# 51131 **Publishing**

# Australian *Journal* of Soil Research



Volume 39, 2001 © CSIRO 2001

An international journal for the publication of original research into all aspects of soil science

**All enquiries and manuscripts should be directed to:**



*Australian Journal of Soil Research* CSIRO Publishing PO Box 1139 (150 Oxford St) Collingwood, Vic. 3066, Australia

Telephone: +61 3 9662 7628 Fax: +61 3 9662 7611 Email: sr@publish.csiro.au

Published by CSIRO Publishing for CSIRO and the Australian Academy of Science

www.publish.csiro.au/journals/ajsr

# **Soil organic matter composition, transformation, and microbial colonisation of Gelic Podzols in the coastal region of East Antarctica**

## *Lothar Beyer*A*, Daniel M. White*B*, and Manfred Bölter*A

A Institute of Polar Ecology, University Kiel, Wischhofstraße 1–3, Building 12, D-24148 Kiel, Germany; email: Lbeyer@ipoe.um-kiel.de.

B College of Science, Engineering and Mathematics/Institute of Northern Engineering, University of Alaska Fairbanks, USA.

#### *Abstract*

During recent soil geographical expeditions to Casey Station (Coastal Antarctica), soils with the morphological features of Gelic Podzols (WRB: Spodic Haplic Cryosols) were found to be widespread. The purpose of this paper is to provide further information on these unique soils with respect to soil organic matter (SOM), microbiology, and soil formation. Antarctic Podzols develop on solid rock, outwash sediments, and abandoned penguin rookeries. A comparison of different SOM depth profiles, however, revealed carbon (C) and nitrogen (N) of unknown origin. The SOM composition was characterised by a mean C/N ratio of 10, with a high content of carboxyl-C units, probably derived from amino acids, organic acids, and oxidised carbohydrates. Pyrolysis-GC/MS and NMR showed a notable variation between SOM in depth profiles and the horizons within each profile. Microbial colonisation was affected by the surface vegetation, content of organic C, and the influence of seabirds. Correlations between selected SOM compounds and bacteria on the vegetated soils suggested that algal and moss C influence SOM to a great extent. Most of the long-chain C moieties in the antarctic Podzols appeared to contain multiple oxygen- and N-containing functional groups, cyclic ionised and heterocyclic structures, and alkylations. Data suggest that, along with the podzolisation process, organic acids, non-humified carbohydrates, and N-containing moieties migrated from the topsoil into the spodic horizons. The results are discussed with respect to (*i*) soil formation and (*ii*) microbial colonisation in the cold climate. The Gelic Podzols hold huge amounts of C and N but their origin is poorly understood. Explaining the origin of the SOM should be a focus for future research in antarctic soil biogeochemistry.

*Additional keywords:* microbial counts and abundance, CPMAS carbon-13 NMR spectroscopy, pyrolysis-GC mass spectrometry, soil ecology, soil formation, podzolisation.

# **Introduction**

Antarctic Podzols contain high concentrations of carbon (C) and nitrogen (N) (Blume *et al.* 1996; Beyer *et al.* 1998). Blume *et al.* (1997) and Beyer *et al.* (2000*a*) suggested that the occurrence and intensity of podzolisation is determined by microclimate, parent materials, and soil microbial effects. However, coherent and confirmed information on podzolisation processes is still missing. In previous work, the soil organic matter (SOM) of the spodic horizons was characterised by a narrow C/N ratio (<10) with potentially high bioavailability, probably derived from amino acids, other organic acids, and oxidised carbohydrates (Beyer *et al.* 1997). Compared with similar soils from temperate climates, the SOM profiles with depth suggested atypical C and N moieties of unknown origin (Post *et al.* 1988). Knowledge on antarctic soils and especially on the SOM of these soils is still scarce (Seppelt and Broady 1988). More information on SOM in terrestrial ecosystems of East Antarctica is desirable since biological observations suggest that SOM transfer may play an important role in nutrient cycles in the terrestrial Antarctic ecosystem (Smith 1985).

For this reason, some antarctic Podzols from different parent material were investigated with respect to SOM quality using cross polarisation magic angle spinning  $^{13}$ C nuclear magnetic resonance spectroscopy (CPMAS 13C NMR) and pyrolysis gas chromatography mass spectrometry (Py-GC/MS). The results are discussed with respect to SOM quality, transformation, and translocation in the cold climate of Antarctica.

#### **Materials and methods**

#### *Site*

Soils were collected near the Australian Casey Station on Bailey Peninsula (66°18´S, 110°32´E) at Wilkes Land in coastal East Antarctica about 700 m from the shore (Fig. 1). Soil C11 and D3 are located on specific observation sites close to the main station building (Fig. 1: squares C and D). Soil WP5 is located on Clark Peninsula somewhat further north from Bailey (Fig. 1). The parent material is composed of weathered gneiss and schist, moraine deposits, outwash sediments (e.g. Paul *et al.* 1995), and marine deposits by seabirds (Campbell and Claridge 1987). The coastal landscape was partly deglaciated between 5000 and 6000 years BP (Goodwin 1993) and an elevation of terraces occured. The annual precipitation (180 mm) falls mainly as snow. Because of strong drift due to persistently strong winds (Pickard 1986), seawater is heterogeneously distributed on land (Beyer *et al.* 2000*b*). The mean annual ambient temperature is –9.3°C. During the antarctic summer of nearly 6 weeks, temperatures are above the freezing point (e.g. the mean January temperature is +0.2°C). Plant communities of mosses (e.g. *Bryum pseudotriquetrum, Ceratodon pupureus, Schistidium antarcticum*), lichens (e.g. *Usnea sphacelata, Pseudephebe minuscula, Umbilicaria decussata*), and soil algae have become established (Seppelt 1984; Smith 1990).

#### *Sampling, soil survey, and general soil investigations*

Sampling was carried out during January and February 1996. The soils were originally classified as Sandy or Loamy Mixed Lithic or Pergelic Haplocryods (Beyer *et al.* 2000*a*) according to the 7th edition of Soil Taxonomy (Soil Survey Staff 1996). However, using the new Gelisol order for permafrost-affected soils in the recently adopted 8th edition of Soil Taxonomy no adequate classification seemed possible (Beyer *et al.* 2000*a*). According to the World Reference Base of Soil Resources (WRB) these soils have to be classified as Spodic Haplic Cryosols because they are characterised by permafrost within the first metre (Deckers *et al.* 1998). Because only the recently rejected FAO classification includes the name Podzol, a soil type most geoscientists are familar with, the name *Gelic Podzol* has been used (i.e. a Podzol having permafrost in the first 2 m) (FAO 1997) in this paper.

