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Soils in the southern Brazilian highlands: genesis, soil organic matter composition, and relations to vegetation history

Alexander Bruno Dümig

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SUMMARY

Soils in the highlands of north-eastern Rio Grande do Sul (Brazil) show dark-coloured topsoils which are light and very rich in organic matter. They are distributed in a mosaic of grassland, deciduous forest with the conifer *Araucaria angustifolia* and several anthropogenic vegetation forms. The climate is humid and temperate without marked dry periods.

The objectives of this study were (1) to identify the relationships between vegetation mosaic and soil properties, (2) to reconstruct the vegetation history, (3) to investigate if the composition of soil organic matter is associated with vegetation changes and (4) to characterise lignin sources and to evaluate if lignins contribute to ^{13}C depletion in grassland soils.

Twenty-seven soils were characterized and classified to investigate the relationships between present and past vegetation pattern and soil properties. All soils are strongly acidic with high clay contents, low bulk densities and most of them show high phosphate retentions. X-ray diffraction indicates the presence of quartz, kaolinite, secondary chlorite and gibbsite. Selective extractions with pyrophosphate (p), dithionite-citrate-bicarbonate (d) and acid oxalate (o) give in most horizons the following relationships: $Fe_d > Fe_p > Fe_o$ and $Al_p > Al_d > Al_o$. Despite the possible Al release from gibbsite, the high Al_p concentrations were attributed mainly to high amounts of Al humus complexes. The absence of allophane and imogolite was confirmed by the very low Si_o and Si_d concentrations. 21 soils have andic properties according to World Reference Base for Soil Resources (WRB) (IUSS Working Group WRB, 2006) at least for some depth range, 15 of them fulfil the minimum thickness and depth requirements of Andosols. They belong to the aluandic type and are the first detected Andosols in South America outside the areas of recent volcanism in the Andes. The other soils are Umbrisols (11) and Cambisols (1). In grassland soils, andic properties start at or near the soil surface, in forest soils they are only present in subsurface layers, especially in buried A horizons. The latter differ from their actual topsoils by some characteristics which they have in common with the grassland soils like deep black colours and low melanic indexes. This may indicates that Araucaria forest expanded on grassland. In this environment a grass vegetation seems to favour formation and permanence of Andosols whereas a change into forest starts a process of losing andic properties. Most soils without andic properties or with andic properties of insufficient thickness only fail the required minimum concentrations of Al_o and Fe_o. On the other hand, they all show similar concentrations of Al_d and Fe_d. Therefore, the loss of andic properties with forest proliferation is caused by crystallization of Al and Fe oxides which seems to be easier under forest.

It was uncertain, whether the grasslands (C_4) represent relics of drier periods in the Holocene or if they are the result of Araucaria forest (C_3) deforestation in recent times. Thus, plant tissues from gramineous and woody species, organic surface layers, as well as soil organic matter of 13 Andosols and Umbrisols in grassland, shrubland, pine plantations and *Araucaria* forest were analyzed for stable carbon isotope ratios ($\delta^{13}C$) and ^{14}C activity. The soil organic matter was separated into a free light organic matter (LF) and a heavy, organo-mineral fraction by density fractionation. All grassland soils have consistently $\delta^{13}C$ values of -18.7 to -14.3 ‰ typical for C_4 grasses. In *Araucaria* forests and forest patches within grassland the $\delta^{13}C$ values of both, the LF throughout the soil and the organic surface layers, are characteristic for the present below- and above-ground input from C_3 trees. The C_3- and C_4-derived SOC stocks reflect expansion of *Araucaria* forest on grassland, which started after 1300 yr BP. The youngest forests are found at the forest border and in forest patches. Grassland soils lose their typically black colour from the top downwards after shrub encroachment or establishment of forest as indicated by increasing melanic indexes which are closely related to the $\delta^{13}C$ values. The natural ^{13}C depletion with depth in grassland soils counteracts the enrichment of ^{13}C in the subsoils of present *Araucaria* forest. The results clearly indicate that current grasslands represent relics at least from the early and mid Holocene period (6000 – 8000 yr BP) and are not the result of recent deforestation. The heavy organo-mineral fractions were grouped according to source vegetation by using the $^{13}C/^{12}C$ isotopic signature to investigate if *Araucaria* forest (C_3) expansion on frequently burned grassland (C_4) is linked to the chemical composition of soil organic matter (SOM). ^{13}C NMR spectroscopy, lignin analyses (CuO oxidation) and measurement of soil lightness was used to characterise their chemical compositions. Large proportions of aromatic C combined with low contents of lignin-derived phenols in the heavy fractions of grassland soils (C_4) and grass-derived lower horizons of *Araucaria* forest soils (C_3) indicate the presence of charred grass residues in SOM. The contribution of this material may have led to the uncommon increase of C/N ratios with depth in burned grassland soils and to the differentiation of C_3- and C_4-derived SOM, because heavy fractions from unburned Araucaria forest and shrubland soils have lower proportions of aromatic C, lower C/N ratios and are less dark compared to those with C_4 signature. Lignins are not applicable as biomarker for plant origin in these soils as the aboveground plant-specific lignin patterns are absent in heavy fractions. In contrast, the characteristic contents of alkyl C and O/N-alkyl C of C_3 trees or shrubs and C_4 grasses are reflected by heavy fractions. They show consistent changes of the (alkyl C)/(O/N-alkyl C) ratio and the $^{13}C/^{12}C$ isotopic signature with soil depth indicating their association with C_4 and

C_3 vegetation origin. This study demonstrates that soils may preserve organic matter components from earlier vegetation and land use indicating that the knowledge of past vegetation covers is necessary to interpret SOM composition.

