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# Ornithogenic Gelisols (Cryosols) from Maritime Antarctica: Pedogenesis, Vegetation, and Carbon Studies

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#### ABSTRACT

In terrestrial ecosystems of Maritime Antarctica (King George Island), the transference of primary marine production to the land promoted by penguins (Pygoscelis adeliae) and other birds, appears to influence soil formation and chemical weathering to a greater extent than formerly predicted. This paper summarizes the results of pedological investigations on the vicinity of the American Pieter J. Lenie Field Station (62°10' S, 58°28' W), discussing soil formation processes related to vegetation succession in the studied area. Soil organic matter (SOM) accumulation and associated phosphatization are marked soil-forming processes in ice-free areas once colonized by penguins. Also there is a high correlation between soil development and vegetation patterns. Nutrient supply in these cryogenic soils is affected by low pH following nitrification and high contents of P, K, Ca, and Mg due to seabirds' inputs. Lithic Umbriturbels and Glacic Haploturbels are the most common ornithogenic soils, followed by Lithic Fibristels and Psammentic Aquiturbels. In all soils phosphatization and ornithogenesis occurs in varying degrees. However, the recent Gelisols order of Soil Taxonomy does not consider the influence of ornithogenesis or phosphatization in its framework, so that a more detailed classification of such soils is not possible.

**TRYOGENIC** SOILS (Gelisols—Soil Taxonomy, Cryosols-FAO) affected by rich nutrient inputs from penguin rookeries, have been reported in several studies in Antarctica (Tedrow and Ugolini, 1966; McCraw, 1967; Ugolini, 1972; Myrcha et al., 1983; Tatur and Myrcha, 1984; Campbell and Claridge, 1987; Blume et al., 2002; Schaefer et al., 2004). With deglaciation and the resulting glacio-isostatic uplift during the Holocene, a large number of penguin rookeries moved from upland areas onto newly exposed terraces, closer to the emerging coast, and on rock outcrops (Tatur et al., 1996). Subsequentially, abandoned sites became vegetated and subject to pedogenesis. In these areas of former rookeries, a particular type of Cryogenic soil evolved, tentatively classified as Ornithogenic Cryosols, based on peculiar physicochemical attributes related to bird excreta accumulation and transformation in breeding places along the Antarctic coast (Tatur, 1997). These soils are generally characterized by low surface pH, very high P contents, high Al<sup>3</sup> availability, and variable, but usually high, amounts of exchangeable Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup>. Large areas of aban-

Published in Soil Sci. Soc. Am. J. 70:1370–1376 (2006).
Pedology
doi:10.2136/sssaj2005.0178
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677 S. Segoe Rd., Madison, WI 53711 USA

doned penguin rockeries and Skua (*Catharacta spp.*) nesting sites present fossil soils with clear ornithogenic features, such as nesting pebbles and thick histic/organic overlying horizons (Schaefer et al., 2004).

The active nesting area is entirely devoid of vegetation, due to toxic overmanuring and trampling by penguins (Tatur et al., 1996); on the other hand, marginal areas and abandoned sites with moderate to high abundance of nutrients show more diverse vegetation. Several studies performed by the Polish scientists in Maritime Antarctica have proved that guano leachates strongly react with the underling bedrock, forming a layer of phosphatized material that can be subdivided into genetic horizons of different mineral composition (Tatur and Barczuc, 1983; Tatur and Myrcha, 1993a). This particular soil forming process, called phosphatization (Schaefer et al., 2004), is possible due to the intensive seasonal input of P-rich organic material during the summer. Tatur and Myrcha (1993b) estimated  $\sim 10$  kg m<sup>-2</sup> of bird droppings (dry weight) are added each year. On these sites, an oasis of vegetation cover develops, where one can observe greater biological activity, higher temperature, and thicker active layer (Myrcha et al., 1983).

The understanding of physical and chemical weathering, organic matter dynamics, and biogeochemical cycling in polar environments is very important, not only to the environmental preservation, but also to a better understanding of pedogenesis in extreme cold environments. Little is known regarding soil C dynamics in Antarctic soils and its role in global C cycle, compared with soil environments from elsewhere. An understanding of the C cycle in ornithogenic soils of Antarctica, where C immobilization is locally high, is important for understanding the effects of global warming on the coastal Antarctic environment.

