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RADIOCARBON DATING OF SOIL ORGANIC MATTER FRACTIONS IN ANDOSOLS IN NORTHERN ECUADOR

Femke H Tonneijck[1,2] • Johannes van der Plicht[3] • Boris Jansen[1] • Jacobus M Verstraten[1] • Henry Hooghiemstra[1]

ABSTRACT. Volcanic ash soils (Andosols) may offer great opportunities for paleoecological studies, as suggested by their characteristic accumulation of organic matter (OM). However, understanding of the chronostratigraphy of soil organic matter (SOM) is required. Therefore, radiocarbon dating of SOM is necessary, but unfortunately not straightforward. Dating of fractions of SOM obtained by alkali-acid extraction is promising, but which fraction (humic acid or humin) renders the most accurate ^{14}C dates is still subject to debate. To determine which fraction should be used for ^{14}C dating of Andosols and to evaluate if the chronostratigraphy of SOM is suitable for paleoecological research, we measured ^{14}C ages of both fractions and related calibrated ages to soil depth for Andosols in northern Ecuador. We compared the time frames covered by the Andosols with those of peat sequences nearby to provide independent evidence. Humic acid (HA) was significantly older than humin, except for the mineral soil samples just beneath a forest floor (organic horizons), where the opposite was true. In peat sections, ^{14}C ages of HA and humin were equally accurate. In the soils, calibrated ages increased significantly with increasing depth. Age inversions and homogenization were not observed at the applied sampling distances. We conclude that in Andosols lacking a thick organic horizon, dating of HA renders the most accurate results, since humin was contaminated by roots. On the other hand, in mineral soil samples just beneath a forest floor, humin ages were more accurate because HA was then contaminated by younger HA illuviated from the organic horizons. Overall, the chronostratigraphy of SOM in the studied Andosols appears to be suitable for paleoecological research.

INTRODUCTION

In the Ecuadorian Andes, the rise in deforestation, grazing, and burning as a result of the increase in population pressure during the last 500 yr severely disturbed the Upper Forest Line (UFL) (Ellenberg 1979; Hofstede 1995). Therefore, the natural altitudinal position of the UFL is subject to debate (Laegaard 1992; Wille et al. 2000). In the last decade, negative impacts of deforestation were recognized and efforts made to forest degraded lands; however, forestation of tropical alpine grasslands (páramo), that under natural circumstances would not be forest, damages that ecosystem. To support sustainable forestation, we need to examine the natural dynamics of the UFL by investigating the local vegetation history.

Traditionally, vegetation history is reconstructed by analyzing fossil pollen records in peat bogs or lake sediments (e.g. Erdtman 1943; Birks and Birks 1980; Moore et al. 1991; Bradley 1999). To better understand UFL dynamics, our investigation would ideally be concentrated around the hypothetical UFL. Unfortunately, conventional polliniferous deposits are not necessarily located there.

Alternatively, Andosols, the dominant soil type in the high Andes, could provide great opportunities for paleoecological studies, including pollen analyses (Bakker and Salomons 1989). Andosols accumulate vast amounts of OM (Shoji et al. 1993), which is related to low temperatures, acidic soil pH, and the formation of organo-metallic or organo-mineral complexes that resist decomposition (Shoji et al. 1993; Torn et al. 1997). These conditions also favor pollen preservation (Moore et al. 1991), which has been demonstrated in Andosols above 3000 m asl in Colombia (Salomons 1986).

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However, to link soil pollen records to a time scale, understanding of the stratification of SOM in the soil and its age-depth relationship in particular is required (Davidson et al. 1999; Keatinge 1983). Furthermore, since pollen analysis in terrestrial soils is not a widely applied method yet, verification of the results is necessary (e.g. by comparing the pollen records from soils to those from nearby peat bogs). For such a comparison, an accurate chronology of either record is crucial. Since peat bogs and Andosols are both rich in organic carbon, measuring of radiocarbon activities offers a suitable dating method.

Unfortunately, ^{14}C dating of SOM is not straightforward (e.g. Mook and Streurman 1983; Scharpenseel and Becker-Heidmann 1992; Pessenda et al. 2001). SOM consists of a range of complex organic molecules varying in decomposition phase. The continuous input of fresh OM into soils causes the measured ^{14}C ages of bulk SOM to be somewhat younger than the depositional age (Wang et al. 1996). In addition, input of young roots into older soil horizons, leaching of mobile organic compounds through the soil profile, bioturbation, and deposition of allochtonous OM may also contaminate SOM ages (Mook and Streurman 1983; Pessenda et al. 2001). The relative importance of these pedogenetic processes, which determine the measured age of SOM, depends on soil properties and vegetation type among other factors. Therefore, interpretation of ^{14}C dates must be tailored to the specific soil ecosystem under study.

If macroremains of vegetation are lacking in the soil, dating of chemical fractions of SOM (humic substances) obtained by the standard alkali-acid extraction (Schnitzer 1982), instead of dating bulk SOM, offers the opportunity to select the fraction yielding a more accurate ^{14}C age as based on a qualitative evaluation on the validity of dating (Orlova and Panychev 1993; Kristiansen et al. 2003). However, which fraction provides the most accurate dates is not obvious. ^{14}C dating of humic substances rendered more accurate results in a range of soil types (Pessenda et al. 2001; Kovda et al. 2001; Dalsgaard and Odgaard 2001; van Mourik et al. 1995), but Andosols were not yet investigated. Dating peat bog sediments by ^{14}C analysis is generally more straightforward than dating terrestrial soils, as peat sequences are much less disturbed.

The aims of this current paper are 1) to determine which fraction of SOM (HA or humin) renders more accurate ^{14}C dates in Andosols and 2) to evaluate whether the age-depth relationship of SOM in the Andosols of our study area is suitable for paleoecological research such as the reconstruction of the natural position of the UFL. The results are compared to ^{14}C ages of similar OM fractions from nearby peat bogs, to assess whether the pollen records from those peat sequences can be used to verify the soil pollen records. By fulfilling these aims, the current paper will make an indispensable first step towards reconstruction of the UFL in northern Ecuador.

DESCRIPTIVE BACKGROUND

The study sites are located within 3 nature protection areas in northern Ecuador, near the border with Colombia (Figure 1, Table 1). The Guandera Biological Station lies in the Eastern Cordillera (mountain range) and preserves a (semi-)natural UFL at ~3650 m asl. The transition from forest to páramo is abrupt, probably indicating at least some human influence (Laegaard 1992), but the forest still contains trees with a considerable diameter at breast height (dbh) of 70 cm. Some forest patches occur above the current UFL. The dominant species within the forest are *Clusia flaviflora* Engl., *Weinmannia cochensis* Hieron., and *Ilex colombiana* Cuatrec., and the páramo is characterized by *Calamagrostis effusa* Kunth (Steud.) bunch-grass and *Espeletia pycnophylla* Cuatrec. stem-rosette.