Compound-specific gas chromatography-combustion-isotope-ratio mass spectrometry (GC/C-IRMS) was applied in combination with alkaline CuO oxidation to determine the stable isotope composition of lignin-derived phenols in heavy organo-mineral fractions from topsoils under Araucaria forest (C_3) and grassland (C_4). Our objectives were to characterise lignin sources and to evaluate if the prevailing ^{13}C depletion in grassland soils could be related to lignin preservation in the organo-mineral fraction. Total organic carbon and lignins show consistent isotopic differences between C_4 grassland and C_3 forest soils. Lignins of plants and heavy organo-mineral fractions are isotopically lighter relative to total organic carbon. The ^{13}C depletion of C_4 grassland soils may therefore be explained by lignin preservation in the organo-mineral fraction. In contrast, forest soils show prevailing enrichment of ^{13}C from plant to the upper mineral soil as the extent of ^{13}C enrichment is markedly larger compared to C_4 grasslands when comparing roots with leaves and lignins from heavy fractions with those of aboveground plant inputs. Lignins of C_3- and C_4-derived heavy fractions have higher $\delta\ ^{13}C$ values compared to lignins of the respective aboveground plant litter. For total organic carbon, similar ^{13}C enrichments show roots from grasses and trees compared to aboveground plant litter. Thus, the data suggest that roots may be the principal lignin source in mineral soil.

Overall, the results of this investigation are important contributions for a better understanding of vegetation history in the southern Brazilian highlands. This was achieved by characterising soil organic matter, especially by the combined evaluation of the chemical composition and the carbon isotope signatures. In addition, this study revealed that the formation and permanence of nonallophanic Andosols is related to grass vegetation, whereas Araucaria forest establishment results in the development of Umbrisols and the loss of andic properties.

ZUSAMMENFASSUNG

Die Landschaft im subtropischen Hochland von Rio Grande do Sul (Brasilien) wird von einem mosaikartigen Wechsel von Grasland und Laubwald mit der Konifere *Araucaria angustifolia* bestimmt. Die Böden entwickelten sich aus Rhyodazit und wurden durch ihre schwarzen und sehr humusreichen Oberböden bisher als Humic Cambisole oder Leptosole eingestuft. Diese Arbeit hatte als Ziel, (1) die Beziehungen zwischen Vegetationsmuster und Bodeneigenschaften zu identifizieren, (2) die Vegetationsgeschichte zu rekonstruieren, (3) den Einfluss von Vegetationswechsel auf die chemische Zusammensetzung der organischen Bodensubstanz zu untersuchen und (4) die Herkunft von Lignin in Böden und dessen Bedeutung für den Verlauf der $^{13}C/^{12}C$ Isotopensignatur festzustellen.

Es wurden 27 Böden unter Weideland (2), ungenutztem Grasland mit und ohne Sträucher (9), Araukarienwald (12), Buschland (2) und Kiefernplantage (2) charakterisiert, um die Zusammenhänge zwischen Vegetationsmuster und chemischen, physikalischen und morphologischen Bodeneigenschaften zu untersuchen. Alle Böden zeigen eine saure Bodenreaktion, hohe Tongehalte, geringe Lagerungsdichten und die meisten haben hohe Phosphatretentionen. Der Mineralbestand setzt sich zusammen aus Quartz, Kaolinit, sekundärem Chlorit und Gibbsit. In den meisten Horizonten ergaben sich aus den Extraktionen mit Pyrophosphat (p), Dithionit-Citrat-Bicarbonat (d) und Oxalat (o) folgende Beziehungen: $Fe_d > Fe_p > Fe_o$ und $Al_p > Al_d > Al_o$. Trotz der möglichen Al-Freisetzung aus Gibbsit durch Pyrophosphat weisen die hohen Konzentationen von Al_p auf das Vorherrschen von Al-Humus-Komplexe hin. Die sehr geringen Konzentrationen von Si_o und Si_d zeigen an, dass die Böden keine Allophane und Imogolite enthalten. Das Klassifizieren der 27 Böden nach der World Reference Base for Soil Resources (WRB) (IUSS Working Group WRB, 2006) führte zur erstmaligen Beschreibung von Andosolen (nonallophanic, aluandic) außerhalb der Vulkanregionen der Anden in Südamerika. Die 15 Andosole sind eingebunden in einem Mosaik mit Umbrisolen (11) und einem Cambisol, wobei die meisten Umbrisole in bestimmten Tiefenbereichen ebenfalls andic properties und stets hohe Phosphat-Retentionen aufweisen. Graslandböden zeigen andic properties über größere Tiefenbereiche hinweg und direkt unter oder nahe der Bodenoberfläche, während in Waldböden diese nur in größerer Tiefe, vor allem in begrabenen Ah Horizonten, zu finden sind. Der melanic index der organischen Bodensubstanz lässt Schlussfolgerungen auf deren Herkunft zu, da typischerweise Graslandböden niedrigere Werte aufweisen als Waldböden. Im Gegensatz zu den dunkelbraunen Waldoberböden mit hohem melanic index haben die tieferen und begrabenen Horizonte unter Wald eine ähnliche schwarze Färbung und niedrigen melanic index wie die

Graslandböden. Daher ist zu vermuten, dass andic properties unter Grasland entstanden sind. Die Oberböden im Araukarienwald haben deutlich geringere Gehalte an oxalatlöslichem Al und Fe, sowie niedrigere Phosphat-Retentionen als Oberböden im Grasland. Dagegen sind die Gehalte an dithionit-löslichem Fe ähnlich. Tensiometermessungen der FH Rottenburg zeigten eine bessere Durchlüftung von Waldböden im Vergleich zu den häufiger wassergesättigten Graslandböden an. Dies deutet auf eine höhere Kristallisation von Fe und Al Oxiden in den Waldoberböden hin, während in Graslandböden die Kristallisation gehemmt scheint. Demnach begünstigt Grasvegetation die Bildung und Erhaltung von Andosolen und die Ausbreitung von Araukarienwald ist mit dem Verlust von andic properties verbunden.