The aim of this study is to characterize the vegetation and pedogenesis of a toposequence of soils under the influence of penguins on abandoned rookery ecosystems on King George Island, emphasizing the biogeochemical cycling of nutrients, the main processes involved in their genesis and their classification.

## MATERIALS AND METHODS

#### **Study Sites**

The studied soils are located in King George Island, Admiralty Bay, near the American Pieter J. Lenie Field Station, (62°10′ S, 58°28′ W), also known as "Copacabana." The parent materials are ground moraines of varying depths, overlaying weathered volcanic rocks, mainly andesitic basalts, and outwash gravels from upland, older moraines of the Ecology Glacier. The

**Abbreviations:** DSC, differential scanning calorimetry; OC, organic matter; SOM, soil organic matter.

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mean annual precipitation is 367 mm, but the actual soil water regime is variable due to abundant melting water from upland permafrost during the summer. Monthly temperatures range from -6.4 in July, to  $2.3^{\circ}$ C in February (meteorological data from nearby Comandante Ferraz station). The temperature stays above freezing point throughout the summer, so that plant communities, mainly mosses, lichens, and algae, can establish and grow vigorously during this period (Schaefer et al., 2004).

Soil P1 (Glacic Haploturbels) is located at the highest level, at about 98 m above sea, on a ground moraine with no apparent influence of ornithogenesis and permafrost present at the depth of 70 cm. Soil P2 (Lithic Umbriturbels), at a height of 64 m above sea, is located on a former lateral moraine covered by debris from an upland Petrel nesting area, with permafrost at 70- to 75-cm depths; Soil P3 (Lithic Fibristels) is located on a flat ground moraine, near a present-day penguin rookery; the lowermost Soil P4 (Psammentic Aquiturbels) is located in a hydromorphic area, at 28 m above sea level, on the lower terrace just below the present-day penguin rookery. Permafrost level is lower at P3 and P4, due to high organic C (OC) accumulation and greater insulation from summer heat. The active layer thickness at P1, at the highest level, was apparently shallower than in the others (usually at 60–65 cm from the surface).

#### Methods

Soil surveying and sampling were performed during the austral summer, between December 2002 and January 2003, enabling detailed soil and geomorphology mapping. The landscape is typical of most ice-free, vegetated areas on the west side of Admiralty Bay, where land exposure is quite old (6000 YBP). Sampling pits were dug to the depth of permafrost, followed by morphological description following recommendations of Bockheim and Tarnocai (1998). Samples of soil horizons were collected from the pit face at 10-cm intervals, down to permafrost level, kept refrigerated and submitted to chemical and physical analysis. The assessment of particle size was based on wet sieving and ultrasonic dispersion adapted from EMBRAPA (1997). The clay and silt fractions were separated by sedimentation, followed by siphoning the <0.002-mm fraction (clay). All routine analytical chemical and physical determinations were obtained using standard procedures (Klute, 1986; EMBRAPA, 1997); the samples were air-dried and passed through a 2-mm plastic sieve. Exchangeable Ca<sup>2+</sup> and Mg<sup>2</sup> were extracted with 1 M KCl and determined by atomic absorption. Other elements ( $Fe^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ , and  $K^+$ ) were extracted with 0.05 *M* HC1 + 0.025 *M* H<sub>2</sub>SO<sub>4</sub>, and K<sup>+</sup> determined by flame photometry, whereas microelements were determined using inductively coupled spectroscopy. Base sum (BS) was computed as the sum of  $Ca^{2+}$ ,  $K^+$ , and  $Mg^{2+}$  and  $Na^+$ . Ammonium was not determined, though significant, due to losses during previous air-dry sample preparation. Soil textural classes were determined using the soil textural chart of the Keys of Soil Taxonomy (Soil Survey Staff, 2003). The chemical fractioning and purification of soil humic substances were done according to Swift (1996), although samples were not demineralized. Organic C was determined by the wet combustion method of Nelson and Sommers (1982), and also by Yoemens and Bremner (1988). Thermodecomposition curves of humic acids (HA) were obtained by a TGA-50 SHIMADZU thermogravimetric analyzer (Shimadzu, Kyoto, Japan) using 3.3 ± 0.1-mg samples over static air according Benites et al. (2005b). The initial weight was stabilized at 30°C and heating curve was obtained, by 5°C min<sup>-1</sup> increments, to 105°C, with a holding time of 10 min, followed by heating at 5°C min<sup>-1</sup> rate up to 650°C. The first derivative curves (DTG) were obtained from the thermodecomposition curves. The weight loss at 105°C was considered as sample moisture. After complete burning, the residue was considered as the ash content. The weight loss between 105 and 350°C and between 350 and 650°C was determined. The ratio of these two thermo-decomposition events was calculated and defined as a thermogravimetric index (TGI) (Benites et al., 2005b).