The El Angel Ecological Reserve and the Los Encinos Biological Station are located close to each other in the Western Cordillera and were heavily deforested before conservation; the few remaining

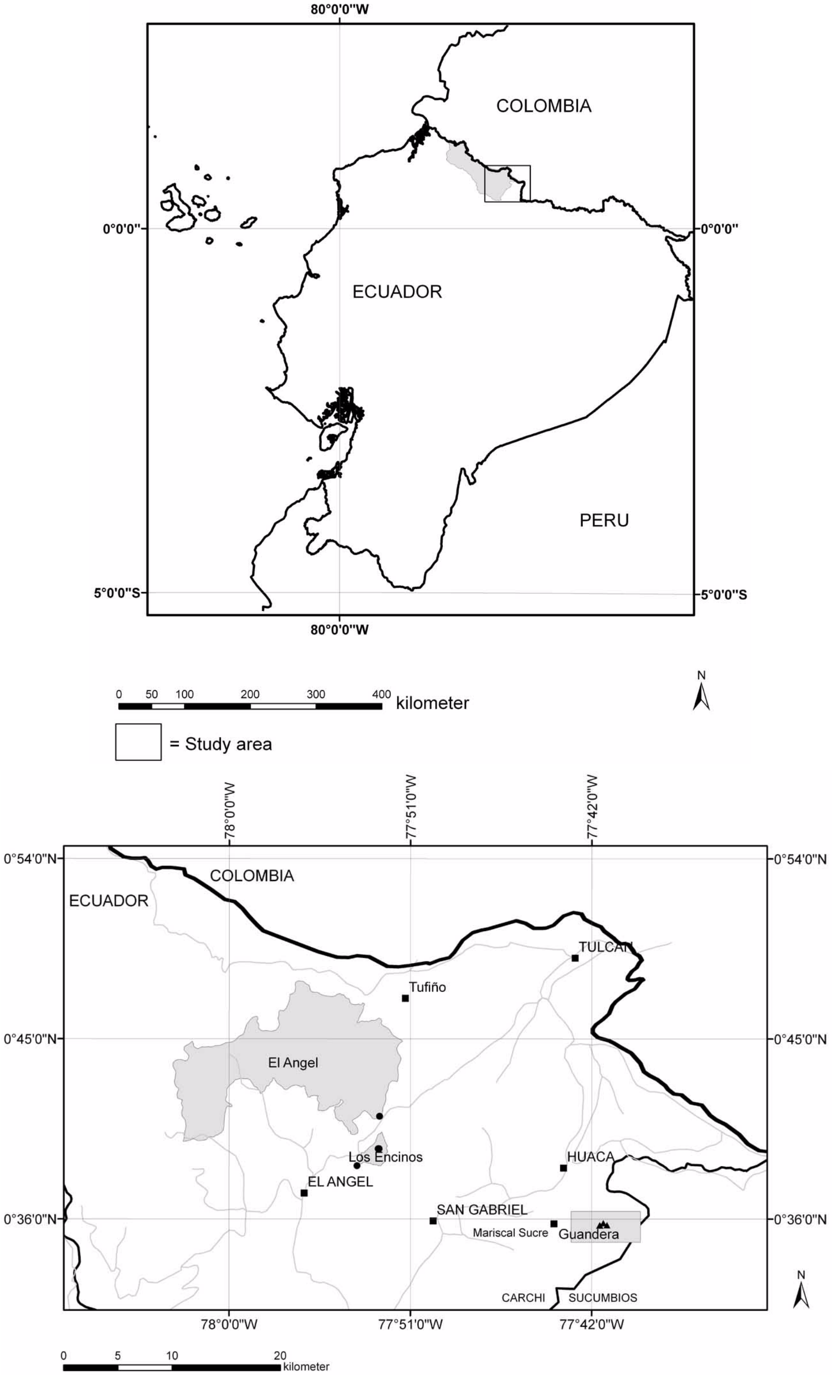

Figure 1 Maps of Ecuador (province of Carchi indicated in gray) and of the location of the National Parks (in gray) and the study sites. ● = site of transect Western Cordillera; ▲ = site of transect Eastern Cordillera; ■ = village or town.

Table 1 Description of study sites.

Soil type (FAO)	Altitude (m asl)	Current vegetation	Coordinates[a]	Cordillera	Site
Andosol	3860	Páramo	N 0°35′48″/ W 77°41′25″	Eastern	G7
Andosol[b]	3697 ± 9 (*n* = 9)	Forest patch in páramo	N 0°35′41″/ W 77°41′36″	Eastern	G5a
Andosol	3694 ± 13 (*n* = 9)	Páramo	N 0°35′41″/ W 77°41′35″	Eastern	G5b
Andosol	3570	Forest patch in páramo	N 0°39′31″/ W 77°52′33″	Western	A7A
Andosol	3570	Páramo	N 0°39′31″/ W 77°52′36″	Western	A7B
Histosol	3869	*Xyris* bog	N 0°35′42″/ W 77°41′14″	Eastern	G8
Histosol	3740	*Oreobolus* bog	N 0°41′16″/ W 77°52′46″	Western	A11
Histosol	3418	*Juncus* bog	N 0°38′40″/ W 77°53′39″	Western	A2

[a] GPS coordinates in WGS 1984, altitudes from altimeter, GPS altitude only used for site G8; *n* = 1 unless stated otherwise.

[b] This profile classifies as (Andic) Cambisol instead of Andosol, but since soil properties are similar to the other soils and for the purpose of simplicity, we refer to the soil as Andosol in the context of this paper.

trees rarely exceed 30 cm dbh. El Angel and Los Encinos are now covered with páramo vegetation and some patches of remnant forest and there is no proper UFL. However, the zonal forest patches that seem to maintain more of the original taxonomic composition of the natural montane forest are located between 3450 and 3600 m asl and dominated by different woody species of the genus *Weinmannia* and *Miconia*, as well as *Clethra crispa* C. Gust. and *Hedyosmum cumbalense* H. Karst. Above this altitude, the páramo vegetation is characterized again by C. *effusa* and E. *pycnophylla*.

The study area in the Eastern Cordillera receives almost double the precipitation annually than the study areas in the Western Cordillera (annual means 1900 mm and 1000 mm, respectively), but mean annual temperatures are similar (from 12 °C at 3400 m asl to 4 °C at 4000 m asl). We did not observe volcanic emanations of (fossil) CO_2 in the field.