Seit der europäischen Kolonisation und der Einfuhr von Rindern im 17. Jahrhundert wurden Araukarienwälder gerodet und in Weideflächen umgewandelt. Von den Araukarienwäldern (C_3) sind mittlerweile nur noch Reste vorhanden. Ohne die Stabilisierung von Grasland (C_4) durch Weide und Feuer würde das immerfeucht-gemäßigte Klima die Waldausbreitung fördern. Es war somit unklar, ob die gegenwärtigen Graslandflächen natürliche Relikte aus einer Zeit trockeneren Klimas sind oder erst seit den Brandrodungen der Kolonisatoren existieren. Zur Rekonstruktion der Vegetationsgeschichte wurde von vorherrschenden Pflanzenarten, organischen Humusauflagen und der organischen Substanz von 13 repräsentativen Böden unter Grasland, Araukarienwald, Buschland und Kiefernplantage die $^{13}C/^{12}C$ Isotopensignatur und die Radiokohlenstoffalter bestimmt. Die Gesamtböden wurden dichtefraktioniert, um das freie und leichte organische Material (LF) von der schweren organisch-mineralischen Fraktion abzutrennen. Die $\delta\ ^{13}C$-Werte von Graslandböden (-18,7 bis -14,3 ‰) sind charakteristisch für organische Bodensubstanz unter C_4-Grasvegetation. Im Araukarienwald zeigen die $\delta\ ^{13}C$-Verhältnisse der leichten Fraktion und der organischen Auflagen den gegenwärtigen ober- und unterirdischen Input von C_3-Bäumen. Der Verlauf der C_3- und C_4-bürtigen Kohlenstoffvorräte mit der Bodentiefe spiegelt die Ausbreitung von Araukarienwald auf Grasland wieder. Nach dem Radiokohlenstoffalter der organischen Bodensubstanz begann die Waldausbreitung vor etwa 1300 Jahren, wobei die jüngsten Wälder am Waldrand und in von Grasland umgebenen Waldinseln zu finden sind. Graslandböden zeigen eine natürliche Verarmung an ^{13}C mit zunehmender Tiefe. Dies wirkt der ^{13}C-Anreicherung von Waldböden in den tieferen Horizonten entgegen, da diese noch alte und unter Grasland entstandene organische Bodensubstanz aufweisen. Die Ergebnisse zeigen deutlich, dass die gegenwärtigen Grasländer Relikte aus dem frühen und mittleren Holozän darstellen (seit 6000 – 8000 Jahren) und nicht durch Rodungen aus der jüngeren Vergangenheit entstanden sind.

Weiterhin wurde untersucht, ob die Ausbreitung von Araukarienwald (C_3) auf häufig gebrannten Graslandböden (C_4) mit einer Änderung der chemischen Zusammensetzung der organischen Bodensubstanz verbunden ist. Hierfür wurden die schweren organisch-mineralischen Fraktionen von acht repräsentativen Böden mittels $^{13}C/^{12}C$ Isotopensignatur nach ihrer Entstehung unter C_4- oder C_3-Vegetation gruppiert. Die chemische Zusammensetzung der organischen Bodensubstanz wurde mit ^{13}C-NMR-Spektroskopie untersucht. Es erfolgte eine Charakterisierung von Lignin (CuO-Oxidation) und die Bestimmung der Bodenhelligkeit (Spektralphotometer). Die schweren Fraktionen von Graslandböden und tieferen Horizonten von Waldböden mit C_4-Signatur zeigen hohe Intensitäten im Aromatenbereich in Verbindung mit geringen Gehalten an lignin-bürtigen Phenolen. Dies weist deutlich auf verbrannte Grasrückstände in der organischen Bodensubstanz hin und erklärt auch die ungewöhnlich ansteigenden C/N-Verhältnisse mit der Bodentiefe in Graslandböden, welche mit dem Aromatengehalt korrelieren. Die häufig gebrannten Graslandböden grenzen sich von nicht gebrannten Böden unter Araukarienwald und Buschland ab, da schwere Fraktionen mit C_3-Signatur geringere Anteile an Aromaten und engere C/N-Verhältnisse aufweisen im Vergleich zu den schweren Fraktionen mit C_4-Signatur. Zudem verfügen schwere Fraktionen mit C_3-Signatur über hellere Bodenfarben als solche mit C_4-Signatur. Oberirdische Pflanzenteile von Gräsern, Sträuchern, Laubhölzern und *Araucaria angustifolia* zeigen eine typische Verteilung an Vanillyl-, Syringyl- und Cinnamyl-Einheiten. Diese pflanzenspezifischen Ligninmuster lassen sich allerdings in den schweren Fraktionen nicht feststellen, wodurch sich die strukturellen Lignineinheiten nicht als Biomarker für die Pflanzenherkunft eignen. Die charakteristischen Unterschiede in den Anteilen an Alkyl-C (überwiegend Lipide) und O/N-Alkyl-C (überwiegend Polysaccharide und Proteine) von Bäumen oder Sträuchern (C_3) und Gräsern (C_4) finden sich auch zwischen den schweren Fraktionen mit C_3- und C_4-Signatur. Die konsistenten Wechsel von (Alkyl-C)/(O/N-Alkyl-C)-Verhältnissen und $^{13}C/^{12}C$ Isotopen-signaturen mit der Bodentiefe zeigen deutlich die Verknüpfung zwischen der chemischen Zusammensetzung der schweren Fraktionen und der Entstehung unter C_4- oder C_3-Vegetation auf. Diese Arbeit stellt heraus, dass organische Komponenten einer früheren Vegetation und Landnutzung in Böden möglicherweise erhalten bleiben. Somit ist die Kenntniss über vergangene Vegetationsbedeckungen notwendig, um die Zusammensetzung der organischen Bodensubstanz beurteilen zu können.