Most soil properties were analysed according to Schlichting *et al.* (1995) on air-dried soil samples. Soil mineral particle composition was determined after sieving at 2 mm by a combination of sieve and elutriate analysis. Soil texture was estimated by using the soil texture chart of the Keys to Soil Taxonomy (Soil Survey Staff 1996: p. 631). The pH was measured in 10 mM CaCl<sub>2</sub> with a commercial glass electrode. Electrical conductivity (EC) was measured in a 1:2.5 water extract. Loss-on-ignition (LOI) was determined gravimetrically after combustion at 650°C in a muffle furnace. Total organic carbon (TOC) was calculated after dry combustion in a Coulomat 702 (Ströhlein, Germany). The samples were heated (600°C) in an induction furnace under oxygen; CO<sub>2</sub> was trapped in Ba(OH)<sub>2</sub> and the remaining Ba(OH)<sub>2</sub> was neutralised by titration. Total nitrogen  $(N_t)$  was digested by the classical Kjeldahl method and determined as nitrate in a flow injection analyser. Pedogenic iron and aluminium oxides were determined after extraction with dithionate–citrate (Fe<sub>d</sub>, Al<sub>d</sub>) and oxalate (Fe<sub>0</sub>, Al<sub>0</sub>). The iron and aluminum bonded to organic matter was determined in an alkaline (NaOH) extract. Alkaline extract was used because sodium pyrophosphate extract overestimates organic iron species by destruction of certain minerals such as olivine (Grimme and Wiechmann 1969; Wiechmann and Grimme 1969). The extinction of the oxalate extract was measured at 472 nm (optical density of oxalate extract, ODOE) according to Daly (1982). The cations  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^2$ <sup>+</sup>, and Ca<sup>2+</sup> were extracted with unbuffered BaCl<sub>2</sub>. Potential H<sup>+</sup> and Al<sup>3+</sup> were extracted with Ca<sup>2+</sup>-acetate and measured as pH and converted into H<sup>+</sup> and  $\overline{A}$ 13<sup>+</sup>. The sum of the cations and potential H<sup>+</sup> +  $\overline{A}$ 13<sup>+</sup> is the potential cation exchange capacity (CEC<sub>p</sub>). The percentage of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> from CEC<sub>p</sub> is the base saturation (BS). The bio-available potassium  $(K_l)$ , magnesium  $(Mg_l)$ , and phosphorus  $(P_l)$  were extracted with  $0.04$  N Ca<sup>2+</sup> lactate + 0.02 N HCl at pH 3.7.  $K_1$  and Mg<sub>l</sub> were determined in an AAS (Perkin Elmer).  $P_1$  was determined colorimetrically as the blue-coloured molybdate–phosphate complex. The immobile P fraction  $(P_c)$  was extracted with 2% citric acid (modified, original 1%) (Van Reeuwijk 1993).



**Fig. 1.** Location of the investigation site in the coastal region of East Antarctica. Squares A–D: specific monitoring sites.

## *CPMAS 13C NMR*

The CPMAS 13C NMR were taken at 2.3 tesla (25.2 MHz) with a Bruker MSL 100 equipped with a commercial 7-mm CPMAS probe at a rotation frequency of 4 kHz. A contact time of 1 ms was used. Due to short relaxation times  $(T<sub>1H</sub>)$  in SOM, a recycle delay of 0.3 s was chosen. The chemical shift is given relative to tetramethylsilane (TMS = 0 ppm) scale. The quantitative data were obtained with the integration routine of the spectrometer. For further details see Fründ and Lüdemann (1989).

#### *Py-GC/MS*

Subsamples with a mass of 25 mg were placed in quartz tubes (2 cm by 2 mm ID) and quantified using a Mettler microbalance. In preliminary research it was determined that samples with a mass <10 mg did not give a signature greater than the baseline and samples >30 mg did not fit entirely within the quartz tube (White and Irvine 1998). The samples were held in place by a plug of quartz wool at each end of the tube. Py-GC/MS was conducted on each sample and used to identify as many compounds as possible. Py-GC/ MS was conducted with a CDS Model 1000 pyrolyser and a Model 1500 GC interface. The interface temperature was set at 280°C. During pyrolysis, the sample was heated from 280°C to 700°C in 0.1 s and held at 700°C for 9.9 s. The pyrolysis reactor was mounted on an HP 5890 Series II GC with a Hewlett Packard HP-1 column (cross-linked methyl-siloxane) 25 m by 0.2 m by 0.33 µm film thickness. The GC temperature program was 35°C for 15 min, 2°C/min ramp to 250°C, and held for 10 min. The GC was plumbed directly to an HP 5971A Series Mass Selective Detector in electron impact mode. The MS scanned mass units 45–650. All mass spectra were compared to the Wiley 138 mass spectral library. Helium was used as the carrier gas at 0.5 cc/min. The sample was injected with a split ratio 1:50. For each sample, the mass spectral signals for all compounds were normalised to the compound of greatest abundance. In this study only those compounds were considered that had a normalised intensity of ≥20%. Each compound was assigned a probable parent (see Table 8). The parent represents a soil biopolymer that was present in the sample prior to pyrolysis. The soil biopolymer classifications used were protein, phenol precursors, carbohydrates, aromatic hydrocarbon precursors (AHP), lipids, and amino-carbohydrates (Bracewell *et al.* 1989). All long-chain hydrocarbons, alcohols, aldehydes and ketones were classified as having lipid parents. Any compound with no assignment to a probable parent was considered unresolved. The relative intensities for all soil biopolymers in each sample were added. Each soil biopolymer class is presented as a percentage of the total on the assigned compounds.