Differential scanning calorimetry (DSC) measurements were performed at the same temperature program described for TG by means of Shimadzu DSC 60 using  $1 \pm 0.1$  mg of HA sample. Measurements were made in an open aluminum crucible with a flow rate of oxygen of 20 mL min<sup>-1</sup>, and an empty pan was used as reference.

The elemental composition of the humic acid fraction was performed by PerkinElmer CHNS 2400 (PekinElmer, Wellesley, MA), and the composition was corrected to a dry and ash free basis. The atomic ratios of C/N, H/C, and O/C were calculated based on the elemental composition thus obtained.

## **RESULTS AND DISCUSSION**

### Soil Morphology and Physical Characteristics

Ornithogenic Cryosols were distinguished by their greater soil depth, thicker active layer, presence of small pebbles down to 30 cm (P-2 and P-3), and brownish humified upper horizons and histic horizons, compared with non-ornithogenic counterparts (P-1). Deeper Ornithogenic Cryosols occur in gentle slopes, on stable sites, long abandoned by penguins, where vegetation attains its maximum height and diversity. Cryoturbation features are also present, with downward mixing of organic and mineral horizons, forming wedges and convoluted horizons. It seems possible to estimate a relative degree of development of these soils based on histic horizon thickness and humification degree of SOM.

P-1 (Glacic Haploturbels) is localized at the upper level of the marginal moraine, and is virtually free of nutrient inputs from penguin droppings. P-1 is a relatively deep soil, covered by sparse Usnea sp. and occasional Deschampsia antarctica. The medium-sized granular structure observed appears to be associated with fine particle flocculation, medium granular structure is typical of Cryosols and can be formed due to freeze-thaw cycles when compression and rapid desiccation of soil aggregates occurs (Schaefer et al., 2004). In the upper part of Profile 2 (Lithic Umbriturbels), the topsoil is formed by a thin layer of fibric remains of dead mosses mixed with loose rock fragments, colonized by mosses and *Deschampsia* (Fig. 1). From 10 to 40 cm it is composed of a stony layer with hydromorphic, gleying features, followed by a dark humified material mixed with pebbles at 40 to 60 cm, with fibric material. There, a possible buried horizon occurs. Profile 3 (Lithic Fibristels) appeared to be the most developed, with uniform color and texture. The upper horizon is formed by fibric remains of mosses, whereas in deeper horizons, organic matter is partly humified, and brownish colored. It is almost exclusively colonized by mosses, due to its poor drainage. However, no clear gleying is noticed.

Profile 4 (Psammentic Aquiturbels) is located close to a melt water channel beneath the present day rookery and above the marine terrace; it does not show ornithogenic features such as nest pebbles, though its chemical data show a clear influence of lateral inputs of guano leachates from upland sources.



Fig. 1. Landscape position of Profile 2 (Copa-2).

The soils have a loamy to loamy sand texture, with silt contents up to 39 g kg<sup>-1</sup>, and clay contents varying between 10 and 20 g kg<sup>-1</sup> (Table 1). These figures are influenced by the low dispersibility of clays in these Cryosols, due to high flocculation and salinity.

