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# Fertilizer effects on phosphorus fractions and organic matter in Andisols

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## Abstract

Andisols are characterized by a high phosphorus (P) fixation capacity, which is a limiting factor for plant production. Continuous application of P fertilizer may result in an accumulation of P associated with soil organic matter (SOM), which further acts to reduce the availability of the added P. The objectives of this study were (1) to evaluate the impact of P fertilizer inputs on the quantities and chemical forms of P, and (2) to investigate relationships between P forms SOM and land use. Topsoil (0-20 cm) and subsoil (20-40 cm) samples were taken from two Andisols series under grassland and arable cropping. Soil P forms were determined using sequential fractionation, while SOM analysis involved a combination of <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy and pyrolysis-GC-mass spectrometry. Fertilization increased total P, total organic P, organic carbon, and inorganic P fractions, mainly in arable soils. Labile P was higher in grassland (3% of total P) than in arable soils (1% of total P). A clear effect of fertilization was observed on organic matter compounds measured by pyrolysis in both soil depths. Interestingly, the polysaccharide-derived compounds increased in fertilized soils and lipid-derived compounds decreased. Thus fertilization principally affected labile P and labile SOM forms, whereas recalcitrant forms of P and SOM remained unchanged.

**Keywords:** Soil phosphorus fractionation, <sup>13</sup>C nuclear magnetic resonance, pyrolysis, phosphorus fertilizer

## 1. Introduction

In most agricultural systems continued inputs of fertilizer phosphorus (P) are required to increase and maintain plant production, although most (>90%) of the applied P remains in the soil as inorganic and organic P (Condrón *et al.*, 2005. Nash *et al.*, 2014).

The fate and bioavailability of fertilizer P in soil-plant systems has been widely studied using a variety of techniques, including sequential fractionation and <sup>31</sup>P nuclear magnetic resonance (NMR) spectroscopy (Hedley *et al.*, 1982; Cross and Schelinger,

1995; Turner *et al.*, 2005; Negassa and Leinweber, 2009. Condon and Newman, 2011). There is a wide description of P forms presents in many soils around the world. However, there are several factors that governed P accumulation in soils including land use, soil depth and soil organic matter (SOM) dynamics, among others.

Soils derived from volcanic ash (Andisols) have a particularly high requirement for fertilizer P inputs to increase plant growth, which has been mainly attributed to the presence of large quantities of amorphous clay minerals resulting in very high P fixation capacities (Dahlgren *et al.*, 2004). This in turn means that many Andisols in agroecosystems contain very high concentrations of P, very little of which is immediately plant available (Borie and Rubio, 2003; Escudey *et al.*, 2001; Pinochet *et al.*, 2001; Briceño *et al.*, 2004; Redel *et al.*, 2007). Soil organic matter plays an important role in P accumulation in Andisols (Escudey *et al.*, 2001; Briceño *et al.*, 2004), and Borie and Zunino, (1983) proposed that P added in fertilizer was stabilized by organic matter through a combination of physicochemical and biological processes. Despite the importance of organic matter for P stabilization in Andisols, up to now no study was carried out to investigate the impact of fertilization on chemical forms of P in relation to SOM composition.

This study investigated the effect of P fertilization on P and SOM in two Andisols under grassland and arable cropping at different soil depths. The specific objectives of this study were to evaluate the impact of P fertilizer inputs on the amount and chemical forms of P, and to investigate their relationship with SOM forms and land use at different soil depths. We hypothesized that increased biological activity in fertilized soil may enhance the contribution of labile P and SOM compounds.