#### *Microbial determinations*

Determination of chlorophylls and phaeopigments were performed according to Jeffrey and Humphrey (1975) and Lorenzen (1967), respectively, in acetone extracts (90%) by spectral photometry. All values were expressed on a dry mass (DM) basis. According to the current literature the occurence of algae is indicated by chlorophyll detection (e.g. Bölter 1990, 1995, 1997). Microorganisms were counted by epifluorescence microscopy. Samples were stained with acridine orange and filtered onto nuclepore polycarbonate membranes. Cells of bacteria and yeasts were identified and counted with respect to their size classes. Biovolumes were calculated by geometrical parameters (Bölter *et al.* 1993). Samples were taken aseptically with a clean spoon and placed in plastic containers.

#### **Results and discussion**

#### *General properties*

All three Podzols showed the typical horizon sequence of AE-Bh(Bhs,Bs)-C with a strong acidification and a Fe<sub>o</sub>/Fe<sub>d</sub> ratio that exceeds 0.5 (Tables 1–3), indicating the existence of short-range-order pedogenic iron compounds (Schlichting *et al.* 1995). Maximum values for most aluminium and iron fractions, the ODOE, LOI, TOC, and total nitrogen  $(N_t)$ occurred in the spodic Bh/Bhs horizons (Tables 1–3). The depth profile for these parameters suggests a translocation of SOM into the subsoil (McKeague *et al.* 1983). Both metals were mainly located in non-crystalline pedogenic oxides ( $Fe<sub>o</sub>$ ,  $Al<sub>o</sub>$ ) or in organic complexes (Fe<sub>NaOH</sub>, Al<sub>NaOH</sub>). However, the high Al<sub>NaOH</sub> values suggest an overestimation of the organically bonded aluminium (Kaiser and Zech 1996) and confirmed the results of Jacobsen (1991) who showed that  $Fe_0$  and  $Al_0$  were higher than  $Fe_d$  and  $Al_d$ . A large amount



**Table 1. Selected properties of a shallow Antarctic Gelic Podzol (C11) from weathered gneiss rock under mosses and lichens in a small depression (sampling** 



Table 2. Selected properties of an Antarctic Gelic Podzol (WP5) from glacial outwash sediments under mosses at a dried-up melt-water lakeside (sampling date<br>EC, electrical conductivity; TOC, total organic carbon; LOI, loss



548 L. Beyer *et al.*



Gelic Podzols in East Antarctica 549

A Term see Bockheim (1997). B Sponge needles.

of P indicated the influence of guano input (Blume *et al.* 1997), and was seen at soil D3 for both P fractions (Table 3). The increase of the P fractions in the subsoil of the Podzol from solid rock (Table 1) also indicates guano input in earlier stages of soil formation.

All suggested spodic Bh/Bhs horizons comply with the criteria of US Soil Taxonomy (Soil Survey Staff 1998). For this reason Blume *et al.* (1997) classifed these soils as Gelic Podzols and Beyer *et al.* (2000*a*) as Haplocryods, recognising unique properties compared to Podzols (Spodosols) in temperate and/or boreal climate regions. The C/N ratios of Podzols in Antarctica were much narrower than those of their temperate counterparts due to their extremely high  $N_t$  contents. This was of course most striking in the Podzol at an abondoned penguin rookery (Table 3).

#### *Microbial abundance*

Tables 4 and 5 show the microbiological properties of the antarctic sites. Chlorophyll *a* content ranges between 0.2 and 9  $\mu$ g/g depending on soil depth and the recent vegetation cover (Table 4). For a comparable site, Roser *et al.* (1993) reported values from 5 µg/g on control sites to 11.2 µg/g on extinct penguin rookeries at Whitney Point. Comparable data of total chlorophyll content (Table 4: chlΣ) were obtained at King George Island in the Maritime Antarctic (Bölter 1997). Here chlorophyll content was within a similar range except in surface horizons with dense cover of higher plants and mosses. At Casey, the same was found in soil with recent vegetation (soil C11, soil WP5). Surprisingly, in soil WP5 the chlorophyll data were highest not in the surface horizon, but in the spodic subsurface horizon, which had the highest value of TOC and chlorophyll of all horizon samples (Table 4). Data of Ohtani *et al.* (1991) from the Yukidori Valley and those of Davey (1988, 1991) from Signy Island also showed similar ranges of total chlorophyll content. The degraded chlorophyll, or phaeopigments (Table 4), however, were much higher in the present Casey data set. In the Maritime Antarctic—at King George Island—phaeopigment content ranged only between 0 and 3.8 µg/g dry mass (DM) (Bölter 1997). The high chlorophyll content in the spodic subsurface horizon of soil WP5 (sample no. WP5.2) suggests that chlorophyll is translocated with the organic matter within the podzolisation process or that the much higher current water content (Table 4) has a direct positive impact on chlorophyll-producing organisms.

Bacterial counts ranged between 91 and 1058  $10^{6}/g$  DM, decreasing with depth (Table 4: TBC), consistent with the distribution of TOC at sites C11 and D3, but not site WP5. This is in agreement with the estimation of the bacterial biovolumes (Table 4). At King George Island, bacterial counts in a Podzol under *Deschampsia antarctica* were found at similar levels (Bölter 1995; Bölter *et al*. 1994, 1997). At Casey, however, no higher plants were present. Roser *et al.* (1993) found high bacterial counts in ornithogenic soils of the Windmill Islands with no vegetation. This is in agreement with the present observations, since soil D3, an abandoned penguin rookery site with no vegetation, showed the highest bacterial counts. In addition, the surface horizon of D3 was the only layer where yeasts were detected (Table 4: TYC).

The mean cell volumes of the bacterial communities range from 59 to 72 nm<sup>3</sup> at site C11, from 55 to 112 nm<sup>3</sup> at site D3 and from 106 to 193 nm<sup>3</sup> site WP5, indicating statistically significant differences between the soils (Table 5). Comparable data from King George Island show values between 50 and 70 nm3 (Bölter *et al.* 1994, 1997). The situation at Whitney Point (WP5) on Clark Peninsula can be attributed to high amounts of large rodshaped bacteria (length  $2-3 \mu m$ ), which contribute between 17% and 34% of the community's biovolume (Table 5). In comparison to other sites, these values are extremely



Gelic Podzols in East Antarctica

5 5 1



and size classes of bacterial colonies of Celic Podzols in East Antarctica **Table 5. Structure and size classes of bacterial colonies of Gelic Podzols in East Antarctica**  $\frac{1}{2}$ Table 5 Stru

high. Elsewhere such high values are mostly found for nutrient-rich microsites such as plant tissue surfaces (Bölter 1995). Similarly, Roser *et al.* (1993) reported cell volumes ranging between 130 and 250 nm3 for communities in the ornithogenic soils of the Windmill Islands. However, at site WP5 no recent or relic penguin influence was detectable (Tables 1–3). Another explanation for this phenomenon might be the high TOC content of the AE horizons, which was  $1.4-1.7\times$  that of soil D3 or C11 (Table 4).

