

# Late Pleistocene and Holocene vegetation changes in the arid Andean piedmont of central Argentina inferred from sediment stable carbon isotopes and C/N ratios



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## ABSTRACT

Stable carbon isotopes ( $\delta^{13}\text{C}$ ) and C/N ratios in bulk sediment organic matter were used as indicators of C<sub>3</sub> and C<sub>4</sub> vegetation functional types in a ca. 40-kyr, predominantly alluvial sequence from Arroyo La Estacada (33.5°S, 69°W), in the arid Andean piedmont of central Argentina. Although this sediment sequence has the potential to contribute to the knowledge of past vegetation dynamics through its fossil pollen content, previous palynological studies provided scant information, constrained to a few time windows, because of poor pollen preservation. Stable isotope results for the total organic carbon fraction from three lithostratigraphic sections that span the past 40 kyr show shifts in  $\delta^{13}\text{C}$  values associated with changing contributions from C<sub>3</sub> and C<sub>4</sub> plants, suggesting this proxy can detect changes in these photosynthetic pathways, representative of Patagonian (and/or stream-margin macrophytes) and Monte phytogeographic units, respectively. Climate and local factors, such as water availability in the basin, are inferred to be the main drivers of vegetation dynamics. The C/N ratios in a few samples show that organic matter sources are algae and/or phytoplankton, not solely C<sub>3</sub> or C<sub>4</sub> vascular plants. The  $\delta^{13}\text{C}$  record from Arroyo La Estacada is an example of how isotope geochemistry has overcome difficulties with pollen analysis and provided a reliable tool to investigate past vegetation changes in regions where C<sub>3</sub> and C<sub>4</sub> are differentially distributed. Isotope values during part of the Marine Isotope Stage 3 (MIS 3) and the middle Holocene are attributed to C<sub>3</sub> local floodplain plants, with a little or no contribution from regional terrestrial (Patagonian) vegetation. Late Pleistocene–Holocene palaeosols have a clear C<sub>4</sub> signal of terrestrial dominance, representative of Monte plants, thus, carbon isotope values constrain the early times of MIS 1, particularly where the Pleistocene–Holocene transition occurs. A mixture of C<sub>3</sub> and C<sub>4</sub> values during the last 3–4 kyr is indicative of environmental conditions that prevail in the region today.

## 1. Introduction

The arid eastern Andean piedmont, between 33° and 35° S in southern South America (Argentina), is an ecotone where grasses with two of the main plant functional types, namely C<sub>3</sub> and C<sub>4</sub>, are distributed according to an east–west climate gradient (Cavagnaro, 1988). The C<sub>3</sub> grasses predominate on the slopes and foothills of the Andes, whereas C<sub>4</sub> grasses are dominant in the lowlands (Cavagnaro, 1988), coincident with Patagonian and Monte phytogeographic units, respectively (Roig et al., 1980). Stable carbon isotopes ( $\delta^{13}\text{C}$ ) can reveal different plant functional types (Boutton, 1996), as C<sub>3</sub> plants present more

negative values (−32‰ to −22‰, average −27‰; O'Leary 1988) than C<sub>4</sub> plants (−17‰ to −9‰, average −13‰; O'Leary 1988), and consequently their changing relative coverage on the landscape can be explored in soil and sediment records. For example, Silva et al. (2011) measured  $\delta^{13}\text{C}$  values in soil samples from Córdoba Province, central Argentina, and documented shifts in C<sub>3</sub>/C<sub>4</sub> plant abundance during the past few millennia.

Because of the geographic position of the south-central Andean piedmont along a desert margin, it is likely that these vegetation types would have reacted sensitively to past environmental changes (Smykatz-Kloss and Felix-Henningsen, 2004). Well-developed late

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Quaternary fluvial and aeolian sequences that span the past 50 kyr provide information on the climate and environmental changes that occurred in this piedmont region during the MIS 3 interstadial, the last glacial maximum (MIS 2) and the current interglacial stage (MIS 1) (Toms et al., 2004; Tripaldi et al., 2011; Zárate and Mehl, 2011; Mehl and Zárate, 2012). Within this context, the sediment sequence at Arroyo La Estacada, composed of alluvial deposits, interbedded with minor aeolian units and palaeosols, offers the potential to explore the climatic, palaeoenvironmental and vegetation history of the area during the past 40 kyr, according to reported ages (De Francesco et al., 2007; Mehl and Zárate, 2012). Previous palynological studies showed that pollen in the deposits is poorly preserved and confined mostly to a few time windows, ca. 13–10 kyr ago, and middle to late Holocene (Zárate and Páez, 2002; Rojo, 2009; Rojo et al., 2012). Therefore, to extend the “palaeo” record beyond the time frame of previous pollen results,  $\delta^{13}\text{C}$  values of bulk sediment organic matter and new pollen samples were obtained to investigate the vegetation history of the area.

The main objective of this study was to reconstruct past vegetation patterns in the eastern Andean piedmont and answer some important questions: 1) Is this currently arid ecotone, and more broadly, are arid ecotones elsewhere, suitable sites to detect past changes in  $\text{C}_3$  and  $\text{C}_4$  plant functional types? 2) Regarding the response of vegetation to climatic and environmental changes, is there coherence between the  $\delta^{13}\text{C}$  and pollen records?, and 3) If so, do  $\text{C}_3$  and  $\text{C}_4$  vegetation proportions reflect the main changes in piedmont palaeoenvironments from MIS 3 to MIS 1?

## 2. Study area and environmental features

The late Pleistocene and Holocene sediment sequence from Arroyo La Estacada (33°29'15" S, 69°01'30" W) is located in the arid eastern Andean piedmont of central Argentina (Fig. 1). La Estacada creek (arroyo) is the main stem of a fluvial system that drains a piedmont area from ~2230 masl closer to the Andes mountain front, to ~848 masl at the mouth of the arroyo in the Tunuyán River to the east, over a distance of approximately 60 km. The arroyo collects water from several minor streams fed by springs located along fault lines and old aggradational levels at higher positions of the piedmont.