#### **Vegetation Distribution**

The successional stages of vegetation observed in the area are consistent with previous observations at nearby

 Table 1. Textural characterization, classification, and color of the profiles.

Horiz.	Color	CS	FS	Silt	Clay	Texture
		g	$kg^{-1}$ —			
P-1						
0-10	10YR5/2	36	6	Haplotu 38	20	loam
10-20	10YR2/2	30	9	35	26	loam
20-30	10YR3/2	32	10	34	24	loam
30-40	10YR3/2	31	10	35	24	loam
40-50	10YR3/2	37	8	33	22	loam
50-60	10YR3/2	32	8	39	21	loam
P-2			Lithic	Umbritu	rbels	
0-10	10YR3/2	59	11	21	9	sandy-Loan
10-20	10YR4/2	51	14	26	9	sandy-Loan
20-30	10YR4/2	49	18	24	9	sandy-Loan
30-40	10YR4/2	56	8	26	10	sandy-Loan
40-50	7.5YR3/3	48	15	24	13	sandy-Loan
50-60	7.5YR3/3	53	10	24	13	sandy-Loan
P-3			Lithi	c Fibrist	els	
0-10	10YR3/3	41	12	27	20	Loam
10-20	10YR3/2	46	11	27	16	sandy-Loan
20-30	10YR2/2	53	11	24	12	sandy-Loan
30-40	7.5YR4/3	41	11	31	17	Loam
40-50	10YR4/3	39	12	34	15	Loam
P-4		F	sammer	ntic Aqui	iturbels	
10-20	10YR3/3	72	3	14	11	Loamy-sand
20-30	10YR3/1	63	9	19	9	Sandy-Loan
30-40	10YR3/1	68	8	14	10	Loamy-sand
40-50	10YR3/1	72	4	15	9	Loamy-sand

CS: Coarse sand (0.2-2 mm); FS: Fine Sand (0.05-0.2 mm); Silt (0.002-0.05 mm); Clay (<0.002 mm).

Stranger Point (Tatur et al., 1996); it begins with a dense mat of green algae *Prasiola crispa*, and crustaceous, epilithic lichens at some distance from the present-day rookeries. In the wetter parts, these are replaced by various types of mosses, especially *Bryum sp.* and various *Polytrichales*, associated with cyanobacteria, close to local depressions and areas of lower redox potentials; welldrained sites are preferentially invaded by higher plants (*Deschampsia antarctica* and *Colobanthus quitensis*). Fruticose lichens (*Usnea spp.*) locally colonize pebbles and rock fragments on sites with varying degree of ornithogenis. Shallow, non-ornithogenic soils and rock outcrops prevail in upland areas exposed to wind ablation. These areas are exclusively colonized by *Usnea spp.* and various crustose lichens.

#### **Soil Chemistry**

At P-1, pH is high, with much greater  $Ca^{2+}$  and  $Mg^{2+}$  values and less exchangeable K<sup>+</sup> than lower soils, due to limited input of seabird droppings (Table 2; mainly Skuas). Low pH values are present in all ornithogenic Gelisols, thus, high guano inputs create an acid environment, which becomes progressively less acid with soil development, following rookery abandonment. The lowest pH values were found at sites recently abandoned (Fig. 2; due to high nitrification degree). Guano is initially alkaline, but microbial degradation generates acidity; however when the sites are abandoned and no fresh guano further input is observed, mineral weathering and high amounts of OC can neutralize part of the acidity, resulting in a more buffered soil.