In both cordilleras, we selected a forest patch and a site with páramo next to it, to determine the effect of the current vegetation on soil profile development and its SOM age-depth relationship. The floristic composition of the forest patch in Guandera is similar to that of the continuous forest belt just below the UFL, the subalpine rainforest, and similarly the forest patch in Los Encinos appears to maintain the original taxonomic composition of the now disappeared forest (Moscol et al., unpublished data). In Guandera, we additionally selected a peat bog at 3869 m asl and a site with páramo next to it. Furthermore, in El Angel 2 peat bogs were investigated, one at 3740 m asl and one at 3418 m asl. The El Angel peat bog at higher altitude is characterized by *Oreobolus obtusangulus* Gaudich and the peat of Guandera by *Xyris subulata* Ruiz & Pav, both small herbs, whereas the El Angel peat bog at lower altitude is dominated by the tall rush species *Juncus balticus* ssp. andicola (Hook) Snogerup. The sites selected for ^{14}C dating belong to 2 transects with sites at altitudinal intervals of 100 m from 3000 to 4000 m asl.

MATERIALS AND METHODS

Sampling Procedures

Soil pits of ~1 m^2 surface area and a depth of 1.5 m to 2 m, depending on the soil profile, were excavated and soil profiles were described according to the guidelines for soil description of the Food and Agricultural Organization (FAO) of the United Nations (FAO 1990) and classified according to the World Reference Base (FAO 1998). In both study areas, 1 paleosol (buried soil) was generally observed beneath the current soil, indicating at least 2 main events of tephra deposition. The current soil was considered sufficiently thick to contain a period without intensive human activities. Therefore, the main focus was on the current soil profile. We took an undisturbed vertical soil sample using a metal gutter of 75 × 5 × 4 cm, and if the current soil was not yet completely covered, a second vertical sample was collected with a small overlap. The gutters were packed in aluminium foil and then plastic foil and finally securely tied with adhesive tape to avoid dislocation and drying during transport. In addition, we took bulk soil samples for chemical analyses (~1 kg field-moist material) and ring samples (with a volume of 100 cm^3) for bulk density determination in the same soil pit at regular depths but respecting horizon boundaries. Each bulk soil sample was obtained from a vertical interval of ~5 cm, the middle of which was noted as the depth of the sample, in order to gather sufficient material. The gutters and soil samples were stored at 2 °C under field-moist conditions prior to analyses. The peat bogs were sampled to their maximum depths with hand-operated Russian augers of 75-mm and 50-mm diameter and a standard length of 50 cm from Wittander Co. (Lund, Sweden). The smaller diameter auger is used when sediments are compact and resistant. The auger is brought to the correct depth by 1-m-long extension rods. The auger segments were wrapped in halved plastic tubes and then packed and stored like the gutter samples.

For ^{14}C dating, at least 3 samples per soil profile were cored from the gutter samples using a corer with 0.5-cm diameter to minimize the time span covered by the sample. Two samples were located in the current soil: one just below the mineral soil surface in the Ah horizon and one at its bottom in the Ah2 or Bw horizon. A third sample was taken at the top of the paleosol, the 2Ahb horizon. Additionally, we took 2 samples from the thick organic horizon in the Guandera forest profile (one in the middle and one at the boundary with the Ah horizon) and one extra sample at the top of the páramo soil profile located next to it. The vertical distance between samples was on average 40 cm. The samples for ^{14}C dating were taken at the same depths as the samples for chemical analyses (except for the sample at the boundary between organic horizon and Ah). In the peat cores, 3 samples at regular spacing were taken using the same 0.5-cm-diameter corer. Fresh roots were removed from the peat sample by hand-picking using a binocular.

Laboratory Procedures

Chemical fractionation of SOM by alkali-acid extraction followed the procedure of Schnitzer (1982), which is the conventional method for OM fractionation (Stevenson 1994). The organic fraction that is soluble in alkali solution and immobile in acid solution is called HA; the residual fraction (immobile in both alkali solution and acid solution) is referred to as humin. Fulvic acid, the OM fraction that is soluble in both alkali solution and acid solution, was discarded because of its inherent mobility in soils. Humin is generally considered to be the most humified (decomposed) OM fraction. Strictly speaking, the division of OM in humic substances is not meaningful in the case of peat, since decomposition is negligible and consequently the composition of OM in peat is not much altered. However, for a proper comparison of soil and peat records we fractionated the peat samples as well, applying the same procedure.

Soil pH was measured with a glass electrode (Consort SP10B, Turnhout, Belgium) in a 0.01M $CaCl_2$ soil solution (w/v 1:5 mineral soil samples and w/v 1:10 organic samples, using field-moist samples) as a measure of actual acidity. Total carbon was measured with a VarioEL (Elementar Analysensysteme GmbH, Hanau, Germany) CNS auto-analyzer. Total carbon equals organic carbon, since carbonates are not present. Dry bulk density was determined by weighing oven-dried samples (105 °C, 44-hr mineral soil samples and 70 °C, 48-hr organic samples) and then dividing the oven-dry weight by the known volume of the sampling ring (100 cm^3).

Radiocarbon Dating

^{14}C analysis was performed by the accelerator mass spectrometry (AMS) facility of Groningen University, the Netherlands (laboratory code GrA). AMS enables the measurement of ^{14}C concentrations in graphite made from milligram-size sample material. After pretreatment as described above, the isolated fraction of the original sample is combusted into CO_2 and purified using an elemental analyzer (EA) (Aerts et al. 2001). The EA provides also quality check parameters such as the organic carbon content and the $\delta^{13}C$ value of the sample. The CO_2 is then collected cryogenically for later graphitization. The graphite powder is pressed into targets that are placed in the sample carousel of ion source of the AMS. The AMS system measures the isotopic ratios $^{14}C/^{12}C$ and $^{13}C/^{12}C$ of the graphite (van der Plicht et al. 2000). Typical measurement errors are 0.4% (Meijer et al. 2006). From these measured isotopic ratios, the ^{14}C activities are calculated (including the correction for isotopic fractionation) and the ^{14}C ages are given in BP.

Telford et al. (2004) explained that mathematical age-depth relationships only make sense when using calibrated ^{14}C ages. Therefore, to evaluate the OM age-depth relationship for the soil and peat sequences, we transformed ^{14}C ages to a calendar year probability distribution (cal AD/BC) with the WinCal25 calibration software (van der Plicht 2005) using the presently recommended IntCal04 calibration data set (Reimer et al. 2004). Some ^{14}C measurements yield activities >100%, which means the samples are modern, containing ^{14}C above the natural level, produced by atmospheric nuclear explosions during the late 1950s and early 1960s—the so-called “bomb peak.” The atmospheric ^{14}C content for these “modern samples” is derived from direct measurements of ^{14}C in atmospheric CO_2, for a variety of locations (e.g. New Zealand: Manning et al. 1990; Norway: Nydal and Lövseth 1983; the Netherlands: Meijer et al. 1995). These records can be used to transfer the ^{14}C activities to calendar ages. Our data contain just a few such modern measurements; since our measurements are within the error, it is not relevant which of these atmospheric data sets are used for our purposes.

