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Do P Cycling Patterns Differ between Ice-Free Areas and Glacial Boundaries in the Maritime Antarctic Region?

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Abstract

Antarctic studies have indicated that during summer, ice-free areas experience greater temperatures than those along the glacial boundaries. This allows for the availability of liquid water and thus influences the biogeochemical processes of Antarctic terrestrial ecosystems. In this study we explore whether the patterns of soil phosphorus cycling differ between the glacial boundary and ice-free areas. To do so, we chose two sites on the Fildes Peninsula in Antarctica, one at the boundary of the Collins Glacier and another within an ice-free area close to Lake Uruguay. In each location, we determined soil phosphorus distribution, iron and aluminum fractions, soil mineralogy, alkaline phosphatase activity, and fluorescein diacetate hydrolysis. The results showed that soils of the ice-free area had a greater content of phosphorus sorbed on iron/aluminum oxyhydroxides and occluded forms. An opposite pattern was obtained for the calcium-bound phosphorus pool. Accordingly, soil samples from the ice-free area showed the greatest levels of iron/aluminum oxyhydroxides and the presence of secondary minerals such as hematite and the intergrade chlorite-vermiculite-montmorillonite. Alkaline phosphatase activity and the fluorescein diacetate hydrolysis were also favored at the ice-free area. The overall results suggest that the less extreme microclimatic conditions and the presence of liquid water in the ice-free area promote the biogeochemical cycling of soil phosphorus. In a context of climate warming this study may contribute to the comprehension of how the expansion of the ice-free areas due to glacial retreat influences biogeochemical cycling of essential nutrients in the Antarctic Peninsula.

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Introduction

A number of studies have concluded that Antarctic soils can sustain communities of heterotrophic organisms in spite of the extremely low temperatures and dry conditions to which they are exposed (i.e., Burkins et al., 2000, 2001; Hopkins et al., 2006a, 2006b; Hopkins et al., 2008). These findings have given rise to several research projects focused on the biotic and/or abiotic factors driving the soil nutrient cycling in the terrestrial ecosystems of this region (i.e. Tscherko et al., 2003; Barrett et al., 2005, 2006; Gajananda, 2007; Hogg et al., 2006; Hopkins et al., 2006a, 2006b; Aislabie et al., 2008; Cannone et al., 2008).

Among the essential nutrients, phosphorus (P) is considered to be the element that most commonly limits net primary productivity in various soil conditions (Vitousek, 1984; Hinsinger, 2001). This is a consequence of its poor mobility due to high reactivity with numerous soil constituents such as iron (Fe) and aluminum (Al) oxyhydroxides, calcium (Ca), organic matter, and clay minerals (Hinsinger, 2001; Chacón and Dezzio, 2004). In soils of the Antarctic continent there is some controversy regarding P as a limitation. In Antarctic field experiments it has been shown that primary productivity increases mainly by the addition of nutrients such as nitrogen (N) and P (Wasley et al., 2006; Hopkins et al., 2008). However, the elevated levels of available P, and the low C:P ratio of these soils, allowed other authors to suggest that P is not biologically limiting in the terrestrial ecosystems of this region (Bate et al., 2008). Nevertheless, it is well recognized that soils

adjacent to Antarctic streams and lakes can be a significant source of available P to these biologically P limiting waters (i.e. Priscu, 1995; Dore and Priscu, 2001; Barrett et al., 2009).

Soil P is generally characterized by various pools that are a function of the state of soil development; whereas the primary inorganic pool is characteristic of young soils, the secondary inorganic- and organic-P pools predominate in more mature soils (Walker and Syers, 1976). Previous studies have shown that soil development is the result of the interplay among parent material, topography, climate, organisms, and time (i.e. Jenny, 1941; Kelly and Yonker, 2005; Bockheim et al., 2005). However, several authors agree that climate (temperature and humidity) plays an important role in soil formation because it controls the rate of physical, chemical, and biological soil processes (Cooper, 1960; Birkeland et al., 1989; Kelly and Yonker, 2005; Egli et al., 2006a; Barrett et al., 2009). In fact, in non-Antarctic cold regions the rate of soil evolution is considered to be distinctly determined by the availability and flow of soil water (Egli et al., 2003; 2006a, 2006b). However, in Antarctic regions, where the liquid water availability is restricted to austral summer (Chen and Blume, 2000; Gooseff et al., 2003), several authors have also recognized that climate is the main driving factor of soil genesis (Ugolini, 1963; Everett, 1976; Matsuoka, 1995; Zhao and Li, 1996; Chen and Blume, 1999; Gooseff et al., 2003; Cannone et al., 2008; Navas et al., 2008; Barrett et al., 2009; Bölter, 2011; López-Martínez et al., 2012).

Taking into account the above findings, in Antarctic terrestrial ecosystems it is expected that P distribution could be affected by

climate. In this region only two studies have reported the soil P fractions (Blecker et al., 2006; Bate et al., 2008), and, in both, authors concluded that this element lies mainly in the primary inorganic pool. However, Blecker et al. (2006) indicated that differences in the weathering intensity between sites account for spatial variability in the soil P pools; while Bate et al. (2008) proposed that geologic legacies strongly influence the soil P distribution. It is noteworthy that these studies are restricted to continental sites in Antarctica, while for maritime Antarctica this question remains unclear.

Based on studies from maritime Antarctica, Ugolini and Bockheim (2008) provided considerable evidence for climate warming in this region. Some authors have characterized these climate conditions as the warmest and moistest within Antarctica (i.e. Ferron et al., 2004; Ugolini and Bockheim, 2008; Navas et al., 2008). Despite their sensitivity to climate warming, most areas of this region are still covered by glaciers (Lee et al., 2004), while the ice- and snow-free areas are scarce (Navas et al., 2008). There are strong microclimatic differences between glaciers and the ice- and snow-free areas. During the summer months, the relatively greater temperature of the ice- and snow-free areas leads to a deep thawing period that produces a more favorable supply of liquid water (Chen and Blume, 2000; Gooseff et al., 2003). In contrast, in terrestrial areas adjacent to subsurface ice, liquid water is limited to the warmest hours of the day (Motta and Motta, 2004).