The Na<sup>+</sup> levels were generally high due to sea saltspray and little leaching due to local aridity. Ornithogenic soils have similar amounts of exchangeable  $Ca^{2+}$ ,  $Mg^{2+}$ , and K<sup>+</sup>, either in recently abandoned areas, or areas subject to lateral movement of bioavailable nutri-

Table 2. Selected chemical properties of ornithogenic Cyosols of King George Island.†

													Micronutrients				
Horiz.	pl	H	Р	K	Na	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	H+Al	BS	CEC	Ν	P-rem	Zn	Fe	Mn	Cu
	H <sub>2</sub> O	KCI	mş	g dm <sup>-3</sup>				— cmol	dm <sup>-3</sup> —	_		%	mg $L^{-1}$		— cmol <sub>c</sub>	$dm^{-3}$	
P-1	Glacic	Haplot	turbels														
0-10	5.9	4.4	185.3	228	396	15.42	5.00	0.2	4.6	22.72	22.92	0.06	33.7	0.88	100.60	80.60	12.97
10-20	7.1	6.1	392.2	244	388	7.83	4.98	0.0	0.0	15.12	15.12	0.01	37.7	0.62	123.80	91.00	17.91
20-30	7.8	5.7	290.3	224	376	8.18	2.69	0.0	0.0	13.07	13.07	0.00	38.3	0.49	131.60	61.10	15.32
30-40	8.2	6.3	245.9	216	320	7.79	4.6	0.0	0.0	14.33	14.33	0.00	38.5	0.36	127.40	64.10	15.33
40-50	8.0	6.4	323.8	244	380	7.86	4.45	0.0	0.0	14.58	14.58	0.00	40.6	0.47	135.90	57.30	17.31
50-60	8.5	6.6	297.7	232	344	7.87	4.42	0.0	0.0	14.38	14.38	0.00	38.4	0.18	131.80	55.50	15.77
P-2	Lithic	Umbrit	urbels														
0-10	4.8	3.3	414.2	200	232	3.58	2.56	5.6	11.9	7.66	13.26	0.08	26.6	3.91	150.80	8.60	10.65
10-20	4.5	3.2	712.4	260	216	2.23	1.15	6.6	28.0	4.98	11.58	0.08	30.9	3.59	158.60	5.50	12.62
20-30	4.3	3.0	1033.6	280	204	1.79	0.72	5.4	33.3	4.12	9.52	0.08	35.9	3.52	165.40	5.60	12.22
30-40	4.2	3.0	945.9	236	152	1.75	0.74	5.2	34.7	3.75	8.95	0.10	38.0	2.42	170.30	5.20	10.56
40-50	4.2	3.3	1118.6	164	90	1.41	0.6	3.8	22.8	2.82	6.62	0.12	37.7	1.48	190.70	5.40	15.42
50-60	4.1	3.2	722.2	170	100	1.67	0.71	4.2	33.0	3.24	7.44	0.09	34.0	2.15	172.10	4.80	12.67
P-3	Lithic	Fibriste	els														
0-10	5.0	3.9	933.0	144	184	3.32	1.39	1.8	18.8	5.88	7.68	0.17	32.8	2.43	117.20	10.30	5.67
10-20	4.8	3.4	561.9	196	162	3.70	1.34	3.8	24.4	6.24	10.04	0.10	39.8	1.57	164.30	9.40	6.41
20-30	4.6	3.4	695.9	198	204	3.85	1.52	4.6	23.8	6.77	11.37	0.15	36.2	1.56	182.90	8.30	6.68
30-40	4.6	3.4	658.4	182	146	3.31	1.11	3.8	29.4	5.52	9.32	0.17	28.0	1.42	151.50	8.20	5.87
40-50	4.3	3.3	950.3	196	174	3.69	1.21	6.2	38.9	6.16	12.36	0.13	23.5	1.58	177.50	8.20	5.32
P-4	Psamn	nentic A	Aquiturbel	s													
10-20	4.2	3.2	819.9	150	146	1.16	0.59	6.8	22.8	2.76	9.56	0.10	34.6	0.84	129.00	1.80	6.33
20-30	4.2	3.1	1002.2	162	164	1.14	0.55	6.8	25.7	2.81	9.61	0.04	29.9	0.91	150.00	1.80	7.22
30-40	4.1	3.0	673.4	150	158	1.31	0.62	8.8	25.7	3.00	11.80	0.04	38.9	0.89	162.20	2.00	5.38
40-50	4.1	3.2	487.3	168	128	1.36	0.65	9.8	24.4	3.00	12.80	0.10	35.1	0.76	169.00	2.30	4.63