## 2. Materials and Methods

### 2.1. Soil sampling and chemical analyses

Soil samples were collected from two Andisols with different land use histories, in order to represent the dominant land use in southern Chile. One soil belonging to Pemehue series, located in Araucania region (PEH, 39°04' S and 72°10' W) had been under wheat cropping for 15 years. The other soil, belong to the Piedras Negras series, located in Los Rios region (PN, 40°23' S and 72°30' W) (CIREN, 2003), had been under permanent grassland for 20 years. Both soils were sampled at two depths, 0-20 cm and 20-40 cm, and from each soil a sample under fertilization (F) and a reference sample without fertilization (UF) were taken. Fertilized sites had received P fertilization, ranging from 90 to 150 kg P ha<sup>-1</sup> as superphosphate (P<sub>2</sub>O<sub>5</sub>) for 8 years. The soils samples were air-dried, sieved <2 mm and stored.

Aluminum (Al) and iron (Fe) were extracted with sodium pyrophosphate (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) and oxalate according to the methods described by Shoumans *et al.* (2000). Aluminum and Fe in pyrophosphate and oxalate extracts were measured by atomic absorption (UNICAM, 969 AA spectrometer) at 309 and 248 nm, respectively. Total Carbon (C) and nitrogen (N) were determined by dry combustion using a CHN auto-analyzer (CHN NA 1500, Carlo Erba). Total P was determined as the the sum of the different fractions of phosphorus fractionation. Total organic P was determined by NaOH-EDTA extraction according to the method described by Cade-Menun and Preston (1996) using a combination of molybdate colorimetry (inorganic P - Murphy and Riley (1962) and ICP-OES (total P), whereby total P – inorganic P = organic P.

## 2.2. Phosphorus fractionation

Soil P fractions were determined according to a modified version of the scheme originally developed by Hedley *et al.*, (1982). Briefly, 1 g soil was extracted first with 30 mL of deionized water for 16 hours at room temperature and then centrifuged at  $5000 \times g$  for 20 min. The solution was filtered ( $0.45 \mu\text{m}$ ) and stored at  $4^\circ\text{C}$  prior to determination of inorganic and organic P - this fraction corresponds to the most readily soluble P pool. The remaining sample was extracted as described above with sodium bicarbonate ( $0.5 \text{ M NaHCO}_3$  - labile P pool), followed by sodium hydroxide ( $0.1 \text{ M NaOH}$  - moderately labile P pool), then hydrochloric acid ( $1 \text{ M HCl}$ ). Phosphorus that remained un-extracted was termed 'residual P' (total soil P - sum of total P in fractions) and is regarded as representing mainly recalcitrant forms of P. Inorganic P and total P in soil extracts were determined by direct molybdate colorimetry after hypobromite oxidation ( $\text{NaBrO}$ ) (Dick and Tabatabai, 1972).

## 2.3. $^{13}\text{C}$ NMR spectroscopy

Prior to solid-state  $^{13}\text{C}$  NMR analysis soil samples were treated with 10% hydrofluoric acid to remove paramagnetic ions and increase C concentration (Skjemstad *et al.*, 1994). The NMR spectra were obtained on a Bruker MSL 100 NMR spectrometer at a frequency of 50.3 MHz and a spinning speed of 6.8 kHz. The chemical shifts were referenced to tetramethylsilane, the characteristics groups were identified by using the integration routine of the spectrometer, whereby four characteristic chemical shifts regions were assigned to alkyl-C (0-45 ppm), O/N-alkyl-C (45-110 ppm), aromatic C (110-160 ppm) and carboxyl-C (160-220 ppm) (Wilson, 1987).

## 2.4. Pyrolysis

Curie-Point pyrolysis of soils was carried out using a coil probe pyrolyzer (CDS Pyroprobe model 5000), and pyrolysis products were determined by gas chromatography mass spectrometry (GC-MS (Agilent 5973). Sample (1 mg) was loaded in a tubular probe and introduced into the pyrolysis unit and heated to  $650^\circ\text{C}$  for 0.15 s (10 s hold).