In Kombination mit CuO-Oxidation wurde die substanzspezifische Stabilisotopenanalyse ($\delta\ ^{13}C$) mittels Gaschromatographie-Verbrennungs-Isotopenverhältnismassenspektrometrie

(GC/C-IRMS) angewandt, um die δ ^{13}C-Werte der Ligninphenole in schweren Fraktionen von Oberböden unter Araukarienwald (C_3) und Grasland (C_4) zu bestimmen. Ziel dieser Untersuchung war es, die Herkunft von Lignin zu charakterisieren und festzustellen, ob die Verarmung an ^{13}C in Graslandböden auf die Erhaltung von Lignin in den organisch-mineralischen Fraktionen zurückzuführen ist. Gesamtkohlenstoff und Lignin zeigen übereinstimmende Unterschiede in der ^{13}C/^{12}C Isotopensignatur zwischen Grasland- und Waldböden. Lignin von Pflanzen und schweren Fraktionen ist isotopisch leichter im Vergleich zum Gesamtkohlenstoff. Somit kann die Verarmung an ^{13}C in Graslandböden auf die Konservierung von Lignin in den organisch-mineralischen Fraktionen zurückgeführt werden. Im Gegensatz zum Grasland findet im Araukarienwald eine ^{13}C-Anreicherung der organischen Substanz von Pflanze zum oberen Mineralboden statt. Dies läßt sich durch die Isotopensignatur von Wurzeln erklären, welche deutlich höhere δ ^{13}C-Werte aufweisen als das oberirdische Pflanzenmaterial. Ein ähnlicher Unterschied in der Isotopensignatur läßt sich zwischen Lignin der schweren Fraktionen und Lignin von oberirdischen Pflanzenteilen feststellen. Gräser zeigen für Gesamtkohlenstoff und Lignin ähnliche Tendenzen, aber die Unterschiede im ^{13}C-Gehalt sind wesentlich geringer zwischen ober- und unterirdischen Pflanzenteilen. Die Ergebnisse deuten darauf hin, dass der Ligningehalt der schweren Fraktionen größtenteils aus dem Eintrag von Wurzelstreu stammt und der Unterschied in der ^{13}C/^{12}C Isotopensignatur zwischen ober- und unterirdischen Pflanzenteilen vor allem in Waldböden für den Verlauf der ^{13}C/^{12}C-Isotopensignatur von Bedeutung ist.

Aufgrund der Ergebnisse ergibt sich als Fazit, dass diese Arbeit einen wichtigen Beitrag für das Erfassen der Vegetationsgeschichte im südbrasilianischen Hochland leistet. Die Grundlage hierfür war die Charakterisierung der organischen Bodensubstanz, insbesondere die Bewertung der chemischen Zusammensetzung in Kombination mit der Signatur der stabilen Kohlenstoffisotope. Diese Untersuchung zeigt außerdem, dass die Bildung und Erhaltung von Andosolen an Grasvegetation geknüpft ist, während unter Araukarienwald sich die Böden zu Umbrisolen entwickeln und ihre andic properties verlieren.

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GLOSSARY

$(Ac/Al)_s$	Acid-to-aldehyde ratio of syringyl units
$(Ac/Al)_v$	Acid-to-aldehyde ratio of vanillyl units
Al_d	Dithionite-extractable aluminium
Al_o	Oxalate-extractable aluminium
Al_p	Pyrophosphate-extractable aluminium
AMS	Accelerator Mass Spectrometry
BD	Bulk density
B.P.	Before present
CEC	Cation exchange capacity
CEC_b	Potential cation exchange capacity
CEC_{eff}	Effective cation exchange capacity
C_F	Amounts of soil C derived from *Araucaria* forest
C_G	Amounts of soil C derived from grassland
CPCN	Centro de Pesquisas e Conservação da Natureza
CPMAS	Cross-polarisation magic angle spinning
C_S	Carbon stocks
FAO	Food and Agricultural Organisation of the United Nations
Fe_d	Dithionite-extractable iron
Fe_o	Oxalate-extractable iron
Fe_p	Pyrophosphate-extractable iron
GC/C-IRMS	Gas chromatography-combustion-isotope-ratio mass spectrometry
GC/FID	Gas chromatography-flame ionization detector
HF	Hydrofluoric acid
ICP-OES	Inductively coupled plasma - optical emission spectroscopy
LF	Light fraction
L-value	Lightness value
MI	Melanic index
NIST	National Institute of Standards and Technology
NMR	Nuclear magnetic resonance spectroscopy
OC	Organic carbon