† All Values are based on the mean of three replicates; CEC: Cation exchange capacity; P. extr: Mehlich-1; BS: Base Sum (Ca<sup>++</sup>+Mg<sup>++</sup>+K<sup>+</sup>+Na<sup>+</sup>).

ents enhanced by ornithogenesis; P-4 showed very high values, which can be related to a till locally richer in basaltic rock fragments in this area, compared with present rookeries, where andesitic fragments are more commonly observed. In the absence of ornithogenic activity, soil chemical weathering is less pronounced and soils present chemical and mineralogical characteristics greatly influenced by the parent material (Simas et al., 2004). In this case, high pH, high  $Ca^{2+}$  and  $Mg^{2+}$  levels, and salinity, are usually observed.

The areas of former penguin rookeries present relic soils with clear ornithogenic features. There, P levels are greater near the present-day rookery (range 562– 1119 mg dm<sup>-3</sup>). P distribution along the profile is irregular; P-2 and P-3 have grater values in deeper layers, which indicate a buried horizon, P-1 has high P values in the uppermost layer, indicating recent ornithogenic influence (Fig. 3). The ornithogenic soils have high  $Al^{3+}$  saturation in the topsoil, increasing with depth for all profiles with spodic features, showing that organic

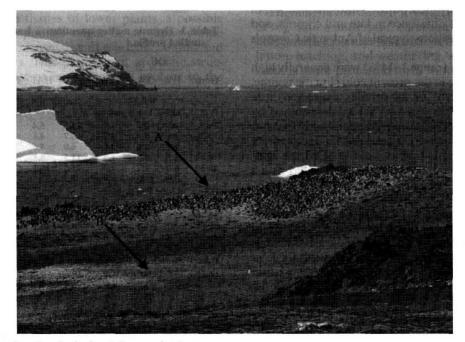


Fig. 2. Former and abandoned rookeries located on marine terraces.



Fig. 3. Landscape position of Profile 1 (Copa-1).

matter can be associated with  $Al^{3+}$  transformation and leaching with depth.

The microelement distribution is fairly irregular, showing greater values of Mn and Cu in more stable areas (P-2 and P-3) with greater redox potentials, Zn values are considerably higher for sites strongly affected by ornithogenesis due to its close relation to marine organisms (Santos et al., 2005). Iron distribution is regular with depth for all profiles, showing slightly greater values for ornithogenic sites.

#### **Organic Carbon and its Fractions**

Due to the intense cryoturbation of these soils, organic matter has been deeply incorporated into the profile. All horizons showed little difference in hue and chroma, and convolute diffuse transitions, typical of Antarctic Cryosols (Simas et al., 2004).

The amounts of OC (range 1-14%) were generally high due to its preservation in the present cold climatic regime, the uppermost horizons of all profiles expressed little difference (around 30%) for OC values determined by Nelson and Sommers (1982) and Yoemans and Bremner (1998) procedures (Table 3). These results demonstrate that even the more stable fractions of the SOM are composed of easily degradable compounds, associated with a fibric matrix.

Humification rates in Maritime Antarctica are controlled by microclimate, soil biota and soil moisture regime. In Antarctica, some areas are virtually free from lignin-producing plants, due to the dominance of lichens and bryophytes. The formation of humic substances in such environments where lignin and lignin-degradation products are not prevalent can only occur through the condensation of sugar-amine compounds, or reactions between quinones and amino acids (Beyer et al., 1995). The HAF/FAF ratio showed values around 1.0 for the surface horizons, increasing rapidly at deeper horizons in Soils P-2 and P-3, reaching 1.39 in the deeper horizons of P-3. This suggests that the organic material is migrating, and reaching deeper layers where policondensation occurs, and recalcitrant humic substances tend to accumulate. The low level of OC in deeper horizons of P-4, compared with the profile's top soil, can be related with the present day input of guano, and low decomposition rate of SOM due to low oxygen and reducing conditions.

There was observed an increase in N concentration in the humic compounds after humification, suggesting an important participation of amino compounds in the humification process in ornithogenic Maritime Antarctica soils.