The pyrolysis products were transferred to the GC-MS system through a splitless injector using helium as carrier gas. A silica capillary column (60 m, 0.32 mm i.d., film thickness 0.25  $\mu\text{m}$ ) was used, coated with a non-polar phase equivalent (5%-phenyl)-polydimethylsiloxane (column BPX5, SGE) was used to separate and identify the pyrolysis products. The temperature program of the GC oven was set with a temperature increase of  $2^\circ\text{C}/\text{min}$  from  $30^\circ\text{C}$  to the maximum temperature of the  $350^\circ\text{C}$ , and the final temperature was maintained for 15 min. Compounds were identified based on their mass spectra, GC retention times, and comparison with library mass spectra.

## 2.5. Statistical analysis

The data were tested for normal distribution, and those that were not normally distributed were log transformed. Two-way ANOVA analysis was carried out to determine the significance of differences between means using the Tukey test at 5% probability ( $P < 0.05$ ). Principal component analyses (PCA) were carried out to assess the effect of treatments and depths on eight chemical properties.

### 3. Results

#### 3.1. Chemical properties of Andisols

Selected chemical properties of the soils are shown in Table 1. Total C concentrations were higher in grassland soil (PN) (92.1–120.3 g C kg<sup>-1</sup>; mean 105) compared with arable soil (PEH) (61.2–112.4 g C kg<sup>-1</sup>; mean 90), and were consistently higher in topsoil compared with subsoil and in fertilized compared with unfertilized soils. Total N concentrations ranged between 5.3 and 8.8 g N kg<sup>-1</sup> and followed similar trends to C, while C:N ratio ranged between 11.7 and 14.0 in both soils, with no significant differences observed between depths and treatments. Total P concentrations were generally higher in PEH soils (1935.5–2268.3 mg P kg<sup>-1</sup>; mean 2212.7) compared with PN soils (1019.6–2237.3 mg P kg<sup>-1</sup>; mean 1475.6), and as expected were higher in topsoils for fertilized sites compared with unfertilized soils.

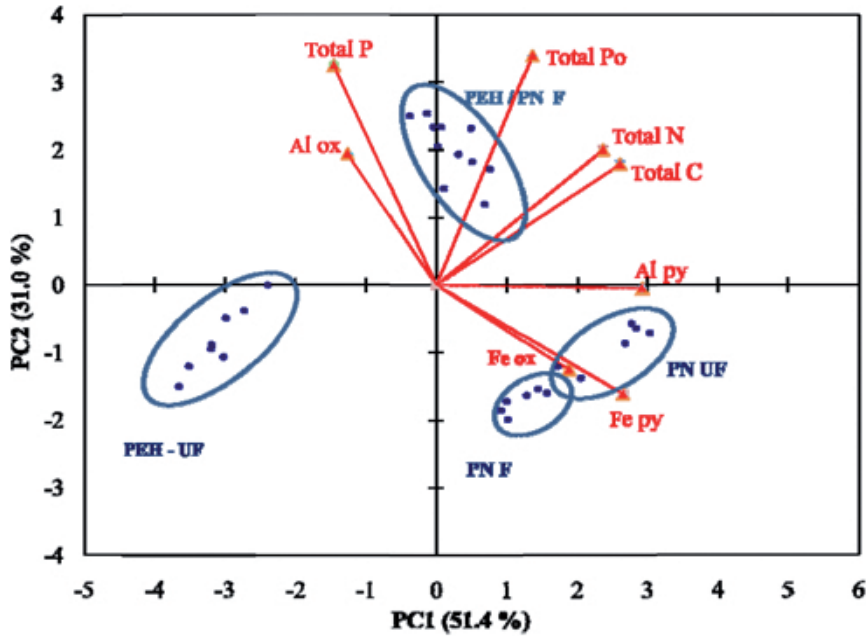
Concentrations of total organic P were similar in both soils and accounted for 25–47% of total P in PN soils compared with 20–30% in PEH soils, although differ-

ences between depths and treatments were similar to those observed for total P. Differences in total C and organic P between soil were reflected in corresponding data for C: organic P which were higher in PN soils (mean 253) compared with PEH soils (mean 217). Pyrophosphate-extractable Al concentrations were higher than pyrophosphate-extractable Fe while the opposite trend occurred for oxalate extractable Al and Fe, ranging for both soils ranged between 6.5 and 11.6 g kg<sup>-1</sup> and between 1.2 and 6.5 g kg<sup>-1</sup>, respectively. Pyrophosphate-extractable Al was lower in unfertilized PEH soils compared with the corresponding fertilized soils at both depths.