Calibrated ^{14}C ages are expressed as the range of calendar years of the 1-σ peak with the largest relative area under the probability distribution, except for the modern samples where the most probable range was selected based on expert knowledge. Since the ranges are small, calculations are performed with the mean and the dots displayed in the graphs represent the whole range of calendar years at the scale of the graph.

Statistical Analysis

Differences in means were considered significant when $p < 0.01$ unless stated otherwise, as determined with a 2-tailed paired-samples test performed with the SPSS Compare Means procedure (SPSS Inc. 2001). Pearson’s correlations (bivariate) between variables were calculated using the SPSS Correlate procedure and considered significant when $p < 0.01$ unless stated otherwise. We performed a linear regression in Graphpad Prism (Graphpad Software Inc. 1999) to evaluate the relationship between calibrated age and depth.

RESULTS AND DISCUSSION

Soil properties are reported in Table 2. The soils in both areas consist of Andosols (FAO 1998) with upper mineral horizons characterized by a very large organic carbon content (9–21%), acidic pH (pH $CaCl_2$ 3.7 to 4.5), and low dry bulk densities (0.4–0.6 g cm^{-3}). The dry bulk densities are similar for all samples and therefore the effect of compaction on the age-depth relationship as described by Hetier et al. (1983) is minimal. The horizon sequence can be summarized as Ah1 - Ah2/Bw - 2Ahb - 2Bwsb - 2BCb, common for Andosols (Shoji et al. 1993). The forest profiles in addition have organic horizons (a forest floor) overlying the mineral horizons. All soils show a multisequum, containing at least 1 paleosol. Roots concentrate in the first Ah horizon of the páramo soils and in the relatively nutrient-rich organic horizons of the forest soils.

^{14}C Ages of HA and Humin in Andosols

The results of ^{14}C dating of the HA and humin fraction of soils collected in the Eastern and Western cordilleras of northern Ecuador are presented in Table 3 and Figure 2. The δ^{13}C values (Table 3) indicate a dominant C3 vegetation, which is to be expected in a humid, cold climate. Humic acid and humin contributed equal proportions (both ~30% organic carbon, data not shown) to the total bulk soil organic carbon, underlining that the impact of contamination of either fraction on bulk SOM age will be considerable.

The HA fraction was significantly ($p = 0.001$) older than the humin fraction, except for the mineral soil samples just beneath a forest floor, where the opposite was found. The difference between the ^{14}C ages of the fractions (hereafter referred to as "age difference") can be used as a measure of contamination with younger material (e.g. by roots). The absolute age difference ranges from 33 ^{14}C yr to 995 ^{14}C yr and increases significantly with increasing ^{14}C age ($r = +0.85$, $p = 0.000$ with ^{14}C age HA and $r = +0.79$, $p = 0.001$ with ^{14}C age humin; mineral soil samples just beneath a forest floor excluded). The ^{14}C age increases significantly with depth for both fractions ($r = +0.93$ with ^{14}C age HA and +0.94 with ^{14}C age humin, both with $p = 0.000$, modern samples excluded).

Contamination with roots may well explain the observed younger ^{14}C ages of humin. Although the humin fraction is often considered as the OM fraction containing the most resistant and immobile organic molecules (Pessenda et al. 2001; Stevenson 1994), some authors report that it is also the fraction that is rejuvenated considerably by the inclusion of relatively young roots (Orlova and Panychev 1993). In accordance, Nierop et al. (1999) and Nierop and Buurman (1999) demonstrated with pyrolysis-gas chromatography/mass spectrometry (GC/MS) that organic molecules of fresh roots accumulate in the humin fraction. The larger age differences with older ^{14}C ages may be explained by the prolonged exposure to contamination by roots. Additionally, the rejuvenating impact of fresh roots is higher on samples with low ^{14}C activity than on samples with high ^{14}C activity (Mook and van de Plassche 1986).

However, how accurate are the ^{14}C ages of the HA fractions? It is highly unlikely that HA is mobile in the mineral part of Andosols because of the high metal/SOM ratio combined with the very low pH in these soils. Therefore, contamination by illuviation of younger HA is negligible. In addition, undisturbed Andosols show strong resistance to water erosion due to rapid rainfall infiltration and high aggregate resistance to dispersion (Shoji et al. 1993). In the field, we did not observe signs of erosion or deposition on our sites. Hence, deposition of allochtonous OM is not expected to have a dominant influence. Some earthworm species are known to burrow up to 1 m depth (Lee and Foster 1991) and Barois et al. (1998) observed earthworm casts up to 60 cm depth in Mexican Andosols at 3100 m asl (mean annual temperature 5–10 °C and pH KCl at 20 cm soil depth = 4.6). However, the

Table 2 Selected soil properties for the Andosols (mean and standard deviations calculated if at least 2 samples were taken within the horizon at different depths).