Finally, we suggest that in the coastal region of Continental Antarctica both vegetation and the influence of seabirds affected soil bacterial colonisation. This is discussed in detail by Beyer *et al.* (2000*b*).

#### *Soil organic matter composition*

Table 6 shows the SOM composition according to the carbon-13 NMR experiments. The increase in alkyl C and simultaneous decrease of O-alkyles is comparable to the pattern observed in Podzols in temperate regimes (Post *et al.* 1988). However, the high level of carboxyl-C in all soil horizons was unexpected. This might be the reason for the somewhat higher  $CEC_p$  in the soil at the abandoned penguin rookeries (Table 3). The abrupt change of the SOM composition within the subsurface Bhs, the IIBs and the IIICw horizons of the Podzol on the penguin rookery (D3) is probably due to different concentrations and quantities of droppings and deposits by penguins in different layers. Beyer *et al.* (1997) suggest for the spodic horizons that, in contrast to those in Germany, the SOM is characterised by a high percentage of amino derivates from proteins, polysaccharides, urates, and chitin, resulting in a mean C/N ratio of 10 and a high content of carboxyl-C units, probably derived from amino and other organic acids. The podzolic soil from solid rock under mosses and lichens (C11) showed an aromatic-C pattern comparable to Podzols in temperate climate regions. However, the aromatic C in the AE was very high and cannot be explained with residual preservation from the recent vegetation. It was unclear if another source of SOM in the area, such as relic organic matter or an input by eolian transport, was contributing. An input by seabirds can be discarded because P contents were low (Table 1). The most substantial similarity of SOM composition with that of Podzols from temperate climates was found in the podzolic soil from outwash sediments under mosses (WP5). However, the comparison of the AE horizons under mosses (WP5-1 and C11-1) confirms the assumption that, in the shallow Podzol from gneiss and schist (C11), a C source other than recent vegetation is likely. Comparing the SOM composition of the soil horizons with the SOM composition (Beyer *et al.* 1995, 1997; White and Beyer 1999) of selected organic parent materials (Table 7) suggests that in soil WP5 the algal and mossy C sources influence SOM to a great extent, whereas in soil D3 and C11 the influence is smaller.

Table 8 shows the major ions found by using Py-GC/MS. In general, there were no indications of lignin in any of the samples. A variety of methylphenols were present, which indicate either protein or lignin. If the methylphenols were derived from lignin, however, methoxylphenols, which were not observed, would have been present (Hempfling and Schulten 1990). The phenols, therefore, were assumed to be derived from proteins. Most of the long carbon-chain molecules in the Antarctic soil samples appeared to contain multiple O- and N-containing functional groups, cyclic ionised and heterocyclic structures, and alkylations. However, the complex and easily ionised compounds and the low C content made mass spectral identification difficult.

In all 3 soils the signal pattern was more detailed in the AE and Bh horizons than in the deeper layers (see example given in Fig. 2), which indicates the direct influence of local vegetation or microbial colonisation, consistent with the NMR data. In soil C11 from



Table 6. Soil organic matter composition according to CPMAS carbon-13 spectroscopy of Gelic Podzols soils in coastal East Antarctica (signal range in ppm **Table 6. Soil organic matter composition according to CPMAS carbon-13 spectroscopy of Gelic Podzols soils in coastal East Antarctica (signal range in ppm** 

5 5 4

L. Beyer *et al.* 

n.d., not determined.

A Adapted from Beyer *et al.* (1995). B Adapted from Beyer *et al.* (1997).

n.d., not determined.<br>A Adapted from Beyer et al. (1995).<br>B Adapted from Beyer et al. (1997).

$\overline{\phantom{a}}$						
Soil	Horizon	$r$ value $_{\rm{algae}}$	$r$ value $_{\rm{mosses}}$			
C11	AE	0.488	0.589			
	Bh	0.480	0.610			
WP <sub>5</sub>	AE	$0.931***$	$0.966***$			
	Bh	$0.911***$	$0.950***$			
	C	$0.800**$	$0.856**$			
D <sub>3</sub>	AE	$0.789**$	$0.807**$			
	Bh	0.613	$0.730*$			
	<b>Bhs</b>	0.356	0.500			
	<b>IIBs</b>	0.498	0.624			
	<b>IIIC</b>	0.041	0.149			

**Table 7. Linear correlation coefficients (***r***) between NMR subunits of the SOM in Gelic Podzols of coastal East Antarctica and the organic matter composition of mosses and algae (data see Table 6,**  *n* **= 9)**

 $*P < 0.05$ ; \*\*  $P < 0.01$ ; \*\*\*  $P < 0.001$ .

weathered gneiss rock under mosses and lichens, only the C11-1 (AE) and C11-2 (Bh) horizons contained smaller molecules such as phenols and single-ring aromatics (Fig. 2: e.g. peaks no. 28, 37), whereas in the deeper C11-3 (BsC) and C11-4 (IIC) horizons, longchain acids, alcohols and ketones were present (Fig. 2; peaks no. 87, 93, 101). Protein precursors (e.g. peaks no. 9, 75) were found only in C11-1 and C11-2, which was in line with a higher occurrence of bacterial microorganisms (Table 4). However, at the same time, peak no. 109 suggested the significance of unresolved compounds, which might have some aromatic structure as suggested by peak 79 (Fig. 2, Table 8) and the NMR data (Table 6).

