suspended particulate material. Anal. Chim. Acta 491 (2), 125–133.
Marra, P.P., Hobson, K.A., Holmes, R.T., 1998. Linking winter and summer events in a migratory bird by using stable-carbon isotopes. Science 282 (5395), 1884–1886.
McDermott, F., 2004. Palaeo-climate reconstruction from stable isotope variations in speleothems: a review. Quat. Sci. Rev. 23 (7), 901–918.
Michelutti, N., Keatley, B.E., Brimble, S., Blais, J.M., Liu, H., Douglas, M.S.V., Mallory, M.L., Macdonald, R.W., Smol, J.P., 2009a. Seabird-driven shifts in Arctic pond ecosystems. Proc. R. Soc. B Biol. Sci. 276 (1656), 591–596.
Michelutti, N., Liu, H., Smol, J.P., Kimpe, L.E., Keatley, B.E., Mallory, M., Macdonald, R.W., Douglas, M.S.V., Blais, J.M., 2009b. Accelerated delivery of polychlorinated biphenyls (PCBs) in recent sediments near a large seabird colony in Arctic Canada. Environ. Pollut. 157 (10), 2769–2775.
Michelutti, N., Simonetti, A., Briner, J.P., Funder, S., Creaser, R.A., Wolfe, A.P., 2009c. Temporal trends of pollution Pb and other metals in east-central Baffin Island inferred from lake sediment geochemistry. Sci. Total Environ. 407 (21), 5653–5662.
Minagawa, M., Wada, E., 1986. Nitrogen isotope ratios of red tide organisms in the East China Sea: a characterization of biological nitrogen fixation. Mar. Chem. 19 (3), 245–259.

Minami, H., Minagawa, M., Ogi, H., 1995. Changes in stable carbon and nitrogen isotope ratios in sooty and short-tailed shearwaters during their northward migration. Condor 565–574.
Mincks, S.L., Smith, C.R., Jeffreys, R.M., Sumida, P.Y.G., 2008. Trophic structure on the West Antarctic Peninsula shelf: Detritivory and benthic inertia revealed by $\delta^{13}C$ and $\delta^{15}N$ analysis. Deep Sea Res. Part II: Top. Stud. Oceanogr. 55 (22), 2502–2514.
Mizota, C., Naikatini, A., 2007. Nitrogen isotope composition of inorganic soil nitrogen and associated vegetation under a sea bird colony on the Hatana islands, Rotuma Group, Fiji. Geochem. J. 41, 297–301.
Mizota, C., 2009a. Temporal variations in the concentration and isotopic signature of ammonium- and nitrate-nitrogen in soils under a breeding colony of Black-tailed Gulls (Larus crassirostris) on Kabushima Island, northeastern Japan. Appl. Geochem. 24, 328–332.
Mizota, C., 2009b. Nitrogen isotopic patterns of vegetation as affected by breeding activity of Black-tailed Gull (*Larus crassirostris*): a coupled analysis of feces, inorganic soil nitrogen and flora. Appl. Geochem. 24 (11), 2027–2033.
Mizutani, H., Wada, E., 1988. Nitrogen and carbon isotope ratios in seabird rookeries and their ecological implications. Ecology 340–349.
Mizutani, H., Hasegawa, H., Wada, E., 1986. High nitrogen isotope ratio for soils of seabird rookeries. Biogeochemistry 2 (3), 221–247.
Mizutani, H., Kabaya, Y., Moors, P.J., Lyon, G.L., 1991a. Nitrogen isotope ratios identify deserted seabird colonies. The Auk 108 (4), 960–964.
Mizutani, H., Kabaya, Y., Wada, E., 1985. Ammonia volatilization and high $^{15}N/^{14}N$ ratio in a penguin rookery in Antarctica. Geochem. J. 19 (6), 323–327.
Mizutani, H., Kabaya, Y., Wada, E., 1991b. Linear correlation between latitude and soil ^{15}N enrichment at seabird rookeries. Naturwissenschaften 78 (1), 34–36.
Monaghan, A.J., Bromwich, D.H., Powers, J.G., Manning, K.W., 2005. The climate of the McMurdo, Antarctica, Region as represented by one year of forecasts from the Antarctic Mesoscale Prediction System. J. Clim. 18 (8), 1174–1189.
Naito, Y.I., Honch, N.V., Chikaraishi, Y., Ohkouchi, N., Yoneda, M., 2010. Quantitative evaluation of marine protein contribution in ancient diets based on nitrogen isotope ratios of individual amino acids in bone collagen: an investigation at the Kitakogane Jomon site. Am. J. Phys. Anthropol. 143 (1), 31–40.