Site	Horizon[a]	Depth (cm)	Bulk density (g cm^{-3})	C_{total} (%)	pH $CaCl_2$	Roots[b]
G7	O	0–1	n.d.	n.d.	4.4	n.d.
	Ah1	1–40	0.35	18.20 ± 2.7	4.0 ± 0.1	common v.f., few f., very few m.
	Ah2	40–70	0.42 ± 0.0	13.07 ± 0.6	4.3 ± 0.0	few v.f., very few f.
	2Ahb	70–130	0.36 ± 0.0	17.62 ± 2.9	4.2 ± 0.1	few v.f., very few f.
	2Bw1b	130–147	0.71	5.30	4.6	few v.f., very few f.
	2Bws2b	147–150	n.d.	n.d.	n.d.	n.o.
	2BC3b	150–170+	0.93	0.38	5.4	n.o.
G5a	O1	0–1	n.d.	n.d.	3.9	n.d.
	O2	1–35	0.10	50.11 ± 0.2	2.5 ± 0.1	common v.f. to f., few m., very few c.
	Ah	35–75	0.45 ± 0.0	15.58 ± 3.0	3.9 ± 0.3	very few v.f. to c.
	Bw	75–105	0.57 ± 0.0	9.51 ± 0.9	4.2 ± 0.0	very few v.f. to m.
	2Ah1b	105–125	0.48	13.34	4.1	very few v.f. to f.
	2Ah2b	125–140	0.44	12.46	4.1	very few v.f. to f.
	2Ah3b	140–175	0.42	12.01	4.3	very few v.f. to f.
	2Bsw1b	175–177	n.d.	n.d.	n.d.	n.o.
	2BC2b	177–190+	0.92	0.35	5.1	n.o.
G5b	O	0–1	n.d.	n.d.	4.1	n.d.
	Ah	1–45	0.37 ± 0.1	17.71 ± 3.7	4.1 ± 0.2	common v.f., few f., very few m. to c.
	Bw1	45–70	0.54	9.15	4.4	few v.f., very few f.
	Bw2	70–115	0.57 ± 0.0	8.48 ± 0.6	4.4 ± 0.0	few v.f., very few f.
	2Ahb	115–175	0.48 ± 0.1	10.92 ± 1.0	4.3 ± 0.1	very few v.f. to f.
	2Bw1b	175–192	0.61	7.13	4.6	n.d.
	2Bws2b	192–194	n.d.	n.d.	n.d.	n.o.
	2BC3b	194–200+	0.94	0.29	5.2	n.o.
A7a	O1	0–1	n.d.	n.d.	3.8	n.d.
	O2	1–5	n.d	42.87	3.7	many v.f. to f., common m., very few c.
	Ah1	5–40	0.42 ± 0.1	20.21 ± 6.6	3.7 ± 0.4	few v.f. to f., very few m.
	Ah2	40–80	0.51 ± 0.1	9.45 ± 2.1	4.2 ± 0.1	few v.f. to f., very few m.
	2Ahb	80–165	0.41 ± 0.0	13.90 ± 2.1	4.2 ± 0.1	very few v.f. to f.
	2ABb	165–175	0.66	5.60	4.5	n.o.
	2BCb	175–195+	0.97	0.70	5.2	n.o.
A7b	O	0–1	n.d.	n.d.	4.6	n.d.
	Ah1	1–25	0.43	16.97	4.1	common v.f. to f., few m., very few c.
	Ah2	25–70	0.52 ± 0.1	9.21 ± 1.6	4.5 ± 0.1	few v.f. to f. and very few m.
	2Ahb	70–135	0.40 ± 0.0	14.61 ± 2.1	4.3 ± 0.0	few v.f. to f. and very few m.
	2ABb	135–155	0.66	6.43	4.7	very few v.f. to f.
	2BCb	155–177	0.99	0.78	5.2	n.o.

[a] Horizons named according to FAO guidelines (1990); horizons sampled for ^{14}C analysis indicated in bold.

[b] As described in the field according to FAO guidelines (1990): v.f. = very fine roots; f. = fine roots; m. = medium roots; c. = coarse roots; n.d. = not determined; n.o. = not observed.

Table 3 ^{14}C ages (BP) and ^{13}C (‰) values of HA and humin in the Andosols.

			Humic acid			Humin		
Site	Horizon	Sample depth (cm)	CIO code GrA-	^{14}C age[a] (BP)	^{13}C (‰)	CIO code GrA-	^{14}C age[a] (BP)	^{13}C (‰)
G7	Ah1	10.0–10.5	28130	180 ± 35	–25.24	28117	45 ± 35	–25.67
G7	Ah2	46.5–47.0	28134	1690 ± 40	–25.22	28131	1405 ± 35	–25.66
G7	2Ahb	89.5–90.0	28126	4910 ± 45	–24.98	28135	4130 ± 40	–25.47
G5a	F	14.5–15.0	30109	–623 ± 35 (108.1 ± 0.4)	–27.46	30108	–656 ± 35 (108.5 ± 0.4)	–28.83
G5a	F	34.0–34.5	30112	–28 ± 35 (100.4 ± 0.4)	–26.39	30110	–218 ± 35 (102.8 ± 0.4)	–26.93
G5a	Ah	45.0–45.5	28102	490 ± 35	–25.67	28101	775 ± 35	–25.93
G5a	Bw	84.5–85.0	28104	2170 ± 35	–25.92	28103	2005 ± 35	–26.56
G5a	2Ah1b	114.5–115.0	28108	4355 ± 40	–25.10	28106	3360 ± 35	–26.13
G5b	Ah	14.5–15.0	30138	590 ± 35	–25.33	30136	425 ± 35	–25.69
G5b	Ah	34.5–35.0	28111	1350 ± 35	–25.45	28109	1270 ± 35	–26.08
G5b	Bw2	75.0–75.5	28113	3465 ± 35	–25.51	28112	2615 ± 35	–26.09
G5b	2Ahb	124.5–125.0	28116	5730 ± 40	–24.91	28115	4945 ± 40	–25.16
A7a	Ah1	30.0–30.5	28129	445 ± 35	–26.08	28127	555 ± 35	–25.95
A7a	Ah2	64.5–65.0	30153	2050 ± 35	–25.24	30154	1505 ± 35	–24.94
A7a	2Ahb	99.5–100.0	28140	4715 ± 40	–24.17	28139	3930 ± 40	–24.56
A7b	Ah1	15.0–15.5	28144	595 ± 35	–24.68	28141	310 ± 35	–25.02
A7b	Ah2	54.5–55.0	28146	2540 ± 40	–25.15	28145	2320 ± 35	–25.60
A7b	2Ahb	85.0–85.5	28149	4060 ± 45	–24.55	28147	3470 ± 40	–24.95

[a] For samples with measured activities higher than the standard, the ^{14}C ages expressed in BP are negative numbers. In these cases, we also show the activity ratios in %.

strong correlation between age and depth in the studied soils indicates that bioturbation did not homogenize SOM at the scale of the applied vertical sampling distances. We thus conclude that the ^{14}C ages of the HA fractions are more accurate than the ^{14}C ages of the humin fractions for all samples except the mineral soil samples just beneath a forest floor.

Two factors may explain the younger ^{14}C age of HA compared to that of humin in the mineral soil samples just beneath a forest floor. Firstly, contrary to the mineral horizons, HA may be mobile in the organic horizons overlying them in the forest. Upon entering the mineral horizon these younger mobile HA form complexes with the abundant metals in Andosols (Al and Fe) and become immobile. Consequently, the ^{14}C age of the HA fraction in that mineral topsoil is lowered. Secondly, roots concentrate in the relatively nutrient-rich organic horizons rather than in the mineral horizons (Table 2), resulting in less contamination of the humin fraction of the mineral horizon. Accordingly, in the organic horizon, HA was again older than or of equal age as humin. Possibly, mobile (younger) HA disappears from the organic horizons by leaching while the residual HA remains immobile and uncontaminated. We therefore conclude that in the mineral soil samples just beneath a forest floor, the humin fraction is more accurate for dating, if roots are removed adequately. In the organic horizons themselves, HA still seems more accurate for dating, but more data is necessary to support this conclusion.