In Table 9 the semi-quantitative data are summarised in per cent of assigned signals. The SOM of the C11-1 (AE) and C11-2 (Bh) horizons were composed of a large percentage of unresolved compounds, but contained some carbohydrates, protein, and/or phenol precursors as well as aromatic hydrocarbon precursors (AHP). For all samples, most of the compounds comprising the unresolved fraction appeared to be heterocyclic or cyclic molecules (Table 8). In addition, NMR data suggested 20–30% aromatic C nature in soil C11 (Table 6). The decrease of phenol precursors and AHP was in agreement with the decrease of aromatic-C units determined by NMR (Table 6). The increase of alkyl-C from AE to Bh, as evaluated from NMR, was not detectable in the lipid fraction of Py-GC/MS.

In soil WP5 from glacial outwash sediments under mosses, lipids were abundant in all samples (Table 9). As observed in soil C11, in soil WP5 the SOM patterns of the upper WP5-1 (AE) and WP5-2 (Bh) horizons were similar, consisting of protein, phenol precursors, carbohydrates, trace amounts of amino carbohydrates, and low amounts of unresolved compounds. In contrast, the SOM in the WP5-3 (C) horizon had an abundance of unresolved carbon units, lipids, and, in contrast to the C horizon of the Podzol C11, amino carbohydrates (Table 9). As observed in soil C11, proteins were found only in the 2 topsoils, probably as a consequence of a higher microbial activity due to more favourable conditions (light, temperature, etc.) in the surface layers (Beyer *et al.* 2000*b*; Bölter 1990; Bölter *et al.* 1997). On the other hand, there might be a certain impact of the vegetation, because no proteins were found in the surface soil in soil D3, which had no plants.

In unvegetated soil D3 at an abondoned penguin rookery there was an abundance of amino carbohydrates in all but the D3-4 (IIBs) horizon. None of the other Podzols contained nearly as high a concentration of amino carbohydrates. This might be due to some degradation products of uric acids (White and Beyer 1999). Uric acid itself might be

# **Table 8. Major ions detected with Py-GC/MS in Gelic Podzols in coastal East Antarctica and their assignment to probable parent compounds**

Ions in highest abundance underlined



hidden in the unresolved fraction and its occurence is suggested to be correlated with the occurrence of heterocyclic moieties (White and Beyer 1999 and Table 8, peaks 78, 79), which could be found in most of the horizons of soil D3 (spectra not shown). This probably reflects the influence of the organic input from guano. In contrast to the other Podzols, miscellaneous carbohydrates are abundant in all 5 horizons without having the clear



Fig. 2. Ion chromatograms of pyrolysis GC/MS of a Gelic Podzol (C11) from weathered gneiss rock under mosses and lichens.

differentiation from the upper soil horizons and the subsoil. NMR and Py-GC/MS suggest the occurrence of a very specific SOM pattern in the D3-4 (IIBs) horizon. The strong decrease of O-alkyl-C units within the soil profile observed by NMR was not found with Py-GC/MS. The minimum of aromatic C in the D3-4 horizon might be correlated to the occurrence of carbohydrates. However, the observed maximum in carbohydrates was in contrast to the NMR data. This suggests that pyrolysis data do not reflect total SOM due to the occurrence of high amounts of unresolved compounds and the undetected SOM fractions (>20%, compare methods). In any case, the data combination suggest that a large

Horizon	Protein	Phenol precursors	Carbo- hydrates	Aromatic hydro- precursors	Lipids	Amino- carbo- hydrates	Unresolved		
Soil from weathered gneiss rock under mosses and lichens in a small depression (C11.1-4)									
AE	9	9	14	3	20	n.d.	46		
Bh	8	n.d.	30	n.d.	15	n.d.	48		
<b>BsC</b>	11	n.d.	n.d.	n.d.	11	n.d.	78		
НC	n.d.	n.d.	n.d.	n.d.	79	n.d.	21		
Soil from glacial outwash sediments under mosses at a dried-up melt water lake side (WP5.1-3)									
AE	5	14	23	n.d.	22	4	32		
Bh	8	10	33	n.d.	25	3	21		
C	n.d.	n.d.	n.d.	n.d.	39	20	42		
Unvegetated soil under a gravel pavement at an abondoned penguin rookery $(D3.1-5)$									
AE	n.d.	n.d.	19	n.d.	16	33	32		
Bh	9	13	24	4	10	10	29		
<b>Bhs</b>		n.d.	30	n.d.	n.d.	22	41		
<b>IIBs</b>	n.d.	n.d.	43	n.d.	34	n.d.	23		
<b>IIICw</b>	n.d.	n.d.	27	n.d.	n.d.	17	56		

**Table 9. Soil organic matter compound classes (% of assigned signals) according to the pyrolysis GC/MS experiments in Gelic Podzols in coastal East Antarctica**

n.d., none detected.

#### *Soil ecology and soil formation*

Frequently the measured microbial properties are highest in the uppermost AE horizons, although TOC was less than in the underlying spodic horizons (Bh/Bhs). The reason may be the rapid temperature decrease over the first few centimeters below the soil surface (Bölter *et al.* 1994), and temperature is more important than TOC for biological activity (Beyer *et al.* 1998). Overall, the microbiological data show values lower than those commonly observed. In cryptogamic crusts on Signy Island, Wynn-Williams (1985) found larger populations of  $450-2180 \times 10^6$  g soil DM. This can be attributed to the much milder climate and higher temperatures in Maritime Antarctica. For soils on the Windmill Islands, Roser *et al.* (1993) gave total bacterial counts of  $4.6 \times 10^{10}$ /g for active and  $3.4 \times 10^{9}$ /g DM for extinct penguin colonies. The latter is greater than in the penguin-affected soil D3. The non-penguin affected control sites of Roser *et al.* (1993) contained 2.6  $\times$  10<sup>9</sup>/g DM, which is greater than in soil D3. For abandoned and active penguin colonies on Ross Island, Ramsay and Stannard (1986) gave bacterial counts similar to those of this study, but the bacterial cell volumes were much greater, indicating a better substrate supply in terms of available organic matter (Bölter 1990). The higher bacterial counts of Roser *et al.* (1993) and the larger bacterial cell volumes described by Ramsay and Stannard (1986) (in a similar climate to Casey) suggest that conditions for bacterial colonisation of soils at Casey are less favourable than elsewhere in the coastal region of Antarctica. However, using the same methods, Bölter (1990) and Bölter *et al.* (1993, 1994) obtained counts near Casey Station of between  $10^6$  and  $10^8$ /g DM in non-podzolic soils, suggesting that the antarctic Podzols have smaller colonies of microbes than other soils in the area.