The PCA results shown in Figure 1 revealed that the fertilized and unfertilized soils were clearly separated along the two components (PC1 and PC2), which explained 51% and 31% of the total variance, respectively. Total P, total organic P, total C, total N and oxalate-Al were positively correlated with PC1 with fertilization in arable and grassland soils, while pyrophosphate-Fe and oxalate-Fe correlated with grassland soil. On the other hand, all properties were negatively correlated with unfertilized PEH soils.

**Table 1.** Chemical properties of fertilized and unfertilized Andisols (PN and PEH) sampled at 0–20 cm and 20–40 cm. Capital letters correspond to differences between treatments for the same depth and lowercase letters correspond to differences between depths for the same treatment.

Soil	Depth	pH	Total C	Total N	Total P	Total Po	C/N	C/Po	Al py	Fe py	Al ox	Fe ox
	cm		---g kg <sup>-1</sup> soil---	----mg kg <sup>-1</sup> soil----					-----g kg <sup>-1</sup> soil-----			
PN	Fertilized	0–20	5.2 106.0 <sup>Ba</sup>	8.1 <sup>Aa</sup>	2237.3 <sup>Aa</sup>	518.6 <sup>Aa</sup>	13.1 <sup>Aa</sup>	204.3 <sup>Aa</sup>	9.3 <sup>Bb</sup>	2.3 <sup>Bb</sup>	17.9 <sup>Aa</sup>	21.2 <sup>Aa</sup>
		20–40	5.0 92.1 <sup>Bb</sup>	6.9 <sup>Bb</sup>	1444.5 <sup>Ab</sup>	356.4 <sup>Ab</sup>	13.4 <sup>Aa</sup>	258.5 <sup>Ab</sup>	10.2 <sup>Ba</sup>	5.7 <sup>Aa</sup>	14.3 <sup>Ab</sup>	22.8 <sup>Ab</sup>
	Unfertilized	0–20	5.1 120.3 <sup>Aa</sup>	8.6 <sup>Aa</sup>	1019.6 <sup>Ba</sup>	433.3 <sup>Ba</sup>	14.0 <sup>Aa</sup>	277.6 <sup>Ba</sup>	11.6 <sup>Aa</sup>	6.5 <sup>Aa</sup>	12.7 <sup>Ba</sup>	21.1 <sup>Aa</sup>
		20–40	5.0 102.7 <sup>Ab</sup>	7.8 <sup>Ab</sup>	1200.9 <sup>Aa</sup>	377.7 <sup>Ab</sup>	13.1 <sup>Aa</sup>	271.9 <sup>Aa</sup>	11.2 <sup>Aa</sup>	5.3 <sup>Ab</sup>	13.0 <sup>Ba</sup>	20.6 <sup>Ba</sup>
PEH	Fertilized	0–20	5.3 112.4 <sup>Aa</sup>	8.8 <sup>Aa</sup>	2009.0 <sup>Ab</sup>	530.0 <sup>Aa</sup>	12.7 <sup>Aa</sup>	212.1 <sup>Aa</sup>	9.5 <sup>Aa</sup>	2.7 <sup>Aa</sup>	14.7 <sup>Aa</sup>	18.3 <sup>Aa</sup>
		20–40	5.3 110.3 <sup>Ab</sup>	8.4 <sup>Aa</sup>	2238.1 <sup>Aa</sup>	516.1 <sup>Aa</sup>	13.2 <sup>Aa</sup>	215.6 <sup>Aa</sup>	9.8 <sup>Aa</sup>	2.6 <sup>Aa</sup>	14.0 <sup>Bb</sup>	17.3 <sup>Bb</sup>
	Unfertilized	0–20	5.9 76.2 <sup>Ba</sup>	5.8 <sup>Ba</sup>	1935.5 <sup>Ab</sup>	337.3 <sup>Ba</sup>	13.2 <sup>Aa</sup>	225.8 <sup>Aa</sup>	6.6 <sup>Ba</sup>	1.3 <sup>Ba</sup>	13.7 <sup>Ba</sup>	16.3 <sup>Bb</sup>
		20–40	5.6 61.2 <sup>Bb</sup>	5.3 <sup>Ba</sup>	2268.3 <sup>Aa</sup>	285.2 <sup>Bb</sup>	11.7 <sup>Aa</sup>	214.6 <sup>Aa</sup>	6.5 <sup>Ba</sup>	1.2 <sup>Ba</sup>	15.6 <sup>Ab</sup>	18.4 <sup>Aa</sup>