Taking into account these findings and the role of water availability in the evolution of the Antarctic soils, we asked whether there were significant differences in the geochemical cycling of soil P between sites near glacial boundaries and those on ice-free areas. Were they to exist, we hypothesized that the concentration of several inorganic P pools defined as P sorbed on amorphous and some crystalline Al and Fe oxyhydroxides and occluded forms should show greater values in the ice-free areas. An opposite trend is expected for the Ca-bound P pool.

In addition to the foregoing hypothesis concerning the chemically defined P fractions, we also hypothesized that biological cycling of P should be favored in the ice-free areas. Support for this assumption comes from the research of Barrett et al. (2006, 2009), Gajananda (2007), Zeglin et al. (2009), and Bölter (2011), who have pointed out that due to the absence of higher plants, soil communities in terrestrial Antarctic ecosystems are largely controlled by abiotic factors. In principle, in those areas with greater liquid water availability due to increasing temperatures, biotic activity would be enhanced. Thus, in order to test these hypotheses, we chose a site along the boundary of the Bellingshausen Ice Dome (Collins Glacier) and another in an ice-free area in the vicinity of Lake Uruguay, Antarctica.

Materials and Methods

STUDY AREA AND SAMPLE COLLECTION

The study site was located in the vicinity of the Artigas Antarctic Scientific Base (Base Científica Antártica Artigas [BCAA]) on the Fildes Peninsula of King George Island, which forms part of the South Shetland Islands in Maritime Antarctica (61°54′–

62°16′S; Fig. 1). The climate is maritime with an annual mean precipitation and temperature of 800 mm and -2°C (1989–2001; Navas et al., 2008), respectively. During summer the temperatures of the surface soils can reach more than 10°C (Zhao and Li, 1996). Vegetation consists of lichens, mosses, algae, and the grass, *Deschampsia antarctica* (Soave et al., 2000).

The Fildes Peninsula, located at the extreme southwest of King George Island, is the largest ice-free area on the island (Soave et al., 2000; Vogt and Braun, 2004). In this region the last deglaciation occurred at 8–5 ka B.P. (López-Martínez et al., 2012). The peninsula consists of a thick subalkaline volcanic rock stratum with intercalations of volcanoclastic rock that characterize the Fildes Peninsula Group (Almeida et al., 2003). According to Zhao and Li (1996), soil development at this site is controlled by the parent material, landforms, and bioclimatic factors. Soils of the Fildes Peninsula are composed of Histosols, Regosols, Cambisols, and Andisols (Chen and Blume, 1999).

The soil samples were collected from two sites in the vicinity of BCAA: one at the boundary of the Collins Glacier (BG: 62°10′49.62″S, 58°54′34.75″W) and the other in an ice-free area (IFA: 62°11′08.33″S, 58°54′33.02″W) near Lake Uruguay (Fig. 1). We considered only one study site for the ice-free area and another one for the boundary of the glacier because genuine replicates of these sites were not feasible in widely spaced geographic areas. The lack of field replication and consequently the risk of pseudo-replication are almost inevitable in the studies of large-scale systems (i.e. rivers, small watersheds, forest patches) (Hargrove and Pickering, 1992; Oksanen, 2001) such as these. We think this level of pseudo-replication in our study does not undermine our results, though it does mean they should be interpreted with caution, as other authors in similar situations have pointed out.

In each study site, we sampled the surface mineral horizon (0–10 cm) from 15 points selected according to a completely random design (total $n = 30$). The sampling depth was limited to 10 cm due to the presence of stones and rocks. The samples were stored in plastic bags. While those samples destined for the analysis of microbial and enzymatic activity were maintained at $+4^{\circ}\text{C}$, the samples for chemical analysis were air dried at room temperature (Tschirko et al., 2003). A preliminary analysis showed that soil textural class was similar between sites; however, other soil properties such as pH and organic carbon content (OC), showed differences (Benzo et al., unpublished data; samples collected in 2009; Table 1). During the sampling, the field temperatures recorded at lakes adjacent to BG and IFA sites were 2.4°C and 5.3°C , respectively.

P FRACTIONS

Soil P fractions were obtained according to the method of Hedley et al. (1982), which was modified by Tiessen and Moir (1993). This procedure uses a sequence of increasingly strong reagents to remove the labile and more stable P forms (Tiessen and Moir, 1993). Aliquots of 0.50 g of dry soil previously ground and sieved (0.43 mm) were sequentially extracted with anion exchange resin, followed by 0.5 M NaHCO_3 , 0.1 M NaOH , 0.5 M HCl , and hot concentrated HCl . Total P was determined in aliquots of each extract by digestion with ammonium persulphate and H_2SO_4 to convert all the organic P forms (Po) to inorganic P forms (Pi).