The study area has a desert climate, with mean annual temperature of 12.5 °C and average annual rainfall of ~200 mm (Norte, 2000). It is crossed in a north–south direction by the South American Arid Diagonal (AD) (Bruniard, 1982), which is the climatic limit of influence of two main sources of humidity in the South American subtropics (Figs. 1A and 2A). To the east of the AD, precipitation comes from the Atlantic Ocean and Amazonia mainly during the summer, whereas the western part receives most of the precipitation in winter from Pacific Ocean air masses (Prohaska, 1976; Garreaud, 2009). This climatic setting coincides with the 12 °C annual isotherm (Labraga and Villalba, 2009) that determines the development of hot or cold deserts, each with its typical vegetation (Rundel et al., 2007; Quinn, 2009). Hot desert develops below 1400/1600 masl to the east of the AD (Fig. 2), represented by Monte vegetation, with xerophytic shrublands dominated by *Larrea divaricata*, mostly associated with *Prosopis flexuosa*, *Atriplex lampa* and *Schinus* spp. (De Marco et al., 1993; Méndez, 2011). Hot desert grasses are dominated by  $\text{C}_4$  plants (Cavagnaro, 1988). In contrast, cold desert is located west of the AD at an altitude above 1400/1600 masl (Fig. 2) and is represented in the eastern Andes slopes and foothills by Patagonian vegetation (= Transition, *sensu* Markgraf 1983; = Andino, *sensu* Méndez 2011), with humid shrublands and grasslands dominated by *Colliguaya integerrima* or *Adesmia pinnifolia*, mainly associated with *Junellia scoparia*, and *Adesmia horrida* (Roig et al., 1980; Méndez, 2011). In the cold desert area, grasslands are dominated by  $\text{C}_3$  plants (Cavagnaro, 1988). Altoandean (= “Altoandino”) grasslands also occur, at altitudes higher than 3000 m asl, associated with cushion plants such as *Azorella monantha*, *Adesmia subterranea*, *Nassauvia la-gascae* and *Senecio crithmoides* (Roig, 1972; Méndez, 2011). Although it

is an arid setting, hydrophytic plant communities (e.g. *Cortaderia* sp. “cortaderales”, *Typha* sp., rushes and sedges) are also present in the area, particularly associated with local water availability such as the floodplains of arroyos and minor streams, and all utilise  $\text{C}_3$  photosynthetic pathways (Smith and Epstein, 1971; Sánchez and Arriaga, 1990).

The Arroyo La Estacada area is characterized by the presence of three landforms (Fig. 3A): a regional aggradational plain part of an alluvial fan, a fill terrace and a present-day floodplain, each with a characteristic sediment record (Zárate and Mehl, 2008; Mehl and Zárate, 2012). The aggradational plain is composed of distal alluvial fan sediments deposited between ~50 kyr BP and the early Holocene, mainly related to overbank sheet overflows, and probably, temporarily inactive channels of sandy braided streams (Fig. 3C) (Mehl and Zárate, 2012). The mid-late Holocene fining-upward alluvial sequence of the fill terrace corresponds to a sinuous fluvial system lithofacies association (Fig. 3C) (Mehl and Zárate, 2012). Vegetation comprising xerophytic shrubs dominated by *Larrea divaricata* (“Jarillales del Monte”) develops on the stabilised surface of these landforms, with minor representation of other taxa such as *Prosopis* sp., *Atriplex* sp. and *Schinus* sp. Together they constitute the typical flora of the Monte vegetation that dominates the arid lowland areas of the region today (Cabrera, 1976).

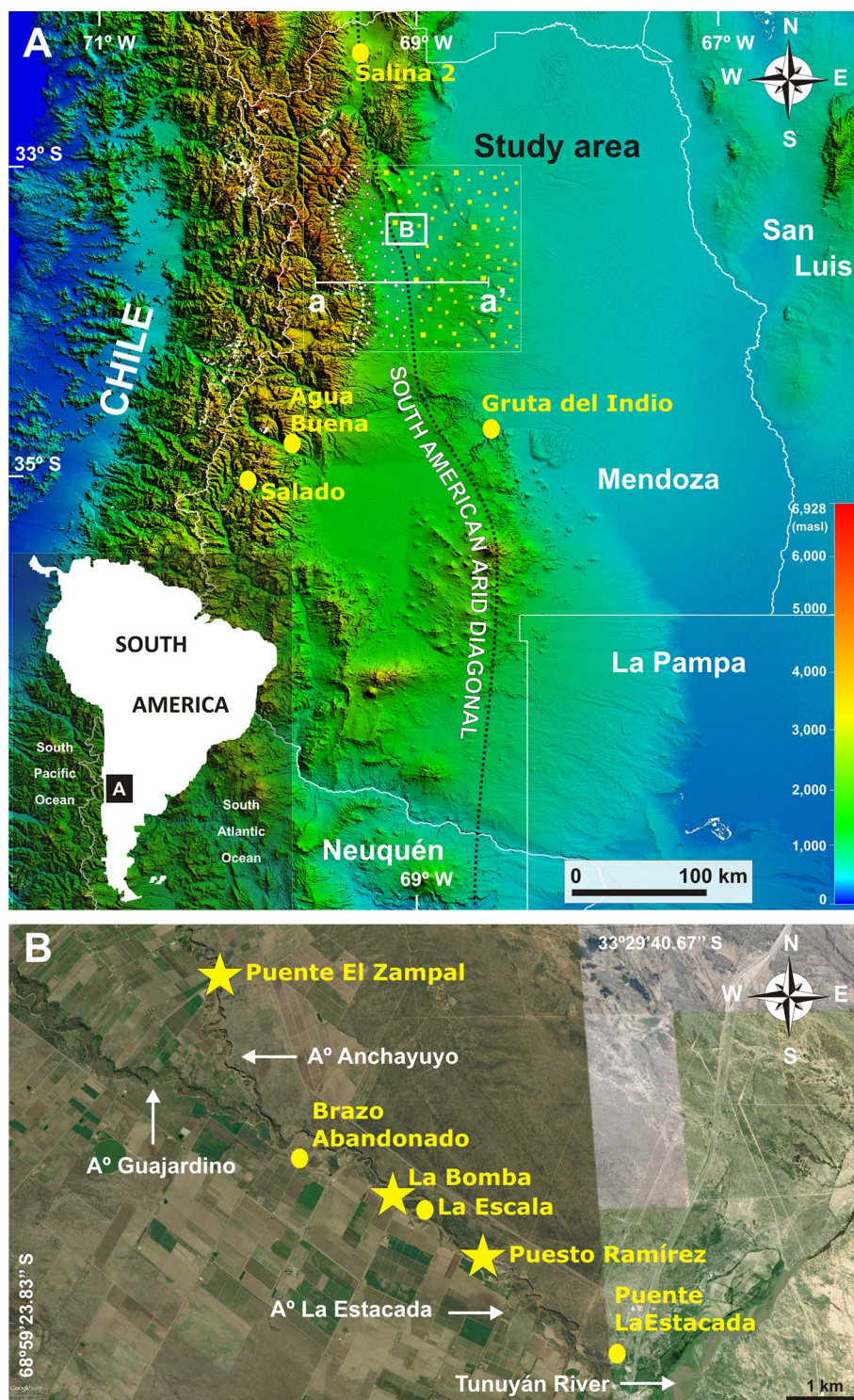
## 3. Materials and methods

Three stratigraphic sections from Arroyo La Estacada, collectively encompass the past ca. 40 cal. kyr and represent the two most conspicuous landforms of the Arroyo *sensu* Mehl and Zárate (2012); La Bomba section (LB; 40–35 cal. kyr BP) and Puente El Zampal section (PEZ; 20–8.9 cal. kyr BP) are situated in the aggradational plain, and the Puesto Ramírez (PR; last ~5 cal. kyr) is a representative section of the fill terrace (Figs. 1, 3B). All radiocarbon dates (and associated  $\delta^{13}\text{C}$  values) in this study were published previously. They are presented as a single data set using the BCal online system and an up-to-date Southern Hemisphere calibration curve, SHCal13 (Hogg et al. 2013) (Table 1). As alluvial sediments are accumulated in pulses, the depositional time intervals are variable, and consequently no age model was built.