The difference in SOM composition and SOM depth profile suggests that parent materials and different C sources influence the mechanisms of humification and translocation in the soil. We suggest that in addition to specific vegetation (e.g. mosses)

microclimate as well as soil microbial decomposition and secondary products are also responsible for the occurrence and intensity of podzolisation and organic matter transformation. For example, total bacterial counts of vegetated soils C11 and WP5 are correlated with selected organic compounds. Total bacterial counts (TBC) and alkyl-C units in a shift range of 0–45 ppm show a weak correlation of  $r = 0.639$ <sup>\*</sup>. When calculated with only the terminal methyl groups  $(0-25$  ppm) r was  $0.674*$ . These correlations suggest that bacterial metabolism affected the SOM composition, or vice versa. For this reason the alkyl-C/O-alkyl-C ratio is correlated to TBC  $(r = 0.709**)$ . The negative correlation of TBC with the signals of the aromatic-C moieties (110–160 ppm) with an *r* value of –0.633\*, especially with respect to olefinic and alkylaromatics (110–140 ppm) with an *r* value of – 0.820\*\*, suggests negative interactions between soil microbes and aromatic SOM compounds. In addition, in soil D3 without any vegetation cover, no correlations between the microbial properties and SOM compounds were present. The high numbers of bacteria may be a response to temperature because no insulating vegetation cushion mitigates a temperature increase in soil (Beyer *et al.* 2000*b*).

Formation of the podzolic soil C11 from weathered gneiss rock under mosses is characterised by a strong decrease of O-alkyl-C and an increase of aromatic- and carboxyl-C units from the recent vegetation (mosses), and probably soil algae, within the humification process. This is why White and Beyer (1999) found a strong correlation between the pyrogram of recent vegetation and the underlying soil horizons by using a Py-GC/FID technique. NMR data and partly this of Py-GC/MS data confirm a different SOM composition between the bleached AE horizon and the dark-coloured spodic Bh horizon suggested with the classification as a Podzol (FAO, 1997). Proteins were located only in the topsoils, probably due to microbial colonisation. Alkyl-C was translocated from the AE to the Bh and probably into deeper subsurface horizons, as the high abundance of lipids in the subsoil suggest. Aromatic compounds were preserved in the uppermost topsoil layer. A high protein content correlates with the extent of algal colonisation. Algae are main precursors of chlorophyll (Bölter 1995; 1997).

Soil formation of WP5 is characterised by a decrease of O-alkyl-C but only a weak increase of aromatic and carboxyl-C units from the recent soil algae colonisation (White and Beyer 1999). Surprisingly, neither NMR nor Py-GC/MS data indicate a different SOM composition between the bleached AE horizon (WP5-1) and the dark-coloured spodic Bh horizon (WP5-2) suggested by Podzol classification within the soil survey. However, both methods suggest a change in SOM quality in the WP5-3 (C) horizon. The higher carbohydrate content found with Py-GC/MS was in agreement with the somewhat higher amount of hydroxyl-C units of NMR (60–90 ppm). However, the increase of the aromatic C from WP5-2 to WP5-3 was not detected as phenol precursors or AHP. As described for the soil C11, these moieties are probably located in the unresolved fraction or in the amino carbohydrate fraction, because for soil D3 the disappearance of amino carbohydrates in the D3-4 horizon (Table 8) was well correlated with a significant decrease of the aromatic-C units (Table 6). In addition, since we are looking at the largest amount of components, some moieties occurring to a lesser extent may have been overlooked. In contrast to soil C11, the increase of the lipid fraction from WP5-1 and WP5-2 to WP5-3 was not detected with NMR. In summary, in the Podzol WP5 from glacial outwash sediments under mosses, the SOM chemistry does not reflect the soil morphology concerning the suggested chemical difference between an albic AE and a spodic Bh as known from temperate climates (Beyer *et al.* 1997). However, the Py-GC/MS data suggest a translocation of alkyl-C moieties in the podzolisation process.

For soil D3, the NMR data suggest that SOM modification from the parent organic matter material (guano) to the soil horizons by a decrease of alkyl-C and increase of carboxyl C units means a reverse relationship between both chemical units. An interpretation of the SOM data with respect to soil formation processes is complicated due to the impact of layering of different deposits by seabirds (Beyer *et al.* 2000*a*). The NMR data indicate a strong downward movement of alkyl-C with a simultaneous enrichment of O-alkyl-C, whereas aromatic and carboxyl-C moieties are stable in the profile. But an influence of layering with a different organic matter source in the deepest horizon is possible. However, Py-GC/MS shows a completely different SOM pattern in most of the 5 soil horizons, which indicates a much stronger influence of seabird-induced layering than an *in-situ* soil formation. In contrast to soil WP5, the SOM chemistry in the unvegetated soil D3 at an abandoned penguin rookery reflects the soil morphology with the assignment of a bleached AE and the dark-coloured spodic Bh horizon.