Páramo fires are common in the northern Andes (Ramsay and Oxley 1996; Hofstede 1995; Laegaard 1992), and they may occur even in protected areas. Fire can cause complex transformations within the humic substances, e.g. from FA to HA and from HA to humin and black carbon (Gonzalez-Perez et al. 2004). Since the original humic substances may differ in ^{14}C age, such fire-induced

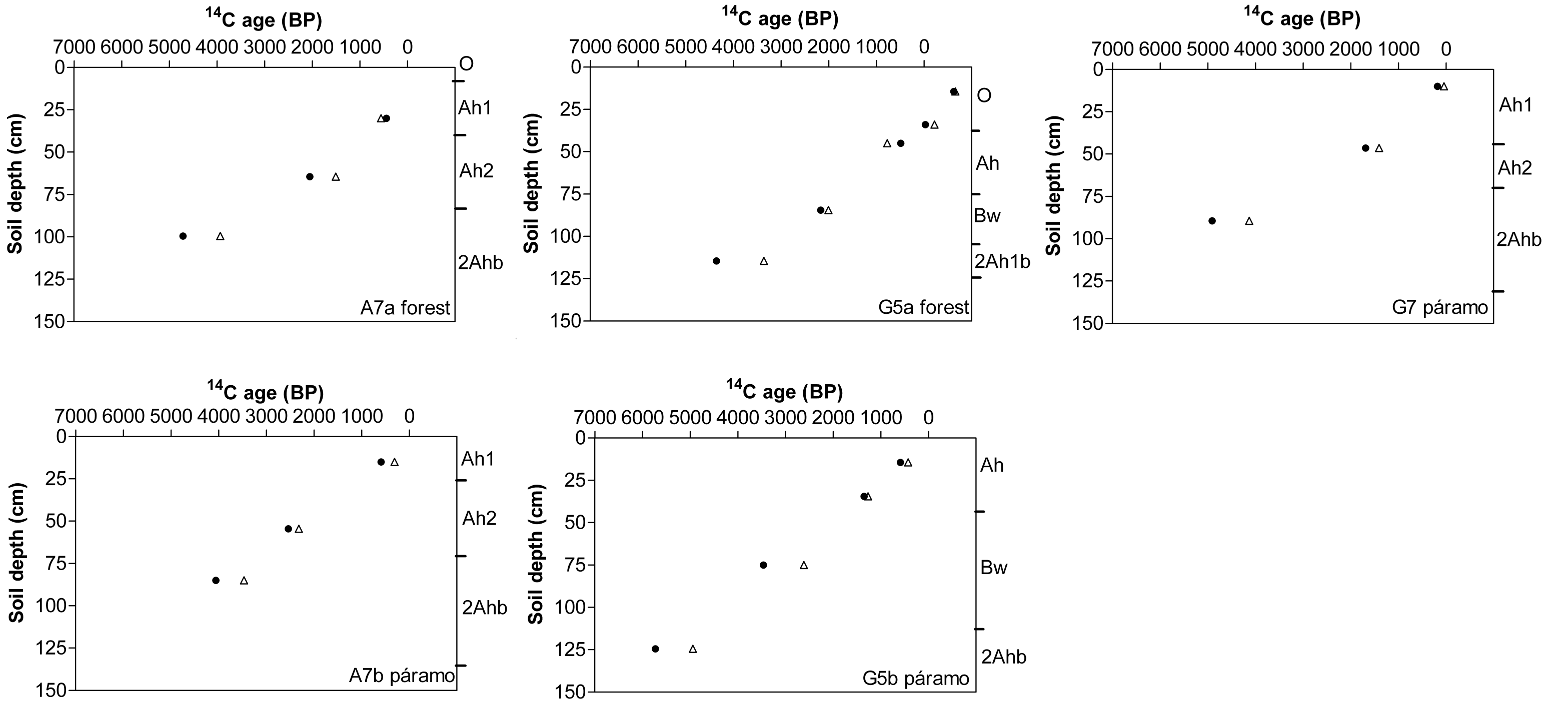

Figure 2 ^{14}C age (BP) and location of the sample in the soil profile, showing that the ^{14}C age of HA is generally older than the ^{14}C age of humin and that the age difference increases with depth. ● = humic acids; △ = humin.

transformations could contaminate the measured ^{14}C age of a specific OM fraction. However, transitions due to fire are much less if OM is complexed with metals or minerals (Gonzalez-Perez et al. 2004) as is the case in Andosols. Furthermore, during a páramo fire, soil temperatures 2 cm below ground remain relatively low, not exceeding 65 °C (Ramsay and Oxley 1996), making such transitions unlikely (Gonzalez-Perez et al. 2004). Therefore, we regard the contaminating effect of fire on ^{14}C age as minimal.

Our results show that *both* HA and humin can be used for ^{14}C dating, but the accuracy of either depends on, for example, soil properties and vegetation type, stressing the necessity for tailor-made research. Additionally, the ^{14}C ages of both HA and humin remain an average, influenced by the continuous input of fresh OM (Wang et al. 1996), and must thus be interpreted as minimum ages.

^{14}C Ages of HA and Humin in Peat

The results of ^{14}C dating of the HA and humin fraction of peat, collected in the Eastern and Western cordilleras of northern Ecuador, are presented in Table 4. The δ^{13}C values in Table 4 are those of a C3 vegetation, which is to be expected in peat.

Table 4 ^{14}C ages (BP) and ^{13}C (‰) values of HA and humin of the peat sequences.

		Humic acid			Humin		
Site	Sample depth (cm)	CIO code GrA-	^{14}C age (BP)	^{13}C (‰)	CIO code GrA-	^{14}C age (BP)	^{13}C (‰)
G8	146.0–147.0	28093	2110 ± 35	–25.19	28092	2110 ± 35	–25.30
G8	196.0–197.0	28097	6075 ± 40	–24.95	28095	5980 ± 40	–25.11
G8	246.0–247.0	28099	8010 ± 50	–25.06	28098	8290 ± 50	–24.92
A11	100.0–101.0	28057	1640 ± 35	–26.20	28055	1610 ± 35	–26.33
A11	160.0–161.0	28059	3450 ± 35	–26.06	28058	3330 ± 35	–26.21
A11	222.0–222.5	28082	7515 ± 45	–26.53	28081	7625 ± 45	–26.89
A2	66.0–66.5	28086	290 ± 35	–26.96	28083	185 ± 35	–26.46
A2	176.5–177.0	28088	1500 ± 35	–27.42	28087	1525 ± 35	–26.58
A2	290.0–290.5	28091	2630 ± 35	–26.78	28089	2940 ± 35	–26.46

Contrary to the soils, the difference between the ^{14}C ages of HA and that of humin is generally small and not significant ($p = 0.459$), although Shore et al. (1995) demonstrated that large age differences (up to 1210 ^{14}C yr) between these fractions can exist in peat samples. Several factors explain the similarity in ^{14}C ages of the humic substances in peat. Firstly, bioturbation is of minor importance. Secondly, the time span of contamination with roots is limited due to the continuous shifting upwards of the active rooting zone during OM accumulation (peat growth). Additionally, the depth of the top samples (varying from 60 cm to 150 cm) is probably already beyond the currently active rooting zone. Finally, although HA mobility cannot be ruled out, its vertical movement may be limited in stagnant water.