OC_{tot}	Total organic carbon
OM	Organic matter
pmC	Percent modern carbon
P_{ret}	Phosphate retention
S	Content of rock fragments (> 2 mm)
S.D.	Standard deviation
SOM	Soil organic matter
SOC	Soil organic carbon
T	Thickness
TC	Total carbon
V-PDB	International Vienna Pee Dee Belemnite standard
VSC	Sum of CuO-oxidation products (Vanillyl, Syringyl- and Cinnamyl units)
WRB	World Reference Base for soil resources
XRD	X-ray diffraction
$\delta^{13}C_{F\text{-}soil}$	Stable carbon isotope value from *Araucaria* forest soil
$\delta^{13}C_{G\text{-}ref}$	Stable carbon isotope value from the grassland reference soil
$\delta^{13}C_{F\text{-}litter}$	Stable carbon isotope value of *Araucaria* forest litter
$\delta^{13}C_{G\text{-}litter}$	Stable carbon isotope value of grassland residues
$\delta^{13}C_{meas}$	Measured $\delta^{13}C$ value
$\delta^{13}C_4$	$\delta^{13}C$ value for C_4 vegetation
$\delta^{13}C_3$	$\delta^{13}C$ value for C_3 vegetation

1 STATE OF THE ART AND OBJECTIVES

1.1 Occurrence of nonallophanic Andosols

Andosols according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006) have andic or vitric properties. A prerequisite for vitric properties is a minimum content of volcanic glasses. Andic properties show low bulk densities, large variable charge and high phosphate retentions which are linked mainly to the accumulation of various reactive forms of Al in the solid phase. Andic properties are distinguished between allophanic, where Al is present mainly in short range order minerals like allophane or imogolite and nonallophanic, where Al in organic complexes predominates (Shoji and Fujiwara, 1984; Dalhgren and Saigusa, 1994). Both types commonly show considerable amounts of ferrihydrite and a striking accumulation of organic carbon (Shoji et al. 1993) and develop preferentially in volcanic ashes frequently containing certain amounts of glasses (Shoji et al., 1996). However, soils with andic properties which developed from other parent material are reported worldwide (Loveland and Bullock, 1976; Hunter et al., 1987; Garcia-Rodeja et al., 1987; Hewitt & Witty, 1988; Alexander et al., 1993; Bäumler & Zech, 1994; Aran et al., 1998; Caner et al., 2000; Delvaux et al., 2004, Bäumler et al., 2005). Their development was attributed to various types of parent materials and climatic conditions with or without short range order minerals.

For soil classification was applied the second edition of the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006). Compared to the first edition an important alteration is the identification of Andosols by andic or vitric properties instead of andic or vitric horizons. Contrary to a diagnostic horizon, a diagnostic property does not have a minimum thickness, and the thickness requirements are given in the key. This allows to comprise within the Andosols soils with several layers with andic or vitric properties (even interrupted by other layers) which in combination fulfil a thickness requirement. The relevant definitions are given here (IUSS Working Group WRB, 2006): Andic properties require:

1. an Al_{ox} + $½Fe_{ox}$ value of 2.0 per cent or more; *and*
2. a bulk density of 0.90 kg dm^{-3} or less; *and*
3. a phosphate retention of 85 per cent or more; *and*
4. if occurring under *tephric material* that meets the requirements of an *albic* horizon, a C_{py}/OC or a C_f/C_{py} of less than 0.5; *and*
5. less than 25 per cent (by mass) organic carbon.

Criterion 4 is obviously irrelevant for our soils. The other requirements have to be checked.

The definition of the Andosols in the key is:

Other soils having

1. one or more layers with *andic or vitric* properties with a combined thickness of *either*
    a. 30 cm or more within 100 cm of the soil surface *and* starting within 25 cm of the soil surface; *or*
    b. 60 per cent or more of the entire thickness of the soil when *continuous rock* or a cemented or indurated layer starts between 25 and 50 cm from the soil surface; *and*
2. no *argic*, *ferralic*, *petroplinthic*, *pisoplinthic*, *plinthic* or *spodic* horizon (unless buried deeper than 50 cm).

Vitric properties and the entire point 2 do not apply for the soils presented here.

In the highlands occur soils with black-coloured, humus-rich and thick topsoils as similar to Umbrisols or Andosols. They did not develop from volcanic ash but from rhyodacite under humid climate. According to the Brazilian system for soil classification (Bertoletti & Teixeira, 1995; Streck et al., 2002) these soils belong mainly to the order “Cambissolo Bruno Húmico Alumínico”, which indicates acid soils with high saturation of Al (≥ 50 %) and the presence of brown B horizons below humus-rich A horizons. The thickness of A and B horizons varies widely. Some of the soils are ”Neossolos” with an A-C sequence and a thickness < 50 cm. The soils are distributed within a vegetation mosaic of grassland, deciduous forest with *Araucaria angustifolia* and shrubland.

1.2 Soil organic matter composition as indicator of vegetation history

The present vegetation of the southern Brazilian highlands in Rio Grande do Sul State is a mosaic of grassland (C_4) and *Araucaria* forest (C_3), which is composed of deciduous trees and the conifer *Araucaria angustifolia*. This subtropical forest is found in southern Brazil between the latitudes 24° and 30° S, mainly at elevations between 1000 and 1400 m a.s.l. (Hueck, 1953) and had originally an extent of about 200 000 km^2 (Hueck, 1966). From the 17th century onwards grazing animals were introduced by European settlers (Rambo, 2000) and the grasslands were used as pastureland with frequent burning. This is one of the reasons why today only some residual areas of the original *Araucaria* forests are still present. The climate is moderate and humid without marked dry periods and favours the expansion of forest onto grassland, if the latter is neither burnt nor grazed (Rambo, 1960; Hueck, 1966). Therefore, the question arises, whether the grasslands are the result of deforestation in recent times or if they represent relics of drier periods in the Holocene. Behling et al. (2001) concluded on the basis of pollen data (one core close to our research area), that the southern Brazilian highlands were dominated by grassland during the early and mid Holocene period (7500 to 4000 ^{14}C yrs BP) due to a dry and warm climate with presumably an annual dry season of about three months. There are indices of climatic and vegetational changes from ca. 4000 ^{14}C yrs BP onwards to wetter conditions and shorter annual dry periods with the appearance of patches of *Araucaria* forest. *Araucaria angustifolia* requires a minimum of 1400 mm annual rainfall without a marked annual dry season (Hueck, 1966), which reflects the change to modern climatic conditions in the late Holocene period.