**Figure 1.** PCA of chemical parameters of fertilized and unfertilized soils. Soils are grouped according to series and fertilizer use (PN-UF, PN-F, PEH-UF, PEH-F) and the chemical parameters are represented by arrows.

### 3.2. Phosphorus fractionation

Table 2 shows data for soil P fractions, which revealed that most soil P was remained in the residual fraction for all soils, accounted for 47-81% of total P (means 60%). Concentrations of inorganic P were higher in arable soil (PEH) (ranged from 416 to 767 mg P kg<sup>-1</sup>) compared with grassland soil (PN) soils (ranged from 141 to 697 mg P kg<sup>-1</sup>). The NaOH extractable P fraction comprised between 11 to 33 % of total P. In this fraction the organic pool (NaOH-P<sub>o</sub>) was higher than the inorganic pool

(NaOH-P<sub>i</sub>) for all soils, ranging between 172.1 and 329.2 mg P kg<sup>-1</sup> (Table 2). The HCl extractable fraction ranged between 100.9 and 486.8 mg P kg<sup>-1</sup>, which are equivalent to 8 and 22% of total P. The lowest P concentrations were found in the NaHCO<sub>3</sub> extractable fraction ranging between 1.6 and 62.1 mg P kg<sup>-1</sup> which on average were equivalent to 2% of total P. For the grassland soil (PN) labile P was higher (29-62 mg P kg<sup>-1</sup>) than arable soil (2-32 mg P kg<sup>-1</sup>) and significant differences ( $p < 0.05$ ) between treatments and depths were observed for the inorganic fraction (NaHCO<sub>3</sub>-Pi) (Table 2).

**Table 2.** Phosphorus fractions (mg P kg<sup>-1</sup> soil) determined for fertilized and unfertilized Andisols (PN and PEH)

Values in parenthesis correspond to percentage of the sum of organic and inorganic P in determined in each fraction as a percentage of total soil P. Capital letters corresponds to differences between treatments for the same depth and lowercase letters correspond to differences between depths for the same treatments.