Only in 2 cases (GrA-28099 and -28091) was the age difference somewhat larger, the differences amounting to 310 and 280 ^{14}C yr, respectively, and humin rendering older ages. These age differences are small compared to the differences occurring in the soils (differences up to 995 ^{14}C yr) as well as compared to the differences reported by Shore et al. (1995) for peat sequences (differences up to 1210 ^{14}C yr). Currently, we have no information on the basis of which we can explain the somewhat larger differences for the 2 samples; therefore, we treat our samples as 1 statistical population and regard the differences as not significant.

Our results show that ^{14}C ages of both HA and humin are equally accurate for the peat bogs, although ages are still averages and should be interpreted as a minimum (Wang et al. 1996). However, in the active rooting zone the humin ages may become less accurate due to contamination by fresh roots.

SOM Age-Depth Relationship in Andosols

To evaluate if the chronostratigraphy of SOM in the studied Andosols is suitable for paleoecological research such as the reconstruction of the natural UFL, we investigated the relationship between age and depth. Calibrated ^{14}C ages and depth are shown in Table 5. We used the calibrated ^{14}C ages of HA for the age-depth relationship in all cases, except for the mineral soil samples just beneath a forest floor, where we used calibrated ^{14}C ages of humin instead. There are no age inversions and no signs of homogenization at the applied sampling distances (see Table 5).

Table 5 Calibrated ^{14}C ages (range and mean, year AD/BC) of the Andosols.

			Calibrated age[a]	
Site	Horizon	Sample depth (cm)	Range (cal AD/BC)	Mean (cal AD/BC)
G7	Ah1	10.0–10.5	cal AD 1761–1789	cal AD 1775
G7	Ah2	46.5–47.0	cal AD 329–407	cal AD 368
G7	2Ahb	89.5–90.0	cal BC 3712–3643	cal BC 3678
G5a	F	14.5–15.0	cal AD 1996–2002	cal AD 1999
G5a	F	34.0–34.5	cal AD 1956–1957	cal AD 1957
G5a	Ah	45.0–45.5	**cal AD 1247–1271**	**cal AD 1259**
G5a	Bw	84.5–85.0	cal BC 352–293	cal BC 323
G5a	2Ah1b	114.5–115.0	cal BC 3015–2944	cal BC 2980
G5b	Ah	14.5–15.0	cal AD 1311–1359	cal AD 1335
G5b	Ah	34.5–35.0	cal AD 648–682	cal AD 665
G5b	Bw2	75.0–75.5	cal BC 1780–1740	cal BC 1760
G5b	2Ahb	124.5–125.0	cal BC 4614–4515	cal BC 4565
A7a	Ah1	30.0–30.5	**cal AD 1392–1418**	**cal AD 1405**
A7a	Ah2	64.5–65.0	cal BC 105–29	cal BC 67
A7a	2Ahb	99.5–100.0	cal BC 3430–3378	cal BC 3404
A7b	Ah1	15.0–15.5	cal AD 1309–1361	cal AD 1335
A7b	Ah2	54.5–55.0	cal BC 797–760	cal BC 779
A7b	2Ahb	85.0–85.5	cal BC 2634–2562	cal BC 2598

[a] Ages derived from humin ^{14}C age instead of humic acid ^{14}C age are depicted in bold.

Since we measured only a few samples per soil profile, we performed linear regressions on the relationship between calibrated age and depth for all soils grouped together, for the soils grouped according to cordillera (Eastern or Western), and for the soils grouped according to current vegetation type (forest or páramo). Therefore, our linear regressions cannot be used to interpolate dates in between measured dates for a given soil profile. However, they can be used to evaluate whether rates of SOM accumulation differ between the cordilleras and between current vegetation types. Shoji et al. (1993) stressed the influence of vegetation on Andosol formation. Results of all linear regressions are presented in Table 6 and the linear regressions according to cordillera are additionally shown in Figure 3. Because of the different nature of the forest floor, we excluded the organic samples from the regressions, but the samples are included in the figures. All these linear regressions have a good fit ($R^2 \geq 0.85$) and a narrow confidence interval (CI). However, Telford et al. (2004) demonstrated that, when the data set is small, no age-depth model provides a good fit to reality and that calculated confidence intervals are too optimistic.

Table 6 Linear regressions of SOM age-depth relationships of the Andosols, showing that the 95% confidence intervals of the slopes are overlapping.

Group	*Y* intercept (cm)	*X* intercept (cal AD)	Slope[a] ± 95% CI	R^2	n[b]
All soils	49.77 ± 3.645	3135	–0.01588 ± 0.00358	0.87	16
Western Cordillera	47.57 ± 4.606	3097	–0.01536 ± 0.00657	0.91	6
Eastern Cordillera	51.16 ± 5.462	3186	–0.01606 ± 0.00544	0.85	10
Forest	62.95 ± 5.647	4292	–0.01467 ± 0.00781	0.87	6
Páramo	41.78 ± 2.461	2515	–0.01661 ± 0.00248	0.97	10

[a] Slope deviates significantly from zero ($p < 0.005$).

[b] Samples from organic horizon excluded from regressions.

The general increase of age with depth (slopes deviate significantly from zero) gives rise to 2 possible scenarios concerning the development of the current soil profile. The first scenario assumes that the current soil consists of only 1 tephra deposit. The observed age-depth relationship can then be explained by continuous burying of OM by younger OM much like in a peat bog. This scenario is possible with and without (shallow) bioturbation, because the zone of active bioturbation could shift upwards during SOM accumulation, resulting in a crude stratification. If bioturbation is present, a step-like curve would appear (for individual soil profiles) when applying smaller sampling distances. The second scenario assumes that the current soil consists of multiple tephra depositions. SOM is then intermittently buried by tephra, and the sedimentation rate mainly determines the age-depth relationship. Again, this scenario is possible with and without (shallow) bioturbation.

The slopes of the linear regressions for both cordilleras were surprisingly uniform (overlapping confidence intervals), suggesting that rates of tephra deposition and SOM incorporation have been similar. The similarity (overlapping confidence intervals) of the slopes according to vegetation type shows that the current vegetation type did not strongly influence the vertical OM distribution in the mineral horizons at the applied sampling distances. However, during soil profile development vegetation could have been different from today. The most notable influence of the current vegetation on soil profile development is the development of organic horizons (dated < cal AD 1957) in the forest. Although we did not include the organic samples in the regression, it is clear that the age-depth relationship in this layer is different, according to expectations. Additionally, the *y* intercept of the linear regression of the forest soils (mineral horizons) is located at somewhat greater depth than the *y* intercepts of the other regressions as a result of the relatively voluminous organic horizons.