The stratigraphic sections were sampled for organic-fraction stable carbon isotopes and palynology at regular intervals and/or following lithostratigraphic characteristics (Fig. 3B). A total of 110 sediment samples, each 1–2 cm thick, were collected and stored in plastic bags. Isotope analyses were performed in the Geochemistry Laboratory of the School of Earth and Environmental Sciences, University of Wollongong. All samples were oven-dried at 60 °C, pre-treated twice with HCl (30%) and rinsed with deionised water each time to eliminate carbonates, and then analysed for  $\delta^{13}\text{C}$  values and C and N contents, using a NA 1500 NCS elemental analyser interfaced to a Micromass PRISM III stable-isotope mass spectrometer operated in continuous-flow mode. The  $\delta^{13}\text{C}$  values are reported as per mil (‰) relative to VPDB. In each daily batch of analyses by mass spectrometry, at least four of the following five reference materials were prepared and analysed as unknowns and used to calibrate for linearity and precision (house urea,  $\delta^{13}\text{C}_{\text{VPDB}} = -36.46\text{‰}$ ; house atropine,  $\delta^{13}\text{C} = -28.53\text{‰}$ ; NIST 1547 peach leaves,  $\delta^{13}\text{C} = -25.88\text{‰}$ ; IAEA-C8 oxalic acid,  $\delta^{13}\text{C} = -18.30\text{‰}$ ; IAEA-CH-6 sucrose,  $\delta^{13}\text{C} = -10.47\text{‰}$ ). Total analytical and sample-preparation precision for  $\delta^{13}\text{C}$  is commonly  $\pm 0.2\text{‰}$ . Thirty samples from the present study were fully duplicated (i.e. separate subsample preparations) and gave maximum replication variation of  $\pm 0.015\text{‰}$  in C content,  $\pm 0.002\text{‰}$  in N content, and  $\pm 0.15\text{‰}$  for  $\delta^{13}\text{C}$ , and commonly half these values. Atomic C/N ratios were obtained by multiplying C/N weight ratios by 1.166185.

Pollen analysis was performed by standard techniques, following the criteria of Faegri and Iversen (1989) at the Museo de Historia Natural de San Rafael Laboratory, using samples from the LB section and from the late Pleistocene interval at the PEZ section. Palynology for





**Fig. 1.** A, Location of the Arroyo La Estacada study area (stippled and labelled 'B') at the foot of the Andes Cordillera. B, Google Earth © satellite image, showing Arroyo La Estacada and its tributaries, Arroyo Anchayuyo and Arroyo Guajardino. The Puente El Zampal, La Bomba and Puesto Ramírez stratigraphic sections are indicated by yellow stars. Fossil pollen sites mentioned in the text are indicated in panels A and B by yellow, filled circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

the PR section is from Rojo et al. (2012). All data were plotted using C2 software version 1.5 (Juggins, 2007).

The  $\delta^{13}\text{C}$  data from the topmost part of the PR section are considered representative of the current vegetation and environmental setting of the study area. Consequently, this  $\delta^{13}\text{C}$  value serves as a modern reference point with which to compare the fossil record.

#### 4. Results

The  $\delta^{13}\text{C}$  values of bulk sediment organic matter (hereafter,  $\delta^{13}\text{C}_{\text{OM}}$ ) from the Arroyo La Estacada sequences (last 40 cal. kyr) range from  $-26\text{‰}$  to  $-15.5\text{‰}$  (Figs. 4–6). Atomic C/N values vary from  $< 10$  to 20, except in palaeosols from the late Pleistocene–Holocene transition (PEZ section), and in the middle Holocene (PR section), where values