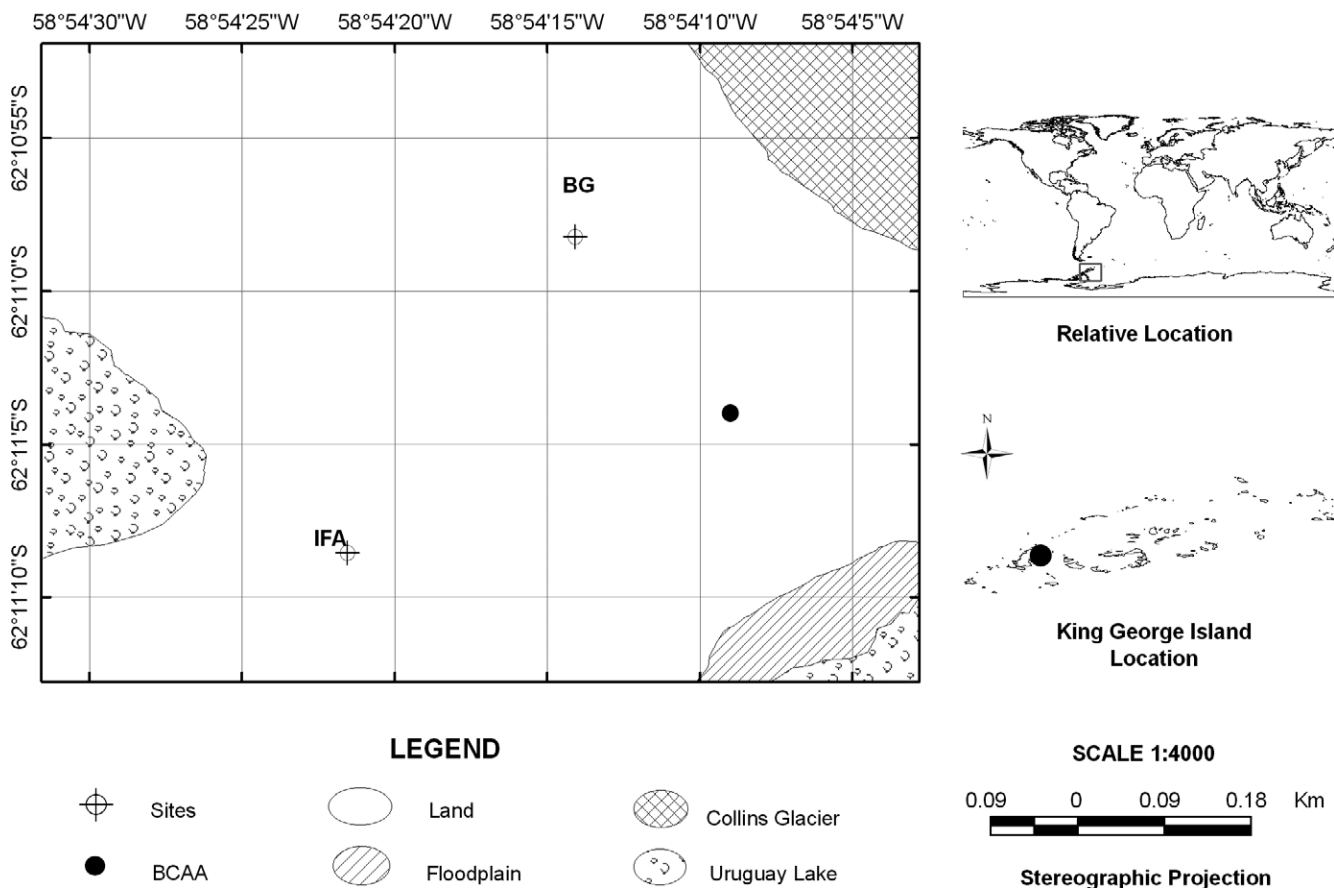


FIGURE 1. Map of King George Island showing the relative locations of the studied sites. BCAA = Base Científica Antártica Artigas, BG = boundary of the glacier, IFA = ice-free area. Digitalized image from the Letter 1111: Artigas Antarctic Scientific Base (Service of Oceanography, Hydrography and Meteorology of the Navy of Uruguay, 1991).

Another aliquot of each extract was used to measure Pi after acidification with H_2SO_4 to precipitate organic matter. In each extract, the pH was adjusted, and the P concentration was determined colorimetrically by means of the molybdate-ascorbic acid procedure (Murphy and Riley, 1962). Organic phosphorus was calculated as the difference between total P and Pi. According to Tiessen and Moir (1993), soil P fractions obtained by this procedure have been associated with the following operationally defined pools: (i) P extracted with resin is often considered as the labile P; (ii) bicarbon-

ate- and hydroxide-extractable P are distinguished as labile and moderately labile P forms respectively, associated to Fe/Al oxyhydroxides; (iii) diluted HCl P is associated with the primary mineral and/or Ca-bound P; and (iv) hot concentrated HCl P is defined as the highly resistant and unavailable P.

Al AND Fe FRACTIONS

A sequential selective dissolution method was used to estimate the organically bound, non-crystalline and crystalline forms of Fe and Al (Wieder and Lang, 1986). Organically bound Fe and Al were extracted with sodium pyrophosphate (Fe_P, Al_P) (McKeague, 1967). Poor crystalline forms of Fe and Al (Fe_O, Al_O) were obtained by extracting the soil with ammonium oxalate (pH = 4 in the dark) (McKeague and Day, 1966), and highly structured Fe and Al associated with crystalline Fe oxides were extracted with dithionite-citrate-bicarbonate (Fe_{DCB}, Al_{DCB}) following the method of Mehra and Jackson (1960). Concentrations of both elements in each extract were determined using atomic absorption spectroscopy.

SOIL MINERALOGY

Soil mineralogy was obtained via X-ray diffraction (XRD) using Cu-K α radiation. Four representative soil samples from each

TABLE 1

Some soil properties in the boundary of the glacier (BG) and in the ice-free area (IFA) (D. Benzo et al., unpublished data).

Soil properties	BG	IFA
pH	8.18 \pm 0.08 ^a	7.18 \pm 0.05 ^b
% OC	1.13 \pm 0.36 ^a	0.09 \pm 0.03 ^b
% Clay	6 ^a	2 ^b
% Silt	8 ^a	3 ^b
% Sand	86 ^b	95 ^a
Textural class	Sandy	Sandy

Mean values \pm 1 SE followed by different letters in rows denote significant differences between sites. OC = organic carbon.

study site were made into pressed powder pellets for XRD analysis. Samples were mounted on glass plates and analyzed from 5° to 90° 2θ with a speed of 2° 2θ per minute. The software code PDFWIN for windows was used for the evaluation of diffraction patterns.

BIOLOGICAL AND BIOCHEMICAL ANALYSIS

In this study, the activity of alkaline phosphatase (AP) was measured as an index of organic P mineralization (Dick and Tabatabai, 1993), while the fluorescein diacetate (FD) hydrolysis was used as a measure of soil microbial activity (Schnürer and Rosswall, 1982; Green et al., 2006). In alkaline soils such as at the two study sites, it is advisable to measure the activity of AP because it is usually greater than that of the acid phosphatase (Eivazi and Tabatabai, 1977). Briefly, aliquots of fresh soil after incubation at +37 °C were used to assess FD hydrolysis and AP activity following the procedures of Schnürer and Rosswall (1982) and Tabatabai and Bremner (1969), respectively.

STATISTICAL ANALYSIS

A one-way analysis of variance (ANOVA) was used to compare soil P fractions, Fe and Al forms, and microbial and biochemical (fluorescein diacetate hydrolysis and alkaline phosphatase) activities. When necessary, data were log-transformed to meet the assumptions of ANOVA (NaOH-Pi, Al_T, FDA). The Tukey Honest Significant Difference (HSD) test was used as a means separation procedure. The Mann Whitney non-parametric test was used when the data did not meet ANOVA assumptions (resin-Pi, NaHCO₃-Pi, NaOH-Po, HCl_{conc}-Po, Al_O, Al_{DCB}, Al_O/Al_{DCB}). Pearson's correlation coefficient (*r*) was used to examine the relationship among parameters (soil P fractions, and microbial and biochemical activities versus P pools). Univariate analyses were performed using STATISTICA for Windows 6.0 (Statistica, 2001).