#### **Conclusions**

In permafrost-affected Podzols at the coast of East Antarctica, soil microbial colonisation with bacteria and algae as indicated by chlorophyll detection is similar to that of soils of the Maritime Antarctic. The highest bacterial colonisation was found in soil D3, the podzolic soil without any vegetation. We suggest that, in the coastal region of the Antarctic continent, not only vegetation but also the influence of seabirds on soil and the content of organic C affect microbial colonisation. The SOM composition is characterised by a high level of carboxylic C and lipidic moieties in all soil horizons, the quantity of which is uncommon compared with temperate climate regions. The correlation of selected SOM compounds and bacteria on the vegetated soils suggests that algal and moss C sources influence SOM to a great extent. The great variety in SOM composition and SOM variation with depth in the profiles suggest that parent materials and different C sources influence the mechanisms of humification and translocation. We think that not only vegetation but predominantly microclimate and soil microbial decomposition and secondary microbial products are responsible for the detailed geochemistry of these processes. The observed pattern variety of long-chain alcohols, acids, and ketones observed with the Py-GC/MS technique are not typical for well-developed soil. Most of the long chains in the Antarctic soil samples appear to contain multiple O- and N-containing functional groups, cyclicionised and heterocyclic structures, and alkylations, which are confirmed by the occurence of 20–40% aromatic NMR C subunits. However, the complex and easily ionised compounds and the low C content made Py-GC/MS identification very difficult, resulting in several unresolved fractions. With respect to soil formation in a Gelic Podzol from weathered gneiss rock under mosses, alkyl-C units must have been translocated from the AE to the Bh and probably into more deeply located horizons, whereas aromatic compounds have been preserved in the uppermost topsoil layer. In a Podzol from glacial outwash sediments under mosses, the SOM chemistry does not reflect the soil morphology. However, the Py-GC/MS data indicate a translocation of alkyl-C moieties within the podsolisation process. The data combination of NMR and Py-GC/MS suggests that a large amount of aromatic C is hidden in the unresolved fraction of Py-GC/MS. In contrast, in an unvegetated Podzol at an abondoned penguin rookery the SOM chemistry reflects the soil morphology with the assignment of a bleached AE and the dark-coloured spodic Bh horizon. However, from the Py-GC/MS data no translocation of lipid moieties was found. For this reason we think that podzolisation in antarctic soils is chemically an ill-defined soil formation process. The processes of formation and translocation of SOM shown are

variable and are affected by the parent materials, the physical and mechanical properties, and by the microclimate and local moisture regime as well as the degree of microbial colonisation.

Regardless of the origin and location of the antarctic Gelic Podzols, these soils store huge amounts of C and N (Beyer *et al.* 1998). SOM depth functions and the comparison of the profiles suggest unknown C and N sources. This puzzle is not solved by our detailed SOM investigation of 3 typical antarctic Podzols. Finding the origin of SOM should be included in future research in antarctic soil science. The results of the analytical approaches and field observations presented in this study suggest that podzolisation and SOM transfer may play an important role in nutrient cycles in antarctic ecosystems. However, little is known about the geo-ecological correlations between soil sources and plant communities in terrestrial Antarctica

#### **Acknowledgment**

This investigation was supported financially by the Australian Antarctic Divison, Kingston, Tasmania, and the German Research Council (DFG) (Be1259/4-1). The Australian Antarctic Research Expeditions and especially the Casey crew in the summer of 1995/1996 supported the field and laboratory work. Some lab work was carried out by Birgit Vogt, Solveig Mevold-Lanzius and Sudelia Kneesch in the Institute of Soil Science of the University of Kiel. Prof. Dr J. G. Bockheim, Madison, improved drafts of the present paper with respect to interpretation and language editing. The authors gratefully acknowledge all of them. Special thanks to Prof. Dr. Dr. h. c. H.-P. Blume; because of his engagement the senior author had the possibility to participate at the field expedition in the Antarctic summer 1995/1996.