In landscapes where C_3 and C_4 plants coexist or may have coexisted, the determination of stable carbon (^{12}C and ^{13}C) isotopic composition of soil organic matter (SOM) represents a powerful method for reconstructing vegetation changes (Deines, 1980; Tieszen and Archer, 1990; Boutton, 1996; Boutton et al., 1998). The extent to which plants discriminate against $^{13}CO_2$ during photosynthesis depends on the photosynthetic pathway type (Vogel, 1980; O`Leary, 1988; Farquhar et al., 1989; Boutton et al., 1998) and the natural isotopic difference is especially high between C_3 (most trees, shrubs, and cool season grasses) and C_4 (most warm season and desert grasses) plants, which show a mean δ^{13}C value of ca. -27 ‰ and -13 ‰, respectively (Martin et al., 1990; Boutton et al., 1998).

Several hypotheses for ^{13}C enrichment or depletion with increasing soil depth regardless of vegetation change are discussed (Balesdent et al., 1993; Boutton, 1996; Balesdent and Mariotti, 1996) and summarized by Ehleringer et al. (2000) and Wynn et al. (2006). In most well-drained mineral soils the organic matter becomes ^{13}C enriched with depth, which usually varies between 1 – 3 ‰ within 1 m depth in temperate and semi-arid soils (Nadelhoffer and Fry, 1988; Becker-Heidmann and Scharpenseel, 1992; Balesdent and Mariotti, 1996), but it can be as high as 6 ‰ for tropical rainforest soils (Krull et al., 2002). As such depth-increasing δ^{13}C values were found in evidently stable C_3 ecosystems (Bird et al., 2003; Krull et al., 2002; Powers and Schlesinger, 2002), ^{13}C enrichment in forest soils (except tropical rainforest) larger than 3 – 4 ‰ is generally attributed to the presence of remaining old C_4-derived soil organic carbon (SOC). In contrast, a lower ^{13}C enrichment reflects the natural depth trend of δ^{13}C values caused by soil-inherent processes without vegetation change (Martin et al., 1990; Mariotti and Peterschmidt, 1994; Victoria et al., 1995; Desjardins et al., 1996; Martinelli et al., 1996; Biggs et al., 2002).

Radiocarbon ages of SOM represent mean ages of a mixture of different carbon pools with varying degrees of stability and turnover rates (O`Brien and Stout, 1978; Balesdent et al., 1988; Trumbore et al., 1989). As soil formation is accompanied by the continuous input and incorporation of new plant material to an older carbon pool, radiocarbon ages are always younger than the age of initial soil formation (Scharpenseel and Becker-Heidmann, 1992; Trumbore, 1996; Boutton et al., 1998). Radiocarbon ages of SOM are usually increasing with depth indicating a high concentration of old and stabilised SOM in deep soil horizons (Rumpel et al., 2002; Krull and Skjemstad, 2003). Radiocarbon dating in combination with stable isotope analysis may therefore yield valuable information about vegetation history in the Southern Brazilian highlands.

Studies of $\delta^{13}C$ values of SOC have not been conducted until now in the highland region of Rio Grande do Sul. In addition, local information about vegetation history on the basis of pollen analyses exist only from one core (Behling et al., 2001). Therefore, plant tissues from gramineous (C_4) and woody (C_3) species, organic surface layers as well as free light fractions (LF) and the heavy organo-mineral fractions were characterized by stable carbon isotope ratios ($\delta^{13}C$) combined with ^{14}C dating. Thirteen soils in grassland, shrubland, pine plantation and *Araucaria* forest were analyzed to explore present and past vegetation patterns in the grassland-*Araucaria* forest mosaic.

The difficulty in stable carbon isotope studies is, that plant tissues do not have a homogeneous ^{13}C content and that $\delta\ ^{13}C$ values should not remain constant during biodegradation if certain chemical compounds are selectively consumed by the decomposing community. The latter process could lead to the relative accumulation of more recalcitrant fractions (e. g. Benner et al., 1987; Melillo et al.1989; Quideau et al., 2003). Thus, the accumulated soil organic matter may differ in their $^{13}C/^{12}C$ isotopic signature from that of the original plant material.

In C_4 grasslands, ^{13}C depletion was detected from plant to heavy organo-mineral fractions of the upper mineral soil and with increasing soil depth. This phenomenon was also found for other C_4 grasslands. It was suggested that the isotopic depletion originates from the relative accumulation of ^{13}C depleted lignins and/or lipids due to a lower decomposition rate compared to the isotopically heavier cellulose, at least in the early stages of biodegradation (Volkoff and Cerri, 1987; Martin et al., 1990; Wedin et al., 1995; Sanaiotti et al., 2002; Henderson et al., 2004). However, the extent at which lignins are degraded or stabilised in soils is still matter for discussion (e. g. Haider, 1992; Quideau et al., 2003; Preston et al., 2005; Dignac et al., 2005).