We used a Principal Component Analysis (PCA) to determine if the concentration of soil inorganic P pools can discriminate between sites influenced by glaciers and the ice-free areas. PCA was performed using the software Multi-Variate Statistical Package (MVSP 3.0 for Windows; Kovach, 1998).

Results

SOIL P FRACTIONS

Concentrations of soil P in the various fractions at both sites are summarized in Table 2. The soil from the BG had less P in the resin-Pi fraction. No difference ($P > 0.05$) between sites was observed among the mean values of NaHCO₃-Pi. None of the sampled sites showed significant differences ($P > 0.05$) in organic P fractions (NaHCO₃-, NaOH-, HCl_{conc}-). The concentration of NaOH-Pi fraction, which is associated with the P strongly chemisorbed on amorphous and some crystalline Al and Fe phosphates (Tiessen et al., 1983), increased significantly in IFA. The soil at IFA also contained greater P in the concentrated HCl-Pi fraction.

TABLE 2

Values of soil phosphorus fractions (mg kg⁻¹) in the boundary of the glacier (BG) and in the ice-free area (IFA).

Fraction	BG	IFA
Resin-Pi	27.48 ± 1.32 ^b	47.88 ± 4.06 ^a
NaHCO ₃ -Pi	0.96 ± 0.19 ^a	3.00 ± 1.34 ^a
NaOH-Pi	2.96 ± 0.43 ^b	24.30 ± 12.91 ^a
HCl(dil)-Pi	385.89 ± 9.21 ^a	281.75 ± 16.72 ^b
HCl(conc)-Pi	26.80 ± 1.97 ^b	39.15 ± 1.68 ^a
NaHCO ₃ -Po	7.95 ± 1.70 ^a	8.46 ± 2.57 ^a
NaOH-Po	1.98 ± 0.41 ^a	9.47 ± 5.97 ^a
HCl-Po	0.68 ± 0.35 ^a	2.52 ± 1.03 ^a

Mean values ± 1 SE followed by different letters in rows denote significant differences between sites. Pi = inorganic phosphorus; Po = organic phosphorus.

One important difference between sites was that soil of the IFA, which contained greater P concentrations in NaOH-Pi and HCl_{conc}-Pi fractions, had lower P in the diluted HCl-Pi fraction, which is linked to unweathered Ca-bound P phases. At this site the weathering of primary minerals seemed to yield soluble P because a positive correlation ($r = 0.63$, $P < 0.05$; $n = 15$) was obtained between resin-Pi and the diluted HCl-Pi fractions. Both parameters were not correlated at the BG site ($r = -0.03$, $P > 0.05$; $n = 15$). Soil from the IFA also showed a negative correlation between NaOH-Pi and the diluted HCl-Pi fraction ($r = -0.77$, $P < 0.05$; $n = 15$). This correlation was not observed in the BG soil ($r = 0.09$, $P > 0.05$; $n = 15$).

Principal Component Analyses (PCA) of the soil inorganic P fractions from the two studied sites is shown in Figure 2. Only the first two axes of ordination are illustrated; these accounted for 65.0% of the variance (Table 3). This analysis clearly showed that, whereas the BG site was associated with soils showing high concentration of the diluted HCl-Pi and low concentrations of resin-, NaHCO₃-, NaOH-, and concentrated HCl-Pi fractions, the IFA findings were opposite.

IRON AND ALUMINUM FRACTIONS

The results of the organically bound, non-crystalline and crystalline forms of Fe and Al are presented in Table 4. In the BG site, the content of total extractable iron (Fe_T = Fe_P + Fe_O + Fe_{DCB}) was well above the total extractable aluminum (Al_T = Al_P + Al_O + Al_{DCB}); however, in the IFA they were in the same order of magnitude.

In both sites, the content of organically bound forms of Fe and Al (Fe_P, Al_P) was low and their contributions to the content of Fe_T and Al_T were as follows: BG: Fe_P = 1.8%, Al_P = 11.7%; IFA: Fe_P = 3.2%, Al_P = 13.5%. Comparisons of mean values between BG and IFA revealed no significant differences ($P > 0.05$) for Fe_P, whereas Al_P increased sharply in the IFA soil. Poorly crystalline forms of Fe and Al (Fe_O, Al_O) followed a trend similar to that of the Fe_P and Al_P fractions. The greatest content of crystalline Fe (Fe_{DCB}) was found in the BG soil; however, there was no difference in the content of crystalline Al (Al_{DCB}) between sites. Non-crystallinity ratios (Al_O/Al_{DCB}, Fe_O/Fe_{DCB}), interpreted as the