Soil	Treatment	Depth	NaHCO <sub>3</sub> -			NaOH-			HCl-			Residual P	Total P
		Cm	Pi	Po	Σ	Pi	Po	Σ	Pi	Po	Σ		
PN	Fertilized	0-20	14.2 Aa	47.9 Aa	62.1 (2.8)	291.1 Aa	329.2 Aa	620.3 (27.7)	392.0 Aa	55.7 Aa	447.7 (20.0)	1044.2 Aa (46.7)	2237.3 Aa
		20-40	5.8 Ab	23.5 Aa	29.3 (2.0)	87.8 Ab	208.5 Ab	296.3 (20.5)	57.1 Bb	95.4 Aa	152.5 (10.6)	966.4 Aa (66.9)	1444.5 Ab
	Unfertilized	0-20	3.3 Ba	34.5 Aa	37.8 (3.9)	70.6 Ba	180.5 Bb	251.1 (25.6)	67.2Ba	33.8 Aa	101.0 (9.9)	629.7 Aa (61.8)	1019.6 Ba
		20-40	4.8 Ab	29.5 Aa	34.3 (2.9)	69.2 Ba	217.5 Aa	286.7 (23.9)	73.5 Aa	27.4 Ba	100.9 (8.4)	779.0 Aa (64.9)	1200.9 Aa
PEH	Fertilized	0-20	20.4 Aa	11.5 A	31.9 (1.6)	406.8 Aa	260.1 Aa	666.9 (33.1)	339.9 Aa	52.7 Aa	392.6 (19.5)	917.6 Bb (45.7)	2009.0 Ab
		20-40	13.6 Aa	19.0 A	32.6 (1.5)	339.5 Aa	317.5 Aa	657.0 (29.4)	366.7 Aa	120.1 Aa	486.8 (21.8)	1061.7 Ba (47.4)	2238.1 Aa
	Unfertilized	0-20	12.9 Aa	--	12.9 (0.7)	159.6 Ba	255.4 Aa	415.0 (21.4)	243.3Ba	50.3 Aa	293.6 (15.2)	1214.0 Ab (62.7)	1935.5 Ab
		20-40	1.6 Bb	--	1.6 (0.1)	65.4 Bb	172.1 Bb	237.5 (10.5)	163.1Bb	27.4 Ba	190.5 (8.4)	1838.7 Aa (81.0)	2268.3 Aa

**Table 3.** Integrals of <sup>13</sup>C CPMAS NMR spectra of fertilized (F) and unfertilized (UF) Andisols (PN and PEH) sampled at 0-20 cm and 20-40 cm

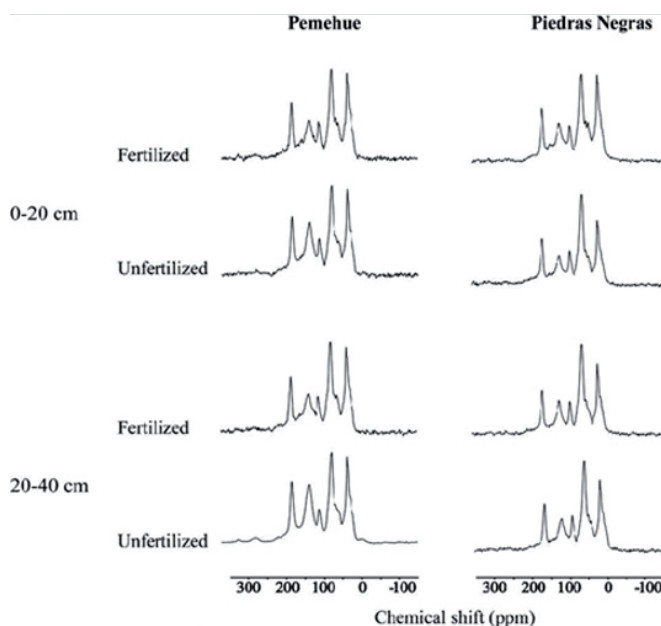
Depth		Alkyl C	O-alkyl C	Aromatic C	Carboxylic C	alkylC/O-alkylC
(cm)		10–45 ppm	45–110 ppm	110–160 ppm	160–220 ppm	
0–20	F	26.5	39.3	19.8	14.4	0.67
	UF	22.4	45.6	16.9	15.1	0.49
20-40	F	23.9	44.6	17.8	13.7	0.53
	UF	23.7	43.9	18.1	14.2	0.54
0-20	F	24.8	40.6	19.8	14.8	0.61
	UF	22.8	38.9	23.5	14.8	0.58
20-40	F	24.1	40.8	20.2	14.9	0.58
	UF	22.3	33.8	29.6	14.3	0.66

### 3.3. Solid state $^{13}\text{C}$ NMR analysis

$^{13}\text{C}$ -NMR spectra presented in Figure 2 were found to be similar for grassland and arable (PN and PEH) showing typical signals at 178, 130, 107, 72 and 28 ppm assigned to alkyl C, O-alkyl C, aromatic C and carboxylic C functional group. In all soils, quantities of O-alkyl C and alkyl C accounted for 22.8-26.5%

and 33.8-45.6% of total C detected respectively, compared with aromatic C (16.9-29.6%) and carboxylic C (14.2-15.1%).