Compound-specific gas chromatography-combustion-isotope-ratio mass spectrometry (GC/C-IRMS) enables the determination of isotopic compositions from individual chemical compounds (Hayes et al., 1990). Besides marine sediments (Goñi and Eglinton, 1996), compound-specific $\delta\ ^{13}C$ values of individual lignin phenols in soils are only reported for maize and wheat lignins from agricultural soils (Dignac et al., 2005; Bahri et al., 2006). In this study, GC/C-IRMS in combination with alkaline CuO oxidation was applied to determine the isotopic composition of lignin-derived phenols in forest (C_3) and grassland (C_4) derived heavy organo-mineral fractions for the characterisation of lignin sources and the evaluation if lignins contribute to ^{13}C depletion in grassland soils.

Soil Munsell colours showed that grasslands have black and Araucaria forests dark brown topsoils. In patches of Araucaria forest and forest sites bordering to grassland, the pedons get darker with increasing depth and become as black as in grassland. These are first indications that the change from grassland with long-term fire history to unburned Araucaria forest alters the composition of SOM. Therefore, the question arises if vegetation shifts from C_4 grassland to C_3 forest or shrubland are associated with the change of the chemical composition of SOM.

For the first time, heavy organo-mineral fractions were grouped according to the $^{13}C/^{12}C$ isotopic signature to trace C_4- and C_3-derived biomass from vegetation sources to SOM. ^{13}C NMR spectroscopy and lignin analyses (CuO oxidation) were applied to characterise the chemical composition of plants, organic surface layers, light fractions and heavy organo-mineral fractions. Additionally, ^{13}C NMR spectroscopy results were related to spectroscopic measurements of soil lightness values.

1.3 Objectives of the present study

The characterization and classification of the soils in the *Araucaria* forest – grassland mosaic of the southern Brazilian highlands led to the first detection of Andosols in South America outside the active volcanic areas in the Andes. These Andosols are associated with Umbrisols and to a lesser extent with Cambisols, which mostly show andic properties for at least some depth range, too. Twenty-seven soils with different vegetation cover were studied to investigate

- the relationships between soil properties, genesis and vegetation. Which present or past vegetation favours the genesis and permanence of Andosols?
- the past vegetation patterns in the grassland-*Araucaria* forest mosaic (13 selected soils). Are grasslands the result of deforestation in recent times or present since the Holocene period?
- the associations between vegetation shifts and the chemical composition of soil organic matter (8 selected soils). Which characteristics of soil organic matter reflect vegetation source and land-use?
- the origin of lignins in topsoils (selected heavy fractions from 5 soils).
  Do lignins contribute to ^{13}C depletion in grassland soils?

2 MATERIAL AND METHODS

2.1 The study area and its environment

The study area belongs to the northern highlands of the southern Brazilian state of Rio Grande do Sul (29°28`- 29` S, 50°10`- 13` W) as shown by Figure 1. Our soils are located in and around the forest reserve CPCN Pró-Mata (Centro de Pesquisas e Conservação da Natureza), which is about 35 km East of the city of São Francisco de Paula and 110 km from the capital Porto Alegre (Figure 1). All soils lie in a smoothly undulating land surface at 900 - 950 m a.s.l. and developed from rhyodacite (Jurassic-Cretaceous volcanism), which has a SiO_2 content of > 63 % (Roisenberg, 1989) and high contents of weatherable minerals, above all plagioclases and pyroxenes (Roisenberg, 1989; Ebner, 2001). Soil temperature and soil moisture regimes are thermic and udic, respectively (USDA, 1999).

Figure 1: Location of the study area Pró-Mata.

The high precipitation (annual mean 2252 mm), the moderate temperature (annual mean 14.5° C), the relative humidity of 84 % (Bertoletti & Teixeira, 1995) and frequent fogs (92 fog days per year) (Moreno, 1961) indicate a humid character without a pronounced dry period. Climate data are documented from the São Francisco de Paula station (912 m a. s. l.). In each year, several days with frost and sometimes snowfall can occur. The local climate of

Pró-Mata probably shows even higher precipitation and more frequent fogs, because Pró-Mata is directly located at the steep brink of the highland and the transport of moist tropical air masses against the brink by the South Atlantic anticyclone leads to relief rainfall the entire year. The present vegetation is a mosaic of grasslands and disturbed *Araucaria* forest (deciduous forest with the conifer *Araucaria angustifolia*). Grasslands which are used for pasture are usually burned once per year. They are composed mainly of species of the families of *Poaceae*, *Asteraceae*, *Fabaceae*, *Apiaceae*, *Cyperaceae* and *Eriocaulaceae* (Boldrini, 1997; Behling et al., 2001). Natural pastures possess high structural diversity and they are dominated by C_4 grass species in summer, whereas C_3 grass species increasingly appear in the short winter period due to the highland climate (Nabinger et al., 2000). The *Araucaria* forest is composed of deciduous trees and the conifer *Araucaria angustifolia*. Harvesting large and best developed *Araucaria* trees resulted in a heterogeneous and generally low occurrence of this conifer. Other frequently occurring species of the *Araucaria* forest are the tree fern *Dicksonia sellowiana* and bamboo. The latter occurs in form of clusters at former gaps after cutting *Araucaria* trees. In the forest reserve Pró-Mata all forms of land use, for example tree felling or grazing and burning of grassland, terminated in 1992. This led to diverse types of successions by shrubs (mainly *Baccharis* sp.) and pioneer trees on grassland (Figure 2).