Nie, Y., Liu, X., Sun, L., Emslie, S.D., 2012. Effect of penguin and seal excrement on mercury distribution in sediments from the Ross Sea region, East Antarctica. Sci. Total Environ. 433, 132–140.
Peterson, B.J., Fry, B., 1987. Stable isotopes in ecosystem studies. Annu. Rev. Ecol. Syst. 433, 293–320.
Polito, M., Emslie, S.D., Walker, W., 2002. A 1000-year record of Adélie penguin diets in the southern Ross Sea. Antarct. Sci. 14 (04), 327–332.
Robinson, D., 2001. $\delta^{15}N$ as an integrator of the nitrogen cycle. Trends Ecol. Evol. 16 (3), 153–162.
Robinson, R.S., Kienast, M., Albuquerque, A.L., Altabet, M., Contreras, S., Holz, R.D.P., Dubois, N., Francois, R., Galbraith, E., Hsu, T.C., 2012. A review of nitrogen isotopic alteration in marine sediments. Paleoceanography 27 (4) PA4203.
Rozanski, K., Johnsen, S.J., Schotterer, U., Thompson, L.G., 1997. Reconstruction of past climates from stable isotope records of palaeo-precipitation preserved in continental archives. Hydrol. Sci. J. 42 (5), 725–745.
Schmidt, M.W.I., Gleixner, G., 2004. Carbon and nitrogen isotope composition of bulk soils, particle-size fractions and organic material after treatment with hydrofluoric acid. Eur. J. Soil Sci. 56 (3), 407–416.
Schmidt, S., Dennison, W.C., Moss, G.J., Stewart, G.R., 2004. Nitrogen ecophysiology of Heron Island, a subtropical coral cay of the Great Barrier Reef, Australia. Funct. Plant Biol. 31 (5), 517–528.
Schmitz, O.J., Hawlena, D., Trussell, G.C., 2010. Predator control of ecosystem nutrient dynamics. Ecol. Lett. 13 (10), 1199–1209.
Speir, T., Cowling, J.C., 1984. Ornithogenic soils of the Cape Bird Adélie penguin rookeries, Antarctica. 1. Chemical properties. Polar Biol. 2 (4), 199–205.
Speir, T.W., Ross, D.J., 1984. Ornithogenic soils of the Cape Bird Adélie penguin rookeries, Antarctica. 2. Ammonia evolution and enzyme activities. Polar Biol. 2 (4), 207–212.
Strauch, G., Haendel, D., Maaß, I., Mühle, K., Runge, A., 2011. Isotope variations of hydrogen, carbon and nitrogen in florae from the Schirmacher Oasis, East Antarctica. Isot. Environ. Health Stud. 47 (3), 280–285.
Sun, L., Emslie, S.D., Huang, T., Blais, J.M., Xie, Z., Liu, X., Yin, X., 2013. Vertebrate records in polar sediments: biological responses to past climate change and human activities. Earth Sci. Rev. 126, 147–155.
Sun, L., Xie, Z., Zhao, J., 2000. Palaeoecology: a 3,000-year record of penguin populations. Nature 407 (6806), 858-858.
Szpak, P., Longstaffe, F.J., Millaire, J.F., White, C.D., 2012a. Stable isotope biogeochemistry of seabird guano fertilization: results from growth chamber studies with Maize (Zea Mays). PLoS ONE 7 (3), e33741.
Szpak, P., Millaire, J.F., White, C.D., Longstaffe, F.J., 2012b. Influence of Seabird guano and Camelid dung fertilization on the nitrogen isotopic composition of field-grown maize (Zea Mays). J. Arch. Sci. 39, 3721–3740.
Ugolini, F.C., 1972. Ornithogenic Soils of Antarctica. In: Llano, A. (Ed.), Antarctic Terrestrial Biology, vol. 20. AGU, Washington, D.C., pp. 181–193.
Wada, E., Mizutani, H., Minagawa, M., 1991. The use of stable isotopes for food web analysis. Crit. Rev. Food Sci. Nutr. 30 (4), 361–371.
Wada, E., Shibata, R., Torii, T., 1981. ^{15}N abundance in Antarctica: origin of soil nitrogen and ecological implications. Nature 292, 327–329.
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 (05), 427–438.
Zhu, R., Sun, J., Liu, Y., Gong, Z., Sun, L., 2010. Potential ammonia emissions from penguin guano, ornithogenic soils and seal colony soils in coastal Antarctica: effects of freezing-thawing cycles and selected environmental variables. Antarct. Sci. 23 (1), 78.