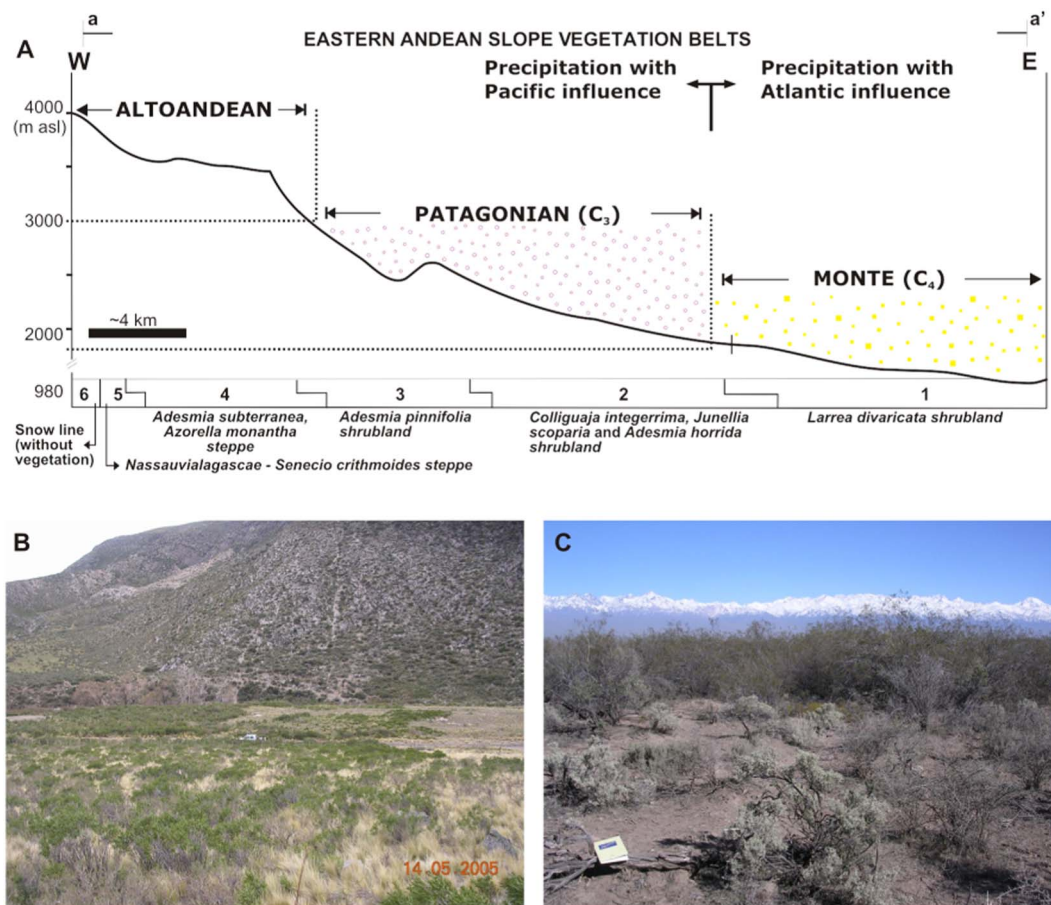


Fig. 2. A, Altitudinal vegetation distribution and ecotones at the eastern Andean slopes between 33°–35° S (a–a' transect in Fig. 1A) and their relationship with the precipitation regime (adapted from Méndez, 2011). Patagonian and Monte stippled colours according to Fig. 1A. B–C, Views of Patagonian (near Arroyo Grande) and Monte vegetation (near Arroyo La Estacada), respectively, in the study area.

are equal to or > 20.

In the LB section (~40–35 cal. kyr BP),  $\delta^{13}\text{C}_{\text{OM}}$  values are between  $-25.5\text{‰}$  and  $-21\text{‰}$ , with higher values at the base of the section and lower values nearer the top (Fig. 4). Atomic C/N values are > 10, following a trend similar to the  $\delta^{13}\text{C}_{\text{OM}}$  values. Total organic carbon (TOC) content is < 0.3 wt% throughout the section.

In the PEZ section (~20–8.9 cal. kyr BP),  $\delta^{13}\text{C}_{\text{OM}}$  values generally vary between  $-25\text{‰}$  and  $-21\text{‰}$ . Higher values (up to  $-15.5\text{‰}$ ), however, are recorded in the three palaeosol levels (Fig. 5). The atomic C/N ratios are  $\geq 10$  from the bottom to the middle of the section, between ~20–12 cal. kyr BP, and above that oscillate between  $\geq 10$  and  $\leq 30$ , showing peaks of > 30 at palaeosol levels, particularly those at 11 and 8.9 cal. kyr BP. Exceptions occur in a few intervals (11.1, 10.2, 5.1, 3.9, 2.25–1.8, and 1.2 m depth), which register C/N < 10. The TOC content is < 0.3 wt% from the bottom to the middle part of the section. In the upper part of the section, TOC content fluctuates irregularly, reaching highest values (> 1 wt%) in palaeosol levels.

In the PR section (last ~5 cal. kyr),  $\delta^{13}\text{C}_{\text{OM}}$  values display similar, but slightly lower values compared to the PEZ, ranging between  $-26\text{‰}$  and  $-23.5\text{‰}$  along most of the section, with higher values (>  $-22.6\text{‰}$  and  $-20.7\text{‰}$ ) in palaeosols at 3.3 and 1.2 cal. kyr BP, respectively (Fig. 6). The highest value ( $-19\text{‰}$ ) corresponds to the modern topsoil in the PR fill terrace surface (Fig. 6). Atomic C/N values vary from  $\geq 10$  to < 30 along the lower and middle parts of the section and show constant values of ~10 in the upper part. Similarly, in consonance with the PEZ sequence, some intervals (8.2, 5.7–5.4, 5.1–4.95, 4.5–4.2, and 3 m depth) show atomic C/N values lower than 10. TOC content is < 0.3 wt% at the bottom of the section, with oscillating higher values from the middle to the top of the section.

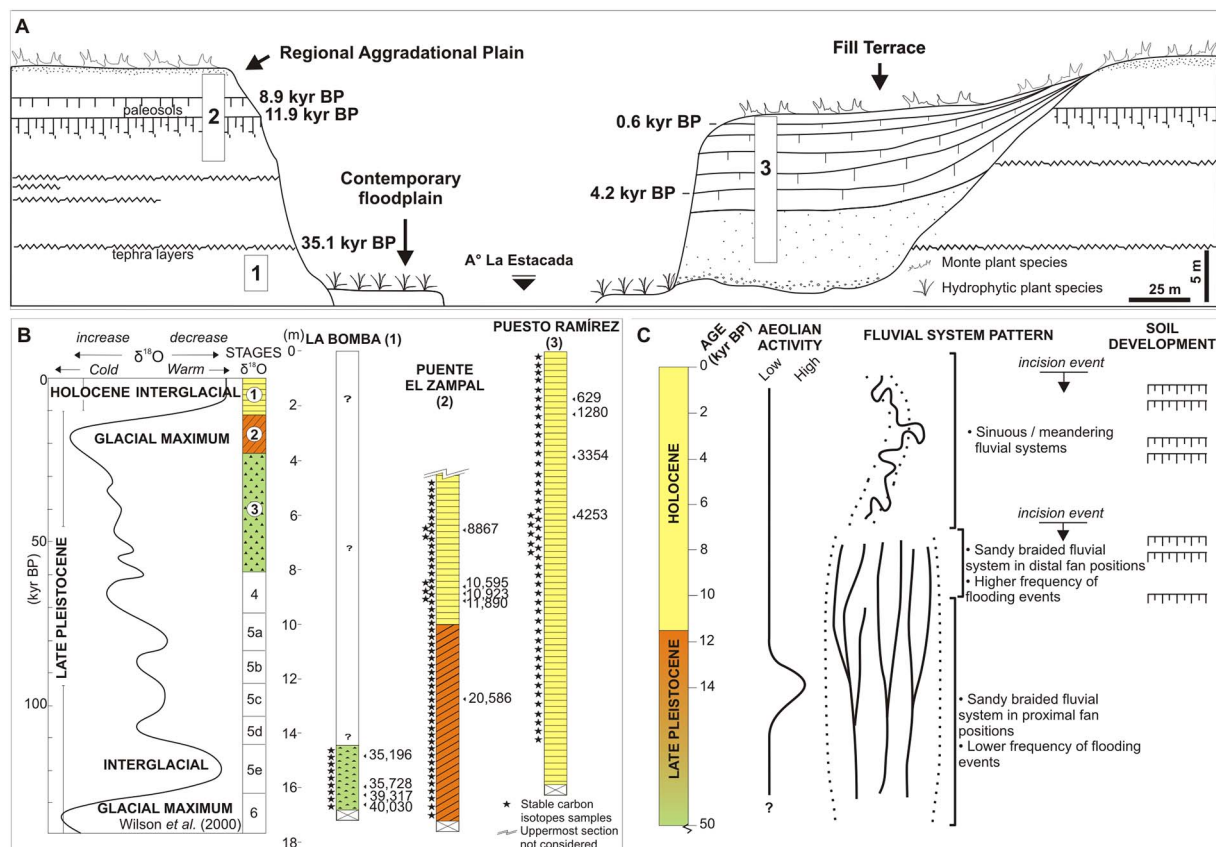
## 5. Discussion

### 5.1. Modern analogue for $\delta^{13}\text{C}_{\text{OM}}$ and C/N interpretation

The prevalent Monte vegetation (with predominance of  $\text{C}_4$  functional types in grasses) on the surface soil of the fill terrace (top of the PR section) is associated with a  $\delta^{13}\text{C}_{\text{OM}}$  value of  $-19\text{‰}$ . Accordingly, less negative  $\delta^{13}\text{C}_{\text{OM}}$  values are interpreted as indicating enrichment with  $\text{C}_4$  plants, reflecting an increase in Monte elements. By contrast, more negative soil  $\delta^{13}\text{C}_{\text{OM}}$  values indicate a greater contribution from  $\text{C}_3$  plants.