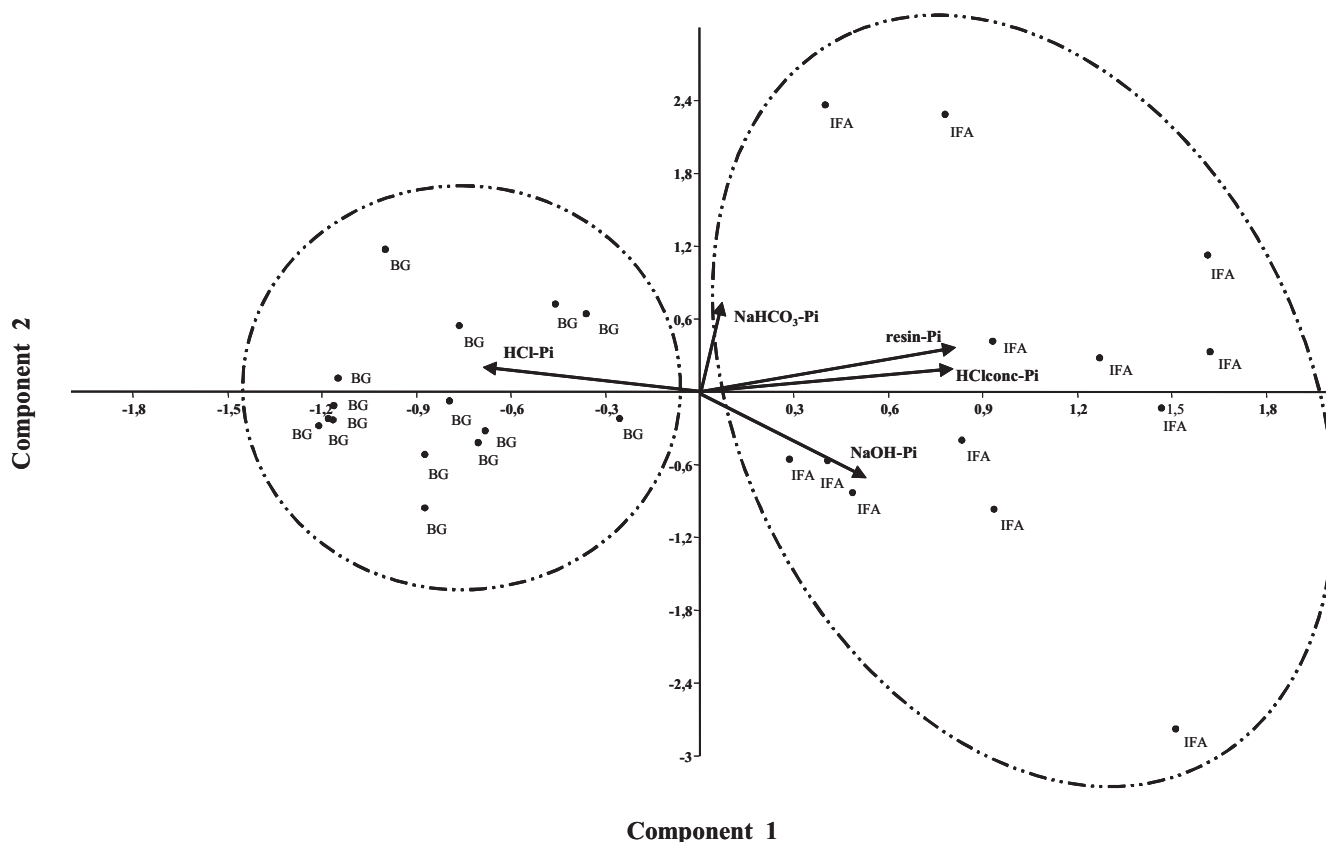


FIGURE 2. Principal Component Analysis for soil P fractions data of the studied sites. IFA = ice-free area, BG = boundary of the glacier.

larger ratio the lower crystallinity (Beck and Elsenbeer, 1999), were greatest in the IFA soil.

SOIL MINERALOGY COMPOSITION

Soil mineralogical composition was different between studied sites. While in the BG site, XRD analysis showed the presence of labradorite, quartz, and the P-bearing mineral hydroxyapatite, the major mineral phases identified in the IFA were labradorite, quartz, and the secondary minerals hematite and chlorite-vermiculite-montmorillonite (Fig. 3; Table 5). Relative abundance of soil minerals at the study sites, as judged from peak heights of the diffractograms, was as follows: BG: labradorite > quartz > hydroxyapatite; IFA: labradorite > hematite > quartz > chlorite-vermiculite-montmorillonite (Fig. 3).

TABLE 3

Eigenvalues and cumulative percentage variance of soil phosphorus fractions for the Principal Component Analysis carried out with data of the studied sites.

Axes	1	2	3	4
Eigenvalues	2.0	1.2	0.9	0.6
Total percentage variance	40.6	24.4	19.0	11.8
Cumulative percentage variance	40.6	65.0	84.0	95.8

ALKALINE PHOSPHATASE AND FLUORESCIN DIACETATE HYDROLYSIS. IMPLICATIONS IN THE GEOCHEMICAL CYCLING OF P

There was a significant difference between sites with respect to enzyme activity and fluorescein diacetate hydrolysis (Table 6). The greatest values for both parameters were detected at the IFA.

TABLE 4

Values of iron and aluminum fractions (mmol kg^{-1}) in the boundary of the glacier (BG) and in the ice-free area (IFA).

Fraction	BG	IFA
Fe_P	3.01 ± 0.39^a	3.92 ± 0.36^a
Fe_O	53.31 ± 1.95^a	55.45 ± 2.76^a
Fe_{DCB}	107.77 ± 3.67^a	61.13 ± 3.49^b
Fe_T	164 ± 4^a	121 ± 5^b
Al_P	3.39 ± 1.50^b	21.21 ± 3.46^a
Al_O	5.45 ± 2.39^b	109.70 ± 9.40^a
Al_{DCB}	20.21 ± 0.62^a	25.68 ± 2.80^a
Al_T	29 ± 3^b	157 ± 12^a
$\text{Fe}_O/\text{Fe}_{\text{DCB}}$	0.50 ± 0.02^b	0.93 ± 0.05^a
$\text{Al}_O/\text{Al}_{\text{DCB}}$	0.30 ± 0.14^b	4.72 ± 0.54^a

Mean values ± 1 SE followed by different letters in rows denote significant differences between sites. $\text{Fe}_O\text{-Al}_O$, $\text{Fe}_{\text{DCB}}\text{-Al}_{\text{DCB}}$, and $\text{Fe}_P\text{-Al}_P$ = ammonium-oxalate, dithionite-citrate-bicarbonate, and pyrophosphate extractable Fe or Al, respectively; $\text{Fe}_T\text{-Al}_T = \sum \text{Fe}_O\text{-Al}_O$, $\text{Fe}_{\text{DCB}}\text{-Al}_{\text{DCB}}$, and $\text{Fe}_P\text{-Al}_P$, respectively.