Fertilization showed an effect in C compounds and the corresponding alkylC/O-alkylC ratio in topsoil of grassland, with a higher ratio (0.67) compared with unfertilized plot (0.49) and arable soil (0.61), at the same depth.



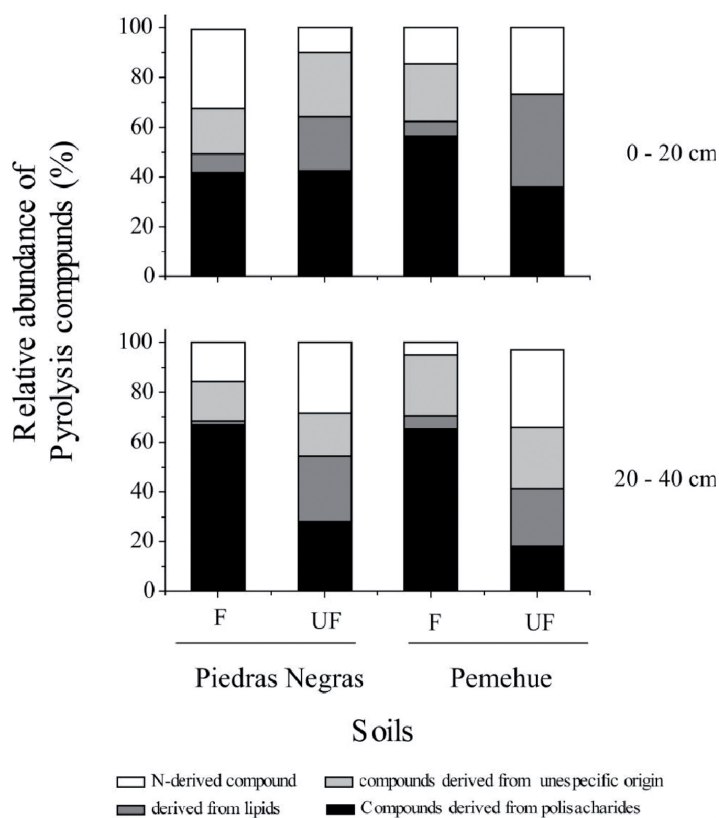
**Figure 2.** Solid-state  $^{13}\text{C}$  NMR spectra obtained for fertilized and unfertilized Andisols (PN and PEH) sampled at 0-20 cm and 20-40

### 3.4. Pyrolysis-GC/MS

The pyrograms obtained for the soils are dominated by compounds derived from polysaccharides, ranging between 36 and 67% of relative abundance (Figure 3). A clear distribution of compounds was observed with depth. Compounds derived from lipids were higher in arable and grassland soils in unfertilized plots (PN 22% and PEH 37% of relative abundance)

respect to fertilized ones (PN 7% and PEH 6% of relative abundance) in topsoil. Whereas, in subsoil an increment in compounds derived from polysaccharides was observed with the fertilization in both soils with a relative abundance of 67% in PN and 65% PEH. The compounds derived from unspecific origin remained constant in all soils, ranged between 16 and 26 % of relative abundance (Figure 3).





**Figure 3.** Relative abundance of pyrolysis products determined for fertilized (F) and unfertilized (UF) Andisols (Piedras Negras and Pemehue) sampled at 0-20 cm and 20-40 cm

#### 4. Discussion

Chemical parameters showed an increase in total P, total organic P, total C and total N in response to fertilization for both soil series and depths, independent of land use. Land use and fertilization response in soils could be separated in the PCA plan due to their contrasting content of iron and aluminium oxides (Figure 1). In grassland soil (PN) there is a clear correlation with Fe ox and Fe py, this may be explained by the fact that repeated fertilization produced a fixation by

sorption of P in mineral phases, which is especially important in Andisols due to the high content of short range order minerals and efficiently C sequestration (Calabi-Floody *et al.*, 2011; Matus *et al.*, 2014; Celi *et al.*, 1999).