Several organic matter sources could potentially contribute to the  $\text{C}_3$  component of the  $\delta^{13}\text{C}_{\text{OM}}$  value, such as terrestrial Patagonian-Altoandean plant species, stream-margin plants (including macrophytes) of the Arroyo La Estacada, and/or algae from within the creek. The C/N ratio, however, helps identify the source of organic matter, as organic matter from aquatic algae and/or phytoplankton has a C/N ratio of ~4–10, whereas higher plants such as macrophytes of the floodplain, soils and/or leaf detritus from the uplands have C/N ratios  $\geq 10$  (Finlay and Kendall, 2007). Additionally, for C/N values < 10, Meyers and Teranes (2001) note that if the TOC content is < 0.3 wt%, the C/N ratio could be artificially low, resulting from the different C and N determination methods. Considering that TOC was measured after removing inorganic carbon (carbonate) and N includes both organic and inorganic fractions (e.g. there are micaceous metamorphic rocks in the upper mountain catchment area as potential inorganic N sources), sediment samples from the Arroyo La Estacada with very low TOC content ( $\leq 0.3$  wt%) could indicate that the C/N ratio is artificially low. Consequently, caution is required when ascribing plant origins to





**Fig. 3.** A, Cross-section of the Arroyo La Estacada valley showing the main geomorphological units identified (adapted from Zárate and Páez, 2002) and relative location of the three analysed sections (La Bomba (1), Puente El Zampal (2) and Puesto Ramírez (3)). B, Lithostratigraphic sections involved in this study (modified from Mehl and Zárate, 2012) and their correlation with Marine Isotope Stages (from Wilson et al., 2000). Calibrated weighted average ages are indicated in both A and B (Table 1). C) Scheme with fluvial system patterns, aeolian activity and soil development during the late Pleistocene and Holocene at the Arroyo La Estacada (from Mehl and Zárate, 2012).

such samples, which occur specifically in the PEZ and PR sequences as mentioned in the results section.

5.2. Palaeoenvironment and vegetation reconstruction

The interval between 40 and 35 cal. kyr BP in the LB section (Fig. 4) records part of the MIS 3 and is barren of pollen. The  $\delta^{13}\text{C}_{\text{OM}}$  values in the interval, between  $-25.5\text{‰}$  and  $-21\text{‰}$ , thus constitute an alternative vegetation proxy for the time period. Comparison with the top-most part of the PR section is useful to interpret the information derived from LB, and suggests that  $\delta^{13}\text{C}_{\text{OM}}$  values and associated C/N > 10, indicate predominance of  $\text{C}_3$  plants, likely from terrestrial Patagonian species and/or macrophytes of the stream-margin floodplain

environment. To determine whether the inferred  $\text{C}_3$  vegetation of the LB section is related to Patagonian or macrophyte vegetation, we invoke previous palaeoenvironmental reconstructions from this section based on diatoms, malacology, and  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  values of fossil molluscs (De Francesco et al. 2007, Hassan et al. 2012, De Francesco and Hassan 2013), which favour a local  $\text{C}_3$  origin rather than a regional Patagonian plant influence. The calcareous, siliceous and isotopic proxy data were previously interpreted to indicate a lentic habitat within a freshwater body ca. 40 cal. ka BP, which shifted to a brackish, alkaline system ca. 35 cal. kyr BP, suggesting a mild, humid period with a progressive increase in temperature (De Francesco et al. 2007, Hassan et al. 2012, De Francesco and Hassan 2013). It was also suggested that the area would have been wetter and warmer than present (De Francesco

**Table 1**  
Radiocarbon dates for the analysed stratigraphic sections. (MS: mollusc shell; OM: organic matter).

Section	Laboratory N°	Material	Uncalibrated age ( $^{14}\text{C}$ yr BP)	$\delta^{13}\text{C}$ (‰)	Calibrated weighted average age (cal. yr BP, 2 $\sigma$ interval)	Source
PR	AA61401	MS	731 $\pm$ 41	-4.61	629 (534–778)	Mehl & Zárate (2013)
	LP-1742	OM	1420 $\pm$ 60	-23.8	1280 (983–1544)	Mehl & Zárate (2013)
	AA72822	OM	3148 $\pm$ 34	-22.7	3354 (3081–3571)	Mehl & Zárate (2013)
	NSRL-12642	OM	3880 $\pm$ 30	-25	4253 (3987–4498)	Mehl & Zárate (2013)
PEZ	Beta-135581	OM	7890 $\pm$ 50	-25.0	8867 (8405–9006)	Zárate & Mehl (2008)
	Beta-135580	OM	9420 $\pm$ 60	-25.0	10,595 (10,238–11,069)	Zárate & Páez (2002)
	Beta-135579	OM	9610 $\pm$ 60	-25.0	10,923 (10,524–11,235)	Zárate & Páez (2002)
	NSRL-12643	OM	10,250 $\pm$ 40	-15.8	11,890 (11,399–12,362)	Mehl & Zárate (2012)
	Beta-154137	OM	17,110 $\pm$ 70	-21.0	20,586 (20,045–21,076)	Zárate & Páez (2002)
LB	AA61397	OM	31,570 $\pm$ 440	No data	35,196 (33,777–37,202)	De Francesco et al. (2007)
	AA61398	OM	31,520 $\pm$ 520	No data	35,728 (34,183–38,446)	De Francesco et al. (2007)
	AA61399	OM	35,460 $\pm$ 740	No data	39,317 (35,886–41,762)	De Francesco et al. (2007)
	AA61400	OM	35,170 $\pm$ 670	No data	40,030 (36,643–42,320)	De Francesco et al. (2007)