#### **References**

- Beyer L, Blume H-P, Knicker H, Bölter M (1997) Soil organic matter of suggested spodic horizons in relic ornithogenic soils of coastal continental Antarctica (Casey Station, Wilkes Land) and spodic horizons in soils of Germany. *Soil Science* **162**, 518–527.
- Beyer L, Bölter M, Seppelt RD (2000*b*) Thermal regime and microbial biomass and vegetation pattern of soils in the coastal region of Antarctica (Wilkes Land). *Arctic, Antarctic and Alpine Research* **32**, 30–39.
- Beyer L, Pingpank K, Bölter M, Seppelt RD (1998) Small-distance variation of carbon and nitrogen storage in different Antarctic mineral Cryosols near Casey Station. *Zeitschrift für Pflanzenernährung und Bodenkunde* **161**, 211–220.
- Beyer L, Pingpank K, Wriedt G, Bölter M (2000*a*) Soil formation in coastal continental Antarctica. *Geoderma* **95**, 283–304.
- Beyer L, Sorge C, Blume H-P, Schulten H-R (1995) Soil organic matter composition and transformation in gelic Histosols of coastal continental Antarctica. *Soil Biology and Biochemistry* **27**, 1279–1288.
- Blume H-P, Beyer L, Bölter M, Erlenheuser H, Kalk E, Kneesch S, Pfisterer U, Schneider D (1997) Pedogenic zonation in soils of Southern circumpolar region. *Advances in GeoEcology* **30**, 69–90.
- Blume H-P, Schneider D, Bölter M (1996) Organic matter accumulation in and podzolization of antarctic soils. *Zeitschrift für Pflanzenernährung und Bodenkunde* **159**, 411–412.
- Bockheim JG (1997) Properties and classification of cold desert soils from Antarctica. *Soil Science Society of America Journal* **61**, 224–231.
- Bölter M (1990) Microbial ecology of soils from Wilkes Land, Antarctica: 1. The bacterial population and its activity in relation to dissolved organic matter. *Proceedings NIPR Symposium Polar Biology* **3**, 104–119.
- Bölter M (1995) Distribution of bacterial numbers and biomass in soils and on plants from King-George Island (Arctowski Station, Maritime Antarctica). *Polar Biology* **15**, 115–124.
- Bölter M (1997) Microbial communities in soils and on plants from King-George Island (Arctowski Station, Maritime Antarctica). In 'Antarctic communities: species, structure and survival'. (Eds B Battaglia, J Valencia, DWH Walton) pp. 162–169. (University Press: Cambridge)
- Bölter M, Blume H-P, Beyer L, Schneider D (1997) Soil biological investigations in the maritime and continental Antarctic (King George Island and Windmill Islands). 2. Dissolved and particulate organic nutrients. *Polar Biology* **18**, 295–304.
- Bölter M, Blume H-P, Erlenkeuser H (1994) Pedogenic, isotopic and microbiological properties of Antarctic soils. *Polarforschung* **64**, 1–7.
- Bölter M, Möller R, Dzomla W (1993) Determination of bacterial biovolume with epifluorescence microscopy: comparison of size distributions from image analysis and size classifications. *Micron* **24**, 31–40.
- Bracewell JM, Haider J, Larter SR, Schulten HR (1989) Thermal degradation relevant to structural studies of humic substances. In 'Humic Substances II'. (Eds. MBH Hayes, R MacCarthy, RL Malcolm, RS Swift) pp. 181–222. (John Wiley and Sons: New York)
- Campbell IB, Claridge GGC (1987) `Antarctica: soils, weathering processes and environment.' (Elsevier: Amsterdam)
- Daly BK (1982) Identification of Podzols and podzolised soils in New Zealand by relative absorbance of oxalate extracts of A and B horizons. *Geoderma* **28**, 29–38.
- Davey MC (1988) Ecology of terrestrial algae of the fellfield ecosystems of Signy Island, South Orkney Islands. *British Antarctic Survey Bulletin* **81**, 69–74.
- Davey MC (1991) The seasonal periodicity of algae on Antarctic fellfield soils. *Holarctic Ecology* **14**, 112–120.
- Deckers JA, Spaargaren OC, Nachtergale F (1998) World Reference Base for Soil Resources. *World Soil Resources Reports* **84**. FAO, ISRIC, ISSS, Rome.
- FAO (1997) Soil map of the world. *Technical Paper* **20**. ISRIC, Wageningen.
- Fründ R, Lüdemann H-D (1989) The quantitative analysis of the solution- and CPMAS 13C-NMR spectra of humic material. *The Science of the Total Environment* **81/82**, 157–168.
- Goodwin ID (1993) Holocene deglaciation, sea-level change, and the emergence of the Windmill Islands, Budd Coast, Antarctica. *Quaternary Research* **40**, 70–80.
- Grimme H, Wiechmann H (1969) Eine Methode zur Extraktion organisch gebundenen Eisens aus Böden. *Zeitschrift für Pflanzenernährung und Bodenkunde* **122**, 268–279.
- Hempfling R, Schulten H-R (1990) Chemical characterization of the organic matter in forest soils by Curie point pyrolysis-GC/MS and pyrolysis-field ionozation mass spectrometry. *Organic Geochemistry* **15**, 131–145.
- Jeffrey SW, Humphrey GF (1975) New spectroscopic equations for determing chlorophylls *a*, *b*, *c*1, and *c*2 in higher plants, algae and natural phytoplankton. *Biochemie und Physiologie der Pflanze* **167**, 191–194.
- Jacobsen BH (1991) Multiple processes in the formation of subarctic podzols in Greenland. *Soil Science* **152**, 414–426.
- Kaiser K, Zech W (1996) Deffects in estimation of aluminum in humus complexes of the podzolic soils by pyrophosphate extraction. *Soil Science* **161**, 252–258.
- Lorenzen CF (1967) Determination of chlorophyll and phaeopigments: spectroscopic equations. *Limnology and Oceanography* **12**, 343–346.
- McKeague JA, DeConnick F, Franzmeier DP (1983) Spodosols. In 'Pedogenesis and soil taxonomy. II.The soil orders'. (Eds LP Wildung, NE Smeck, GF Hall) pp. 217–252. (Elsevier: Amsterdam)
- Ohtani S, Akiyama M, Kanda H (1991). Analysis of Antarctic algae by direct observation using the contact slide method. *Antarctic Records* **35**, 285–295.
- Paul E, Stüwe K, Teasdale J, Worley B (1995) Structural and metamorphic geology of the Windmill Islands, East Antarctica: field evidence for repeated tectonothermal activity. *Australian Journal of Earth Sciences* **42**, 453–469.
- Pickard J (1986) 'Antarctic oasis. Terrestrial environment and history of the Vestfold Hills.' (Academic Press: London)
- Post B, Hempfling R, Klamberg H, Schulten H-R (1988) Zur Charakterisierung von Boden-Huminstoffen. *Fresenius Zeitschrift für Analytische Chemie* **331**, 273–281.
- Ramsay AJ, Stannard RE (1986) Numbers and viability of bacteria in ornithogenic soils of Antarctica. *Polar Biology* **5**, 195–198.
- Roser DJ, Seppelt RD, Asholt N (1993) The microbiology of ornithogenic soils from the Windmill Islands, Budd Coast, Continental Antarctica: Microbial biomass distribution. *Soil Biology and Biochemistry* **25**, 165–175.
- Seppelt RD (1984) The bryoflora of Vestfold Hills and Ingrid Christensen Coast, Antarctica. *Australian National Antarctic Research Expeditions Research Notes* **20**, 1–31.
- Seppelt RD, Broady PA (1988) Antarctic terrestrial ecosystems: The Vestfold Hills in context. In 'Biology of the Vestfold Hills, Antarctica'. (Eds JM Ferris, HR Burton, IAE Bayly) pp. 177–184. (Kluwer Academic Publisher: Dordrecht)
- Smith RIL (1985) Nutrient cycling in relation to biological productivity in antarctic and sub-antarctic terrestrial and freshwater ecosystems. In 'Antarctic nutrient cycles and food webs'. (Eds WR Siegfried, PR Condy, RM Laws) pp. 138–155. (Springer: Berlin)
- Smith RIL (1990) Plant community dynamics in Wilkes Land, Antarctica. *Proceedings NIPR Symposium Polar Biology* **3**, 229–244.
- Soil Survey Staff (1996) 'Keys to Soil Taxonomy.' 7th edn (USDA-NRCS: Washington)
- Soil Survey Staff (1998) 'Keys to Soil Taxonomy.' 8th edn (USDA-NRCS: Washington)
- Van Reeuwijk L (1993) 'Procedures for soil analysis.' 4th edn (ISRIC: Wageningen)
- White DM, Beyer L (1999) Pyrolysis-GC/MS and GC/FID of three antarctic soils. *Journal of Analytical and Applied Pyrolysis* **50**, 63–76.
- White DM, Irvine RL (1998) Potential applications from pyrolysis-GC/MS in bioremediation. *Journal of Environmental Monitoring and Assessment* **50**, 53–65.
- Wiechmann H, Grimme H (1969) Extraktion von organisch gebundenem Eisen aus Sandböden. *Zeitschrift für Pflanzenernährung und Bodenkunde* **122**, 260–267.
- Wynn-Williams DD (1985) Comparative microbiology of moss-peat decomposition on the Scotia Arc and Antarctic Peninsula. In `Antarctic nutrient cycles and food web´. (Eds WR Siegfried, W PR Condy, RM Laws) pp. 204–210. (Springer: Berlin)

Manuscript received 2 May 2000, accepted 4 October 2000

http://www.publish.csiro.au/journals/ajsr