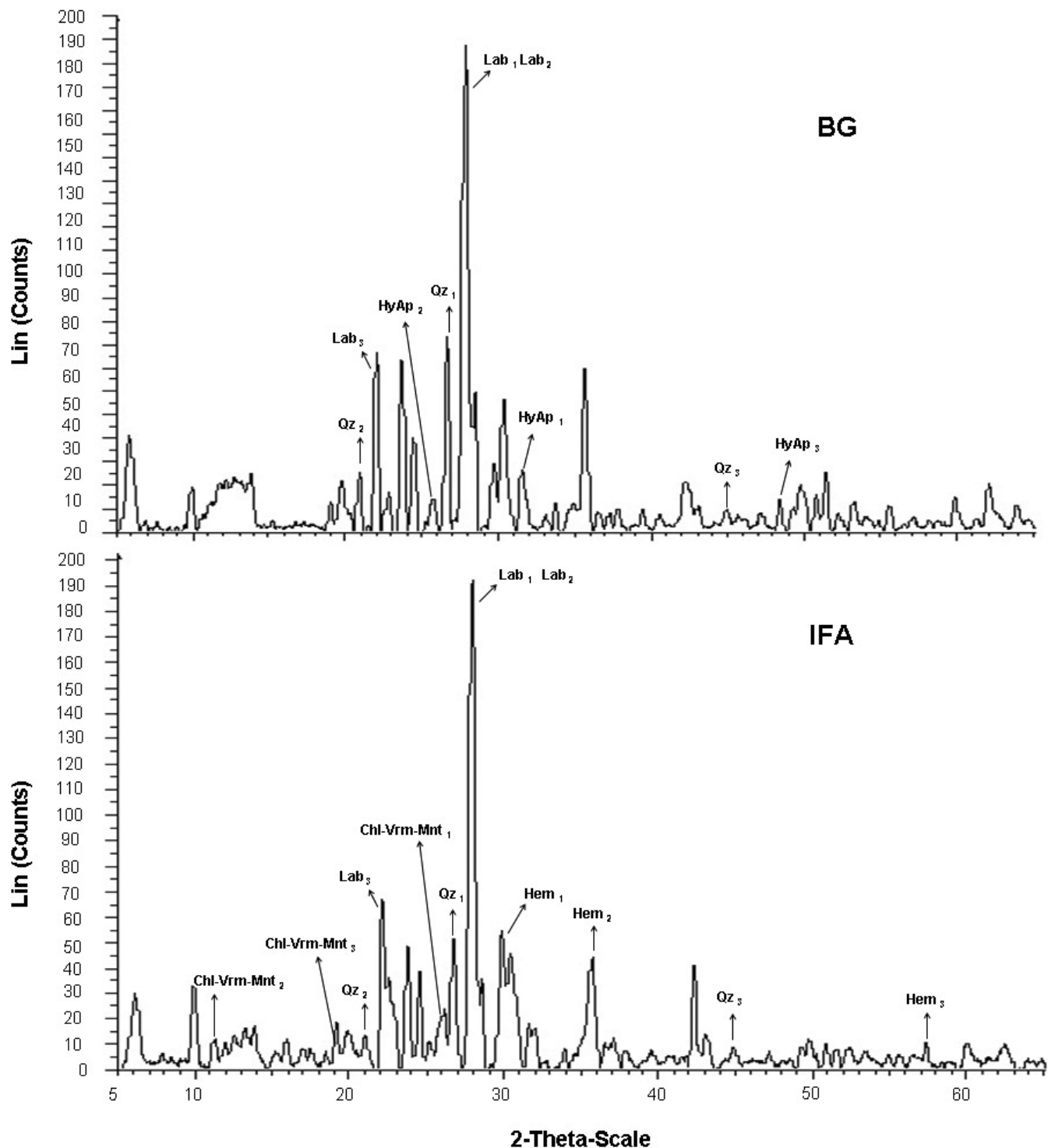


FIGURE 3. Typical X-ray diffraction patterns showing the three main peaks of the identified minerals at the studied sites. IFA = ice-free area, BG = boundary of the glacier, Lab = labradorite, Qz = quartz, Hem = hematite, HyAP = hydroxyapatite, Chl-Vrm-Mnt = chlorite-vermiculite-montmorillonite.

To investigate the relationships between geochemical and biological cycling of P in each site, correlations between chemically defined P pools and the biological parameters (alkaline phosphatase activity and fluorescein diacetate hydrolysis) were established. At the IFA, there was a positive correlation between the activity of AP and the hydrolysis of FD ($r = 0.95$, $P < 0.05$; $n = 15$). For this site, both biological parameters were positively correlated with the

organic and inorganic P fractions obtained in alkali extracts: NaHCO_3 ($r = 0.96$ for AP and $r = 0.91$ for FD in inorganic pool; $r = 0.90$ for AP and $r = 0.92$ for FD in organic pool; $P < 0.05$, $n = 15$) and NaOH ($r = 0.98$ for AP and $r = 0.98$ for FD in inorganic pool; $r = 0.91$ for AP and $r = 0.81$ for FD in organic pool; $P < 0.05$, $n = 15$). The relationships between microbial and enzymatic activities and the soil P pools were not evident at the BG site.

TABLE 5

Chemical composition and d-spacing values (Å) of the three main peaks of identified minerals by XRD analysis in each studied site.

Mineral/Identification card	Chemical composition	PM	BG	IFA
Labradorite/710748	(Na _{0.5} Ca _{0.5})(Al _{1.5} Si _{2.5} O ₈)	3.20	3.21	3.20
		3.18	3.18	3.18
		4.04	4.04	4.03
Quartz/791910	SiO ₂	3.34	3.34	3.34
		4.25	4.25	4.27
		1.81	1.83	1.83
Hydroxiapatite/011008	Ca ₁₀ (OH) ₂ (PO ₄) ₆	2.79	2.83	
		3.44	3.47	
		1.84	1.87	
Hematite/790007	Fe ₂ O ₃	2.69		2.99
		2.51		2.52
		1.69		1.60
Chlorite-vermiculite-montmorillonite/390381	Na _{0.5} Al ₆ (Si,Al) ₈ O ₂₀ (OH) ₁₀ H ₂ O	3.50		3.47
		7.70		7.95
		4.44		4.66

PM = pure minerals, BG = boundary of the glacier, IFA = ice-free area.