Table 3. Organic matter quantitative fractioning for three of the studied profile.<sup>†</sup>

	OC										
Horiz.	WB	YB	YB/WB	FAF	HAF	NEOM	HAF/FAF	OC/N			
		dag k	g <sup>-1</sup>	mg g <sup>-1</sup>							
P 2	Lithi	c Umb	oriturbels								
0-10	4.5	4.7	1.0	11.5	5.4	26.4	0.47	59.6			
10-20	2.8	3.4	1.2	6.7	4.6	17.8	0.69	44.5			
20-30	2.7	2.6	1.0	6.0	4.6	13.6	0.77	34.2			
30-40	2.5	3.8	1.5	11.5	8.5	17.4	0.74	37.4			
40-50	6.0	7.7	1.3	15.5	16.1	39.5	1.04	65.2			
50-60	7.4	10.0	1.4	20.3	21.0	45.2	1.03	111.7			
P 3	Lithi	c Fibri	stels								
0-10	8.6	12.4	1.4	17.6	19.7	65.8	1.12	72.1			
10-20	5.8	7.8	1.3	14.8	18.1	39.4	1.22	75.5			
20-30	4.7	5.4	1.1	13.5	10.2	26.9	0.76	36.0			
30-40	7.7	10.7	1.4	21.6	28.4	51.2	1.31	63.2			
40-50	7.7	9.3	1.2	18.5	25.8	45.5	1.39	70.6			
P 4	Psan	ımenti	c Aquitur	bels							
10-20	3.5	5.6	1.6	10.6	7.4	35.0	0.70	55.7			
20-30	2.7	5.0	1.9	8.4	7.3	29.0	0.87	134.5			
30-40	1.2	2.3	2.0	4.2	4.3	12.6	1.02	53.7			
40-50	1.0	1.2	1.2	2.5	2.2	6.3	0.88	11.2			

† OC: Organic carbon; WB: Walkley Black; YB: Yoemans and Bremen; FAF: Fulvic acid fraction; FAH: Humic acid fraction; NEOM: Non extractable organic matter.

Table 4. Elemental composition of the humic acid fraction, moisture, ash content and termogravimetric index (TGI).<sup>†</sup>

Sample	С	H	H N O Atomic ratio				atio	Moist	Ash	TGI
	% dry ash free basis				H/C	C/N	0/C	%	%	
P-3 0-10	50.3	7.2	7.3	35,2	1.71	8.0	0.52	12.77	3.83	1.17
P-3 10-20	53.3	7.3	7.1	32.4	1.64	8.8	0.46	4.74	15.39	1.60
P-3 20-30	50.2	7.6	7.9	34.3	1.83	7.4	0.51	7.74	10.48	1.01
P-3 30-40	49.8	6.5	6.3	37.4	1.57	9.3	0.56	6.69	13.63	1.22
IHSS	56.4	3.8	3.7	37.3	0.81	17.8	0.50	8.1	1.9	2.74

† IHSS: International Humic Substances Society standard soil HA.

The OC/N ratio is slightly greater than the ratios observed in mineral topsoils like P-1. The high nonextractable organic matter content can be explained by the fibric nature of the material, associated with a small contribution of the macro-organisms and slow decomposition rates imposed by the environment. That leads to light organic matter preservation, for longer periods.

#### **Organic Matter Chemical Characterization**

The elemental analysis of purified humic acids showed their N-rich nature with a high H/C ratio. It indicates that humic acids from ornithogenic Antarctic soils have less aromatic compounds, compared with IHSS Soil Humic Acid standard (Table 4). This agrees with the predominant lower-plant derived humic substances and corroborates previous reports from ornithogenic soils from elsewhere in Antarctica (Beyer et al., 2004; Bölter and Kandeler, 2004).