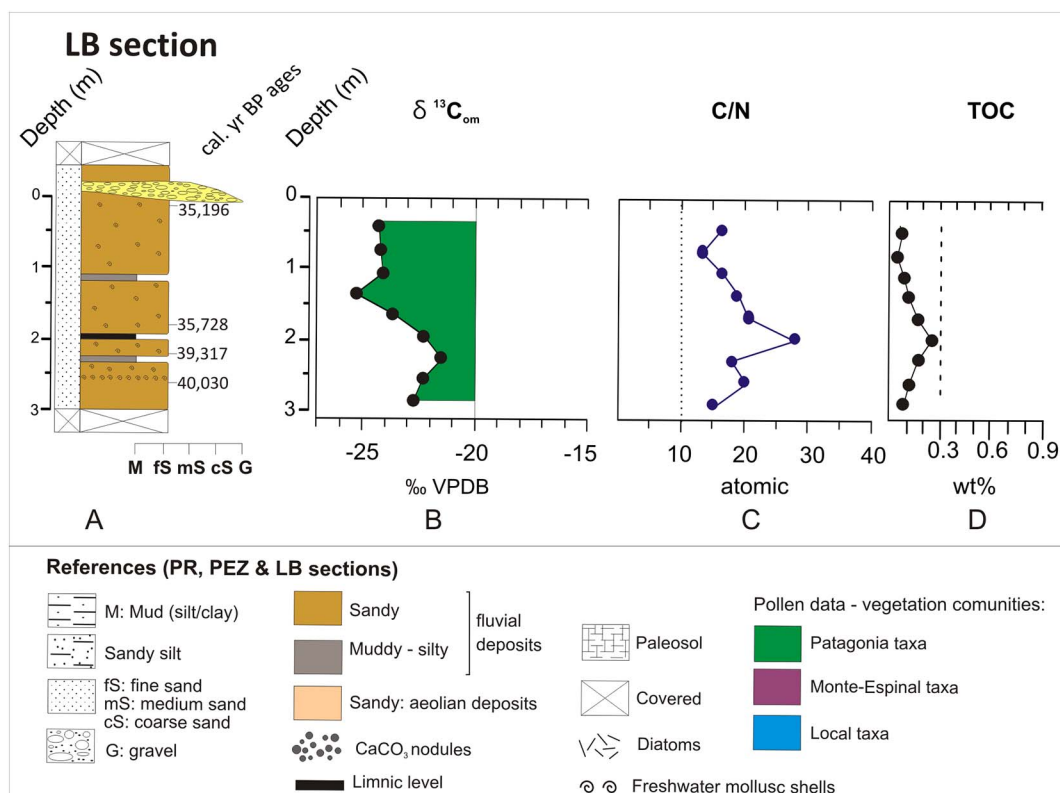


Fig. 4. Schematic representation of La Bomba (LB) lithostratigraphic section (A) and graphs of the variations in carbon stable isotopes ( $\delta^{13}\text{C}_{\text{om}}$ ) (B), atomic C/N ratio (C), and total organic carbon content (D).

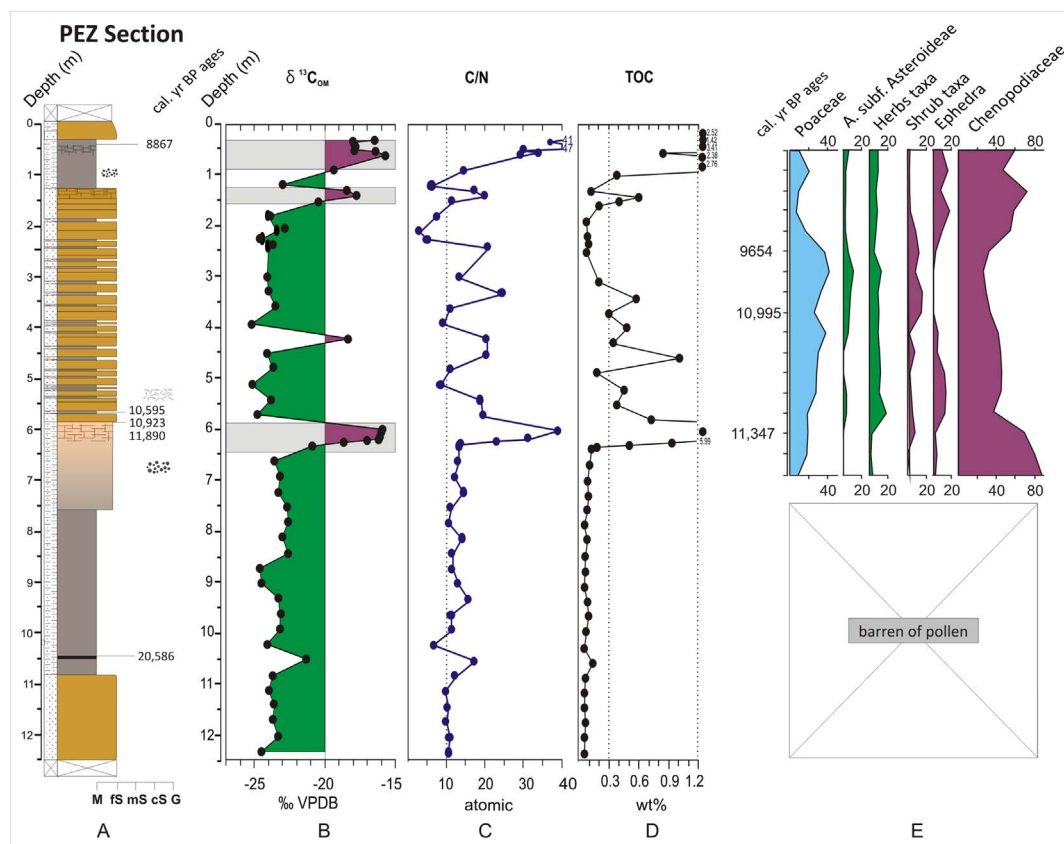


Fig. 5. Schematic representation of the Puente El Zampal (PEZ) lithostratigraphic section (A) and graphs of the variations in carbon stable isotopes ( $\delta^{13}\text{C}_{\text{om}}$ ) (B), atomic C/N ratio (C), and total organic carbon content (D). A pollen diagram for the upper part of the Puente La Estacada section (Zárate and Páez, 2002) is also shown (E).