Discussion

CHANGES IN P POOLS, Fe AND Al FRACTIONS, AND SOIL MINERALOGY FROM THE BOUNDARY OF THE GLACIER TO ICE-FREE AREA

It has been widely accepted that in the Antarctic region the extremely low temperatures and the limited availability of liquid water restricts chemical weathering and consequently soil development (i.e. Ugolini, 1963; Chen and Blume, 1999; Gooseff et al., 2003; Bölter, 2011). However, in some locations, during the summer, soil microclimatic conditions allow the presence of liquid water and favor chemical weathering. This is the case of the ice-free areas at the Fildes Peninsula, which are exposed to a deep thawing period that lasts between 5 and 6 months each year (Chen and Blume, 1999). During this period, soils of these areas are subjected to greater temperatures and availability of free water than at other sites in Antarctica (Zhao and Li, 1996; Chen and Blume, 1999, 2000; Gooseff et al., 2003). In contrast, in terrestrial areas adjacent to subsurface ice, the liquid water content is limited due

to the low air temperature and precipitation (Barrett et al., 2006). During summer, melting water from the glaciated areas may remain in a liquid state only during the warmest hours of the day and refreezes as solar radiation decreases (Motta and Motta, 2004). Taking into account the differences in the microclimatic soil conditions of these two environments, and considering the implications of the water availability in soil chemical processes, we predicted in our first hypothesis that from the boundary of the glacier (BG) to the ice-free area (IFA) P associated with primary minerals should decrease, while P bounded to secondary minerals should increase. To test this, we interpreted our results of soil P fractions along with the contents of secondary minerals (oxyhydroxides of Fe and Al) and soil mineralogy following the theory of Walker and Syers (1976). This theory proposes a conceptual model where availability and forms of soil P vary during its development as a consequence of changes in mineral composition. According to the model, as soil evolution takes place, the weathering of primary minerals (Ca-bound phosphates) releases P, which is readily chemisorbed into the secondary minerals (clay minerals as well as Fe and Al oxyhydroxides).

Our results advance four lines of evidence that help us support our first hypothesis. First, from BG to IFA, the concentration of primary mineral P (diluted HCl-Pi) declined, while the inorganic P chemisorbed and occluded to Fe/Al oxyhydroxides (NaOH- and concentrated HCl-) increased. This pattern led to an inverse relationship between the diluted HCl-Pi and NaOH-Pi at the IFA, but not at the BG site. Such findings were consistent with those obtained using PCA, which showed that inorganic P pools were distinct between the edge of the glacier and the ice-free area. Second, the greatest levels of Fe/Al oxyhydroxides were found in the IFA where the content of NaOH-Pi was also the greatest. Third, at the BG site, the content of Al_T was sixfold lower than that of the Fe_T, and fivefold lower than the content of Al_T in the soils of the IFA.

TABLE 6

Alkaline phosphatase (AP) activity and the fluorescein diacetate (FD) hydrolysis of soils in the boundary of the glacier (BG) and in the ice-free area (IFA).

Soil properties	Units	BG	IFA
AP	μg p-NP g ⁻¹ dry soil h ⁻¹	2.92 ± 0.95 ^b	13.67 ± 3.18 ^a
FD	μg fluorescein g ⁻¹ dry soil h ⁻¹	18.09 ± 2.06 ^b	49.67 ± 16.87 ^a

Mean values ± 1 SE followed by different letters in rows denote significant differences between sites.

In the latter site, the contents of Fe_T and Al_T were similar. The observed trend could be considered a signal of advanced soil development at the IFA because, in the soil environment, high contents of secondary Al minerals are indicative of increased weathering (Hsu, 1977). Fourth, the presence of epigenetic minerals such as hematite and the intergrade chlorite-vermiculite-montmorillonite in the soil of the IFA is strong evidence that chemical alteration of bedrocks seems to be favored in this site. This was not the case at the BG site, where soil mineralogy was characterized by the presence of hydroxyapatite and the absence of chemical weathering products. The soil mineralogy observed at the IFA was in good agreement with the results obtained for other sites in the Antarctic Peninsula (Boyer, 1975; Kuzmann et al., 1998), where chemical weathering is an important pedogenetic process.

Besides the above-mentioned, it is important to note that, according to the theory of Walker and Syers (1976), the chemical alteration of primary minerals provides available P to the soil solution. In this study, this was observed in the IFA soils, since a direct relationship between resin-Pi and the diluted HCl-Pi fraction was obtained. Despite the fact that the alteration of primary minerals increased the available P at the IFA soils, such increase was not reflected in the organic P pool, which was very low and similar between the sites. This result is expected in an environment where the primary productivity is negligible and where, consequently, the content of soil organic matter is low (i.e. Hopkins et al., 2006a, 2006b).

The observed differences in P cycling patterns as well as the formation of epigenetic minerals seem to confirm our first hypothesis. At this point it is important to mention that pedogenetic time was not considered in our discussion, because differences in soil properties could be explained as a function of time when soils are being formed under the same climatic condition (Kelly and Yonker, 2005). However, this is not the case at the studied sites, since, as was mentioned earlier, soils of the ice-free areas are exposed to a less extreme microclimatic soil condition than the terrestrial areas adjacent to subsurface ice.

Despite that soils of the IFA are significantly more developed than soils of the BG site, in this study it is also important to recognize that the alteration of primary minerals in the IFA is still at an early stage since the content of Ca-bound P ($281.75 \pm 16.72 \text{ mg kg}^{-1}$) is at the lower limit of the values reported by other authors (Blecker et al., 2006 [$\approx 267\text{--}349 \text{ mg kg}^{-1}$]; Bate et al., 2008 [$\approx 250\text{--}980 \text{ mg kg}^{-1}$]) for soils of the Antarctic continent, where the weathering is more restricted.

Fe AND Al FRACTIONS AND THEIR IMPLICATIONS ON THE SOIL P CYCLING

The non-crystalline forms of Fe and Al were found to be more abundant in the IFA site, where the chemical weathering was more intense (ΣFe_O-Al_O : BG = $58.76 \text{ mmol kg}^{-1}$, IFA = $165.15 \text{ mmol kg}^{-1}$). As a result, this led to an increase of the non-crystallinity ratios (Al_O/Al_{DCB} , Fe_O/Fe_{DCB}) in the IFA soils. Non-crystalline forms of Fe and Al (Fe_O-Al_O) are considered the main sorbents of phosphate, in relation to crystalline forms, due to their comparatively larger specific surface area (Parfitt, 1989; Ugolini and Dahlgren, 2002).

Whilst the soils of the IFA were enriched with non-crystalline minerals, crystalline forms of Fe were dominant at the BG site. This result seems to be closely related to chemical weathering. According to Ugolini and Dahlgren (2002), when volcanic materials, such as those that make up the Fildes Peninsula Group, are exposed to chemical weathering, the precipitation of non-crystalline minerals is kinetically favored over precipitation of crystalline minerals. In comparison, crystalline minerals are formed at the expense of metastable compounds (Ugolini and Dahlgren, 2002). These authors consider the time of exposure of the weathering processes that are associated with warm and dry soil conditions as the main factor promoting the formation of crystalline minerals. Soils of the BG site are not exposed to warm temperatures, but they are subjected to longer periods of liquid water limitation, which probably favors the formation of crystalline minerals rather than non-crystalline ones.