Thermogravimetric curves show an easily thermodegradable molecule, compared with humic acids extracted from other soils (Benites et al., 2005b). Thermogravimetric data also reveal nonaromatic compounds with thermodegradation peaks up to 300°C (Fig. 4), which are characteristic of aliphatic structures and proteins. On the other hand, aromatic structures are identified in the thermodegradation events higher than 350°C. Despite the lack of lignin in tissues of lower plants, a possible source of these compounds might be aromatic amino acids or products of microbial synthesis from ketonic and carboxylic structures. This pathway of aromatic structures synthesis comes as an alternative process to the

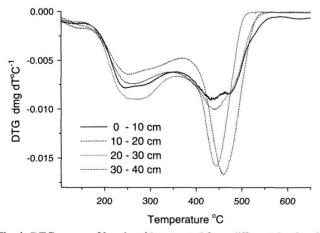


Fig. 4. DTG curves of humic acids extracted from different depths of profile (Copa-3).

more accepted route through the preservation of aromatic structures inherited from lignin. Another possible source of aromaticity is the incorporation of black C particles on the penguin guano. The presence of black C in Antarctic marine water and sediments was reported by Druffel (2004). Small amounts of black C derived humic substances could be co-extracted with the humic acids generating the aromatic signal on the themogravimetric analyses.

Thermal analysis of humic acids reflects the dynamics of SOM development (Kucerik et al., 2004). The amount of heat measured by DSC and calculated as the integration of total area under DSC curve is influenced by the degree of humification and by the amount of oxygen in humic molecules. Greater aromaticity and poorer oxygen content are associated with greater heat evolution. It is noteworthy that a sample from profile 3 (0-10) gave the total amount of heat comparable with the other humic samples characterized by Benites et al. (2005a). The contribution of the first decomposition step is significantly higher in comparison with humic substances samples from elsewere (Fig. 5). On the other hand, the lowest onset temperature suggests a lower stability. Overall, our data indicates that the biological transformation processes are exceptionally low in this Antarctic soil compared with soils from moderate climates, and suggest significantly higher amount of biodegradable compounds in Antarctic humic acids.

#### **CONCLUSIONS**

Formation of soils of maritime Antarctica can be greatly influenced by seabird excreta. Tentatively classified as Ornithogenic Cryosols, these soils occupy lower-lying landscape positions, have higher P levels, lower pH, lower Na<sup>+</sup>, and greater exchangeable  $Al^{3+}$  compared to the nonornithogenic soils of the area.

Higher P levels appear to be an important determinant of vegetation patterns. Continuous plant cover is present only where moisture is sufficient high to promote percolation, leaching, and weathering, and the microenvironment is more protected form wind exposure.

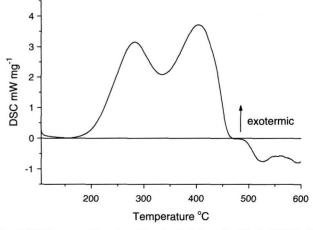


Fig. 5. DSC curve of humic acid extracted from Profile 3 (COPA 3) top horizon.

Primary productivity of ornithogenic soils is much higher than non ornithogenic counterparts; eutrophication of upland marine terraces is due to both *Pygoscelis adeliae* rookeries and *Catharacta spp.* nesting in the vicinity, expanding the affected area.

Soil development, vertical, and lateral movement of bioavailable nutrients is enhanced by ornithogenesis. A close interplay between ornithogenesis, plant diversity and biomass production exists. The acidolysis promoted by biological activity in areas of Penguin rookeries is extreme, and capable of enhancing soil development in these Maritime Antarctica oases of Admiralty Bay.

The humic acids extracted from ornithogenic Cryosols are richer in N and easily thermodegradable compounds, representing a considerable pool of easily degradable C. Data suggest that Ornithogenic Cryosols in this maritime Antarctic environment may be vulnerable to C losses to the atmosphere in response to global warming.

#### ACKNOWLEDGMENTS

We are very grateful for the logistic support from the Brazilian Navy, and financial support from the Brazilian Ministry of Environment (MMA) and Science and Technology (MCT), through the CNPq project 550368 (Cryosols of Maritime Antarctica). We are also very grateful for the DSC analysis performed by Dr. Jiri Kucerik (Brno University of Technology – Czech Republic). Thanks are due to the American personnel (Tracy, Mike, and John) from Peter Lenie Station (Copacabana), who gave us shelter during bad weather times.

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