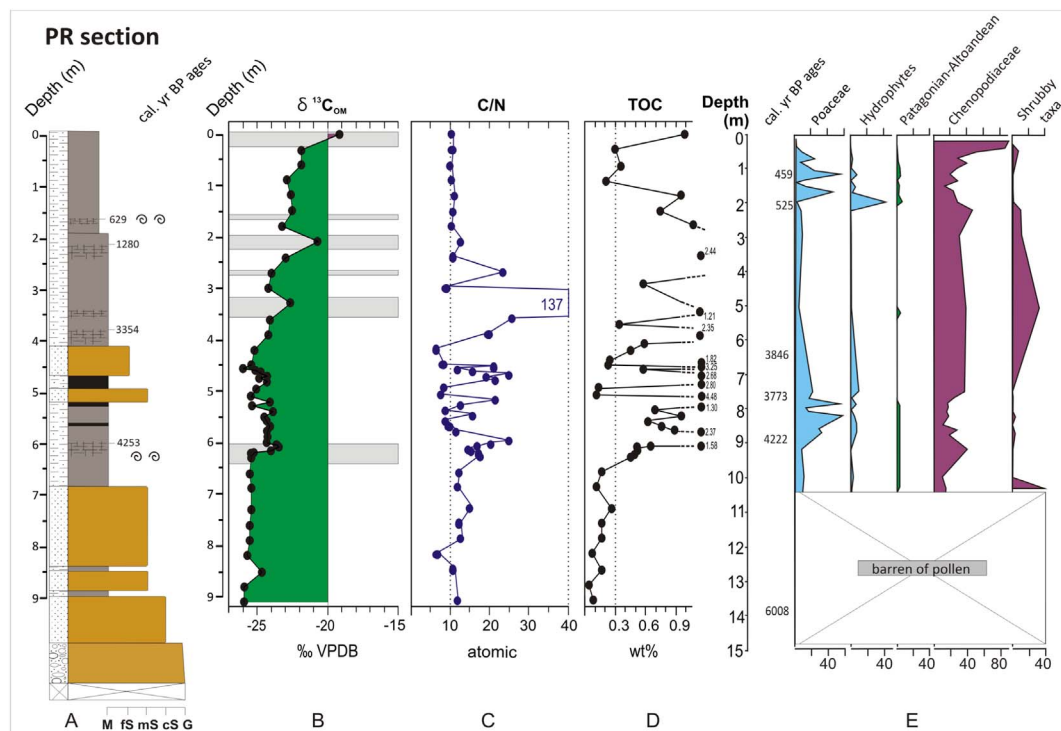


Fig. 6. Schematic representation of the Puesto Ramírez (PR) lithostratigraphic section (A) and graphs of the variations in carbon stable isotopes ( $\delta^{13}C_{OM}$ ) (B), atomic C/N ratio (C), and total organic carbon content (D). A pollen diagram for the upper part of the La Escala section (Rojo et al., 2012) is also shown (E).

and Hassan 2013). As Patagonian-adapted plants are associated nowadays with a colder climate, it is more plausible to interpret the  $C_3$  value from this section as coming from a macrophyte origin. Patagonian vegetation probably had little or no influence on the  $\delta^{13}C$  value. Although De Francesco and Hassan (2013) proposed that conditions were warmer than present, which would imply greater  $C_4$  plant influence in the record and consequently  $\delta^{13}C_{OM}$  values less negative than  $-19\text{‰}$ , this is not the case here.

The interval between  $\sim 20$  and  $12$  cal. kyr BP was also barren of pollen (Fig. 5) in the PEZ sediment section (Zárate and Páez, 2002). Probably, regional MIS 2 aeolian activity (Tripaldi et al., 2011) and/or very low plant cover and/or pollen production could have obscured direct evidence of past vegetation. Therefore, as in the LB section, the  $C_3$  plant type inferred from  $\delta^{13}C_{OM}$  by the end of the late Pleistocene at Arroyo La Estacada constitutes a novel alternative approach to provide insights into past vegetation in the area at that time. As for the interpretation of the LB section data,  $C_3$  predominance is probably a consequence of dominance of floodplain vegetation and/or Patagonian regional taxa. The two levels (11.1 and  $10.2$  m depth) that register  $C/N < 10$  would indicate an algal origin for the organic matter or, that C/N values are an artefact of the differential C and N measurement methods due to TOC content  $< 0.3$  wt% (Meyers and Teranes, 2001).

In a pollen record from the Gruta del Indio archaeological site in the eastern Andean piedmont,  $\sim 150$  km south of Arroyo La Estacada (ca.  $35^\circ$  S; Fig. 1A) (D'Antoni 1983, Markgraf 1983), Patagonian-affinity plant communities are inferred for the late Glacial. Gruta del Indio and Arroyo La Estacada have similar environmental settings, and past environmental/climatic variations are expected to have been broadly similar. Accordingly, it is reasonable to infer that cold-desert Patagonian-affinity vegetation contributed to the  $\delta^{13}C_{OM}$  values measured at Arroyo La Estacada, consistent with the prevailing cold environment for this period. Additional independent fossil records are needed to corroborate the information for the time interval, between  $\sim 20$  and  $12$  cal. kyr BP.

The palaeosol levels interspersed among deposits during the Pleistocene–Holocene transition ( $\sim 12$  to  $8.9$  cal. kyr BP) in the alluvial

PEZ section show the least negative  $\delta^{13}C_{OM}$  values ( $-18\text{‰}$  to  $-15\text{‰}$ ) of the Arroyo La Estacada record. Here, C/N and TOC content support a terrestrial origin for the buried organic matter (Fig. 5C and D). Mehl and Zárate (2012, 2013) suggested that these palaeosols developed because of a change to a warmer climate after the late Pleistocene glacial conditions. Consequently, it is appropriate to interpret these high  $\delta^{13}C_{OM}$  values as the result of a higher contribution of  $C_4$  plants to the sediment TOC content, indicating a major influence of the Monte desert plants by that time. In addition, the  $\delta^{13}C$  data likely suggest an environment warmer than present, with  $\delta^{13}C_{OM}$  values even higher (up to  $-15\text{‰}$ ) than in modern soil ( $-19\text{‰}$ ). The presence of xerophytic Monte taxa (Chenopodiaceae, *Ephedra*, and other shrubby taxa) was indicated in the pollen record for the same oldest palaeosol times (ca.  $12$  cal. kyr BP) and later (Puente La Estacada section, Fig. 1B and 5E; Zárate and Páez, 2002), supporting the interpretation for that period.

At the PR section (last  $\sim 6$  cal. kyr), a broad trend between ca.  $6$  and  $4$  cal. kyr BP with  $\delta^{13}C_{OM}$  values ranging from  $-26\text{‰}$  to  $-23.5\text{‰}$  would indicate predominance (with a decrease to the top) in the contribution from  $C_3$  plants during the middle and late Holocene. Atomic C/N values higher than  $10$  (Fig. 6C) suggest a terrestrial origin for the organic matter. As in the LB sequence and in the bottom and middle section of the PEZ sequence, there still remains the difficulty of distinguishing between macrophytes and terrestrial upland vegetation sources. For the period between  $4$  and  $0.5$  cal. kyr BP, previous pollen evidence from Arroyo La Estacada, analysed in the La Escala and Brazo Abandonado stratigraphic sections (Fig. 1B), showed that the main vegetation changes correspond to floodplain plants of hydrophytic affinity (macrophytes such as sedges, rushes, *Typha* and *Cortaderia* sp.), alternating with Monte taxa, depending on the local water availability (Rojo et al. 2012). Furthermore, regional Patagonian-Altoandean pollen elements are represented in only trace proportions (Fig. 6E). Consequently, as for the LB section, independent proxy records, fossil pollen in this case, favour the interpretation that the more negative  $\delta^{13}C_{OM}$  values in the PR section between  $6$  and  $4$  cal. kyr BP relate to a major contribution from local stream-margin plants, rather than from regional Patagonian-Altoandean elements.