Changes in SOM quantity due to fire may affect soil bulk density and therefore the age-depth relationship. However, Hofstede (1995) demonstrated that soil bulk density was not measurably affected by fire alone in Colombian páramos. As mentioned earlier, the dry bulk densities in the studied soils were similar for all samples. Additionally, the linear regressions of the age-depth relationship were similar for both cordilleras and similar for the current vegetation types, giving no reason to suspect that probable differences in, for example, fire frequency between cordilleras or vegetation types caused changes in the age-depth relationship.

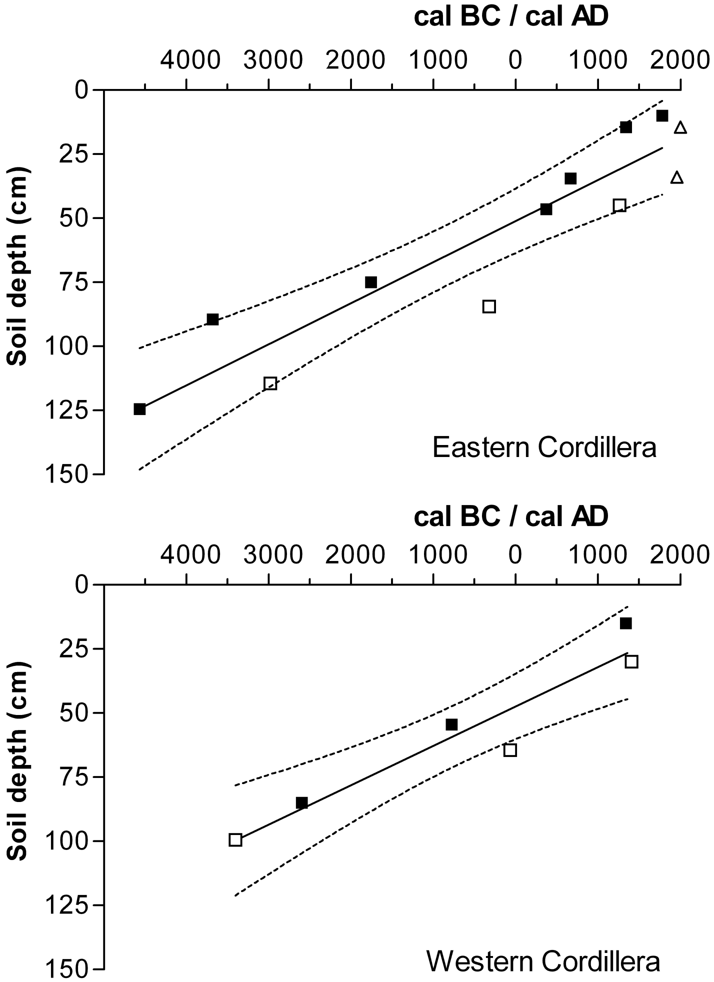

Figure 3 Age-depth relationships for the Eastern Cordillera and Western Cordillera; 95% confidence interval (dashed lines) of linear regression (solid line) included. Regression equations presented in Table 6. ■ = páramo; □ = forest (mineral soil samples); △ = forest (organic samples).

We conclude that the chronostratigraphy of the studied Andosols is very promising for use in paleoecological reconstructions, but more research concerning the tephra stratigraphy is necessary to explain the observed age-depth relationship. The presence of (shallow) bioturbation cannot be ruled out. We recommend applying higher resolution dating of the soil profiles to enable interpolation between dates.

Comparison of Time Frame Soils and Peat Sequences

Calibrated ^{14}C ages (of HA) of the peat cores are reported in Table 7. The calibrated ^{14}C ages of the Andosols were discussed in the previous section. Both the current soils (at least up to 1760 cal BC) and the paleosols (at least up to 4565 cal BC) were found to be of Holocene age. The time frames must be considered as a minimum because we did not date the exact events of tephra deposition or the base of the paleosol. Poulenard et al. (2003) reported similar ^{14}C ages of the bulk SOM fraction

<50 μm of soils in northern Ecuador and dated the base of the paleosol to at least 7838 BP (~6683 cal BC). Similarly, the 3 peat bogs are all of Holocene age, enabling verification of pollen records from soil by comparing them to pollen records from peat bogs. To enhance comparison, the tephra stratigraphy of the peat bogs should ideally be linked to the tephra stratigraphy of the soils. The peat sequences of Guandera and El Angel cover a larger time span (at least up to 6941 cal BC) than the peat of Los Encinos (at least up to 809 cal BC). This independent evidence supports the time frame we report for the studied Andosols.

Table 7 Calibrated ^{14}C ages (range and mean, year AD/BC) of the peat sequences.

		Calibrated age	
Site	Sample depth (cm)	Range (cal AD/BC)	Mean (cal AD/BC)
G8	146.0–147.0	cal BC 180–91	cal BC 136
G8	196.0–197.0	cal BC 5041–4939	cal BC 4990
G8	246.0–247	cal BC 6882–6827	cal BC 6855
A11	100.0–101.0	cal AD 379–434	cal AD 407
A11	160.0–161.0	cal BC 1776–1734	cal BC 1755
A11	222.0–222.5	cal BC 6438–6363	cal BC 6401
A2	66.0–66.5	cal AD 1522–1577	cal AD 1550
A2	176.5–177.0	cal AD 542–603	cal AD 573
A2	290.0–290.5	cal BC 820–797	cal BC 809

CONCLUSIONS

Our results show that in Andosols, ^{14}C dating of the HA fraction renders more accurate results than ^{14}C dating of the humin fraction, except for mineral soil samples just beneath a forest floor, where the opposite holds true. These results demonstrate that the accuracy of the ^{14}C age of a specific OM fraction depends on, e.g., soil properties and vegetation, underlining the necessity of tailor-made ^{14}C dating of soils. In the peat sequences, both OM fractions yield accurate results. The chronostratigraphy of SOM in the studied Andosols appears to be suitable for paleoecological research such as reconstruction of the natural position of the UFL, because age inversions and homogenization were lacking at the applied vertical sampling distances and age increased with depth. However, higher resolution dating of the soil profiles and more research concerning the tephra stratigraphy is necessary to be able to interpolate dates using the age-depth relationship. The time frame covered by the studied Andosols is similar to that of peat sequences nearby, enabling verification of the soil pollen records. With this research, we made an indispensable first step towards reconstruction of the natural position of the UFL in northern Ecuador.

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