In addition to poorly crystalline minerals, the organically bound forms of Fe and Al (Fe_P , Al_P) are also active surfaces that control soil P retention capacity (Gerke and Hermann, 1992; Chacón and Dezzeo, 2004; Chacón et al., 2005a, 2008). In this study, the content of these compounds was low as a result of the generally low content of soil organic matter. However, Al_P was more abundant in the soil from the IFA site than that from the BG site. This finding, along with the great content of non-crystalline minerals obtained for this site, allowed us to conclude that, potentially, IFA soils have a greater P retention capacity than soils at the BG. The implications of these mineral surfaces on P dynamics have been well recognized for highly weathered acid soils (i.e. Schwertmann and Taylor, 1977; Parfitt, 1978; Chacón and Dezzeo, 2004; Chacón et al., 2005a, 2008). However, it is important to bear in mind that these mineral surfaces are positively charged over the whole pH range commonly encountered in the soil (Hinsinger, 2001) and also control the P dynamics of alkaline soils (Matar et al., 1992; Bertrand et al., 1999; Hinsinger, 2001). In fact, in alkaline soils of the Antarctic continent, the increases of Al and Fe phosphates in soils where weathering is less restricted have been explained by the presence of non-crystalline and crystalline Fe and Al oxyhydroxides (Blecker et al., 2006).

ALKALINE PHOSPHATASE AND MICROBIAL ACTIVITY AND THEIR RELATIONSHIP WITH THE BIOGEOCHEMICAL CYCLING OF P

On the basis that biological activities in the terrestrial ecosystems of Antarctic region are largely controlled by abiotic factors (soil temperature and availability of liquid water), we formulated our second hypothesis wherein we predicted an increase in microbial and enzymatic activities for the ice-free area. Indeed, AP activity followed this expected trend. However, before we conclude that such behavior is promoted by the less extreme microclimatic conditions in the IFA, we ascertained within the context of our results, other concepts that could explain the observed pattern with this enzyme.

On a global scale, it has been indicated that extracellular phosphatase activities increase with soil organic matter concentration (Sinsabaugh et al., 2008). In this study, the content of soil organic carbon at the IFA was 13-fold lower than the recorded value at the BG site (Benzo et al., unpublished data; samples collected in 2009),

even though the AP activity was fivefold greater at the IFA than at the BG site. Comparing our findings with results obtained by Sinsabaugh et al. (2008), it can be concluded that in our study sites there is no indication that soil organic carbon plays an important role in the activity of AP. However, other factors inherent to soil matrix could be masking our results. Several studies have found that the interaction of phosphatase enzymes with non-crystalline Al and Fe oxides and clay minerals decreases enzyme activity when compared to the non-immobilized enzyme activity (Huang et al., 1995; Rao et al., 1996, 2000; Shindo et al., 2002; Chacón et al., 2005b). As was already discussed above, soils of the IFA were enriched with non-crystalline compounds, whereas crystalline forms dominated the soils of the BG site. Hence, from this mineralogical composition we could not explain the observed pattern of this soil enzyme. Generally speaking, most secondary minerals are found in the fine fraction of the soil. According to Benzo et al. (unpublished data; samples collected in 2009), soil from the BG site showed a relatively greater content of fine particles (clay) than that from the IFA. In both sites, the correlation of these data with the values of AP activity obtained in this study was not significant (BG: $r = -0.217$, $P > 0.05$, $n = 15$; IFA: $r = 0.117$, $P > 0.05$, $n = 15$). This trend and the previous findings allow us to conclude that soil matrix is not driving the AP activity in the studied sites.

Once the influence of soil matrix on AP activity was discarded, it could be assumed that the activity was likely enhanced by soil microclimate conditions such as humidity and temperature. For Antarctic soils this assumption is reasonable considering that in this harsh environment microbial activities, like carbon and nitrogen mineralization and enzyme production (i.e. alkaline phosphatase), are favored in those areas where temperature allows greater soil water availability (Barrett et al., 2005; Zeglin et al., 2009).

Considering the findings mentioned above and the fact that FD hydrolysis has been widely used to determine the overall soil microbial activity potential (Nannipieri et al., 2003), it was not surprising that this parameter followed the same behavior detected for AP activity. Unfortunately, to the best of our knowledge, for Antarctic soils there are no studies evaluating the influence of soil microclimate conditions on FD hydrolysis. However, for temperate ecosystems it has been reported that suitable conditions of soil temperature and moisture increased the levels of this biochemical parameter (Sidari et al., 2008; Lillo et al., 2011; Reyes et al., 2011).

Finally, it is also important to analyze the positive relationship between biological parameters (AP activity and FD hydrolysis) and both organic and inorganic P pools obtained in alkaline extractants of soils of the IFA. This striking finding suggests that in IFA soils the presence of liquid water allowed the co-occurrence of advanced chemical weathering and a greater biological activity. The conjunction of both factors seems to have a strong influence over the P pools at the IFA.

Conclusions

The changes in the inorganic P pools coupled with the increase in secondary minerals at the IFA soils allowed us to conclude that soils from the IFA showed a greater chemical weathering intensity than soils from the BG. This finding was consistent with the pedogenic theory developed by Walker and Syers (1976). However, the prediction, which states that as soil evolution proceeds organic

P pools increase, could not be verified in this study due to the lack of variation between sites in this P pool. This discrepancy is expected in the harsh environments of Antarctica where reduced input of liquid water is responsible for negligible primary productivity. The biochemical transformation of soil P was also favored in the ice-free area. It is likely that the less restrictive microclimatic conditions, to which the soils of the ice-free areas are exposed during the summer, have a considerable effect on the biogeochemical cycling of soil phosphorus. Taken together, our findings demonstrated that, between the boundary of the glacier and the ice-free area, there are differences in the patterns of soil P cycling. In a scenario of climate warming over the Antarctic Peninsula, this information may contribute to the understanding of how the retreat of the glaciers and consequently the advance of the ice-free areas could be altering the biogeochemical cycling of essential nutrients in this region.

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