After ca. 4 cal. kyr BP, the beginning of a gradual change from most negative to less negative  $\delta^{13}\text{C}_{\text{OM}}$  values,  $\text{C}_3$  to  $\text{C}_4$ , respectively, is evident in the PR section. The C/N values fluctuate from < 10 to 25 between 4 and 3.3 cal. kyr BP, and in the last 1.5 cal. kyr these values were  $\geq 10$ . The TOC content is > 0.3 wt% in much of the section, enabling a confident interpretation that organic matter for the last 4 kyr is composed of a mixture of algae and higher plant sources. It seems, however, that the contribution of Monte  $\text{C}_4$  tends to surpass the macrophyte and algal influence, particularly during the last 1.5 cal. kyr, as is shown by the changing trend towards less negative  $\delta^{13}\text{C}_{\text{OM}}$  values, culminating with  $-19\%$  in the soil of the topmost part of the PR section. The pollen evidence from La Escala and Brazo Abandonado sections (Fig. 6E) supports the inference made about the varying dominance of macrophytes and Monte taxa elements in that period.

For those stratigraphic levels that register C/N < 10 and seemingly indicate an algal origin for the organic matter (8.2, 5.7–5.4, 5.1–4.95, 4.5–4.2, and 3 m depth), there are two with TOC content < 0.3 wt% (5.1–4.95 and 4.5–4.2 m depth) that probably reflect that C/N values are an artefact of the differential C and N determination methods (Meyers and Teranes, 2001). So, as for those similar levels in the lower to middle part of the PEZ sections, these levels yield an ambiguous inference about the origin of the  $\text{C}_3$  signal.

The changing trend in  $\delta^{13}\text{C}_{\text{OM}}$  values from the middle to late Holocene, starting between 4 and 3 cal. kyr BP, is in agreement with pollen records from the eastern Andean slope that also show a significant changing trend in the dominant vegetation ca. 3 kyr BP (Markgraf, 1983; Navarro et al., 2010; Navarro, 2011). In the Salina 2 peat bog (32°15' S, 69°20' W, 2000 masl), close to the Monte/Transition zone vegetation (Fig. 1A), vegetation shifted from grasses, presumed to have  $\text{C}_3$  metabolism, under a higher than present precipitation regime, to Monte taxa, indicating an increase in temperature at 3  $^{14}\text{C}$  kyr BP (Markgraf, 1983). In the high mountain area (Salado peatbog-like deposits; 35°10' S, 70°15' W, 2400 masl; Fig. 1A) there was an increase in Patagonian-Altoandean pollen taxa, also implying higher temperature in those areas at 3 cal. kyr BP (Markgraf, 1983). Similarly, the Agua Buena alluvial fan sequence (34°50' S, 69°56' W, 2100 masl; Fig. 1A) shows a significant change in the pollen record at 2.8 cal. kyr BP, interpreted as a change from wetter to the drier present conditions (Navarro et al., 2010; Navarro, 2011). Although in the PR section the  $\delta^{13}\text{C}_{\text{OM}}$  data show a mixed contribution of local (macrophytes) and regional (Monte) plants, they still support the existence of a regional trend towards present conditions over the last 3 cal. kyr in the eastern Andean piedmont at this latitude.

## 6. Conclusions

Stable isotope ( $\delta^{13}\text{C}$ ) analysis of bulk sediment organic matter proved to be a useful palaeo-vegetation proxy that complements, strengthens and/or substitutes for (particularly in intervals with no pollen data) traditional pollen analysis. Palynology in the arid piedmont setting of central Argentina and other arid areas throughout the world is often difficult owing to low pollen production, poor pollen preservation, and coarse clastic sedimentation. Concerning our initial questions, shifting  $\delta^{13}\text{C}_{\text{OM}}$  values reflect changes in the relative abundance of  $\text{C}_3$  and  $\text{C}_4$  plants and confirm that this piedmont area is suitable to explore past changes in vegetation type. The ecotonal position of the Arroyo La Estacada basin in relation to two different deserts (Patagonian  $\text{C}_3$  and Monte  $\text{C}_4$ ) was crucial to investigate the dynamics of past vegetation in the area. Consistency between  $\delta^{13}\text{C}_{\text{OM}}$  and pollen data reinforce the inference that Arroyo La Estacada alluvial deposits are mainly dominated by local plant communities, whereas regional terrestrial vegetation (Patagonian and/or Monte) had little influence. Nevertheless,  $\delta^{13}\text{C}$  values indicate a clear dominance of terrestrial  $\text{C}_4$  plants (i.e., Monte vegetation), particularly in palaeosols that developed at the late Pleistocene–Holocene transition. Additionally, the  $\delta^{13}\text{C}_{\text{OM}}$  data filled gaps in the pollen records, as those of the LB and the bottom

to the middle parts of the PEZ section, where  $\delta^{13}\text{C}_{\text{OM}}$  data and atomic C/N ratios suggest dominance in the fossil record of local plants and regional terrestrial (Patagonian) vegetation, respectively. Regarding environmental changes from MIS 3 to MIS 1, we found that isotope geochemistry was useful to identify a clear change in the  $\delta^{13}\text{C}_{\text{OM}}$  data at palaeosols developed during the Late Pleistocene–Holocene transition. In the oldest deposits (MIS 3 and MIS 2), however, it was not possible to establish a clear connection between  $\text{C}_3$ – $\text{C}_4$  vegetation dynamics and regional palaeoenvironmental changes, because of the dominance of local plant communities. Finally, more isotope ( $\delta^{13}\text{C}_{\text{OM}}$ ) studies in other sediment archives (e.g. lake and peat bog deposits), and better isotopic characterisation of modern vegetation sources (terrestrial, macrophytes, algae), as well as of modern soils from Patagonian and Monte phytogeographic units are necessary to improve palaeoenvironmental reconstructions for the region. Indeed, the future application of compound-specific  $\delta^{13}\text{C}$  measurements, particularly for long-chain alkanes, may assist in distinguishing among terrestrial, macrophyte and algal sources.

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