The P concentrations recorded in our study were similar to those reported for Chilean Andisols (Borie and Zunino, 1983; Escudey *et al.*, 2001; Pinochet *et al.*, 2001; Briceno *et al.*, 2004). In general, the P distribution showed that after Headley fractionation, more than 40% of P remained in the residual fraction in all

soils, which is in general assumed to comprise organic P forms (Turner *et al.*, 2005; Condon and Newman, 2011). Fertilization increased significantly inorganic P in all fractions, mainly in arable soil (PEH), which suggest a large fertilization input history and a mineralization of soil organic P (Solomon *et al.*, 2000). Labile P, was higher in grassland soil (3% of total P) than in arable soil (1% of total P), this indicate and efficient microbial population in turnover of soil organic P in grassland soil, while in arable soil a depletion of organic P is produced by cultivation and removal of P (Solomon *et al.*, 2000). The inorganic P concentration in HCl fraction were higher than recorded for other studies the P occluded in soil aggregates (Borie and Zumino, 1989) were not released due to the lack of ultrasonication. According the high quantity of P remained in residual fraction and the efficient C sequestration capacity in Andisols, we hypothesize that P is found in residual fractions is forming complexes in organic macromolecules. In this sense, is important to understand the chemical nature of organic matter in order evaluate if fertilization and land use on organic matter composition follow the same pattern that P. Solid-state  $^{13}\text{C}$  NMR spectroscopy showed that chemical composition of soil organic matter is similar for all soils (Figure 2). The spectra showed a high contribution of O-alkyl-C and Alkyl-C groups (means 24 and 41). These peaks generally arise from labile plant or microbial-derived materials such as carbohydrates, proteins and lipids (Kogel-Knabner, 2000; Rumpel *et al.*, 2009). In particular, an effect of fertilization was observed in grassland soil in alkylC/O-alkylC ratio, in topsoil. The alkylC/O-alkylC ratio is a parameter to evaluate the decomposition rate, thus the SOM in grassland soil has efficient microbial recycling in turnover of nutrient, as well as was observed in P. Analytical pyrolysis showed a clear redistribution of compounds according depth. In topsoil, an increase in compounds derived from lipids was

observed in arable and grassland soils in unfertilized plots, which are associated to cell walls. Thus, a slow degradation in unfertilized soils is produced due to a lower microbial activity in comparison with fertilized soils. On the other hand, in subsoil there were no differences between grassland and arable soil in terms of distribution of pyrolysis products. In both soils a high relative abundance of compounds derived from polysaccharides was observed in fertilized soils. These compounds may have been produced by higher plant litter input as well as microbial activity through degradation of fresh OM (Dignac *et al.*, 2005; Gonzalez-Perez *et al.*, 2007). We suggest according to these results that land use and P fertilization had a bigger effect on labile P and SOM compounds than the recalcitrant ones.

## 5. Conclusions

The findings of this study demonstrated that fertilization has an effect on all chemical parameters studied. The P fractionation showed main fertilization effects on inorganic P pools. We did not detect by  $^{13}\text{C}$  NMR any effect of fertilization in functional group composition of SOM. However, an important redistribution of labile SOM forms was observed by analytical pyrolysis. Polysaccharide-derived compound increased substantially in response to fertilizer addition, suggesting enhanced aggregation and thus P stabilization through Al and Fe OM complex formation. However, there were no differences between depths, because soils showed the same response to fertilisation at both depths. Fertilization had a clear effect on labile P as well as labile SOM compounds, whereas recalcitrant organic P and SOM forms were unaffected. Further studies are needed to elucidate the effect of P fertilization on the composition of residual fraction, which comprises most P in Andisols.

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