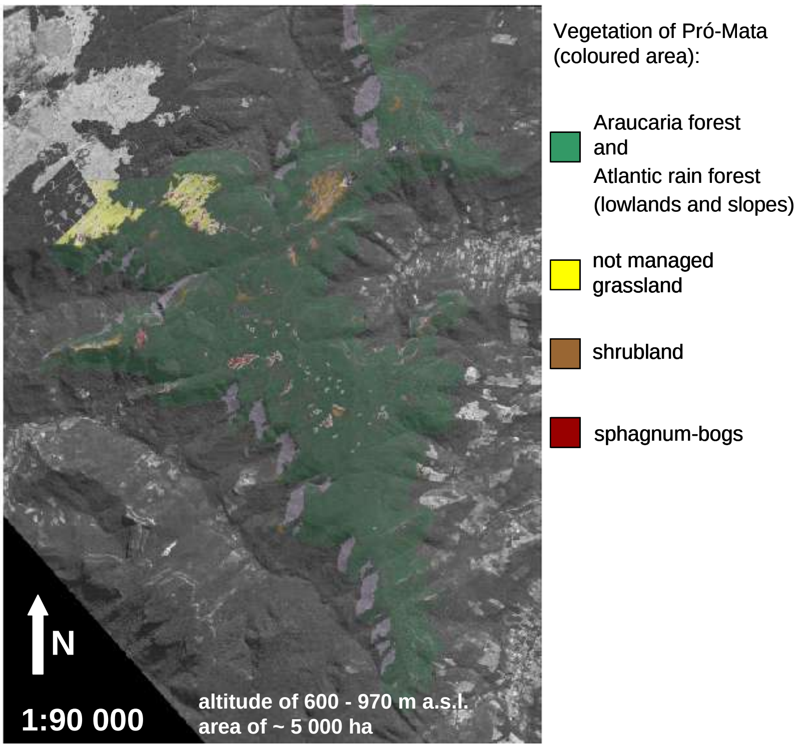
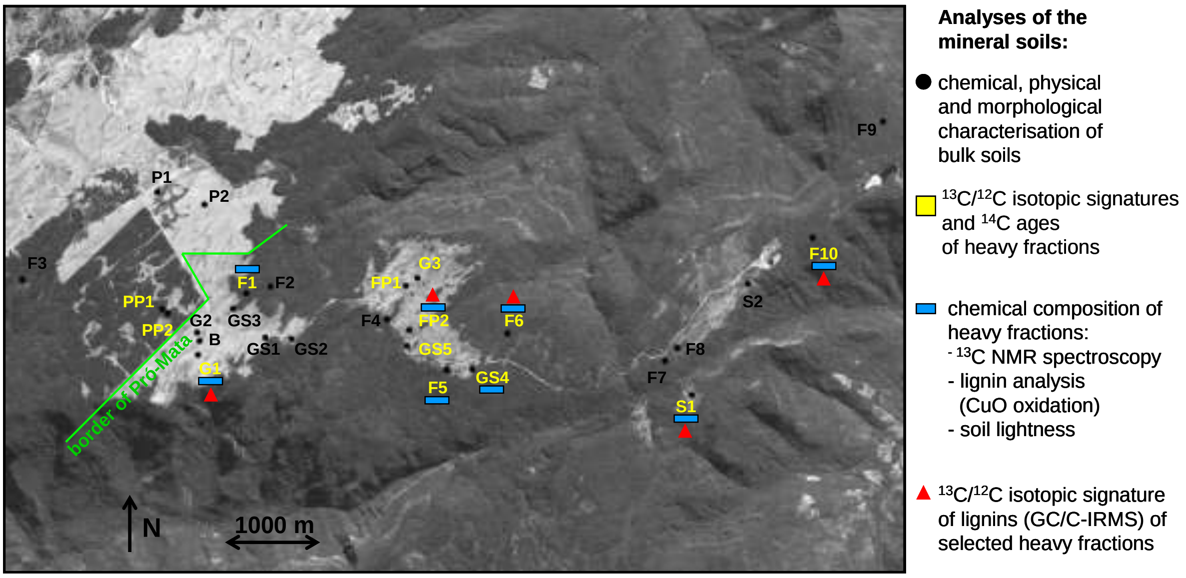


Figure 2: Vegetation of Pró-Mata (orthophoto: courtesy of the University of Applied Forest Sciences, Rottenburg, modified).

In addition, areas with secondary forest and shrubland, established after forest clearing, can be found. Sphagnum bogs with grasses and with or without shrubs are common in basins and sinks. Even outside the reserve area agricultural and pastoral activities are low, but recently afforestation of pastureland with Pinus (mainly *Pinus taeda* and *elliottii*) is increasing.

2.2 Field work, sampling and design of analysis

Sites for detailed sampling were selected after field observations of soil morphology (horizon depths, textures, colours) with an auger, vegetation, topography and representativeness for larger areas. Twenty-seven soils were dug until to the parent rock (rhyodacite) and described in the field according to the draft of the guidelines for soil description of the FAO (Jahn et al., 2003). All soil horizons were sampled conventionally in the centre across the entire front profile wall from the bottom to the top. Soil horizons with small thicknesses were sampled as a whole. In addition, undisturbed samples (100 cm^3 cylinder cores) were collected at field capacity for each soil from the centres of all horizons in triplicate for bulk density measurement. The position of soils, their codes according to the vegetation type and the conducted analysis are shown by Figure 3.



G = not managed grassland without shrubs (3)
GS = not managed grassland with shrubs (5)
P = pastureland (2)
S = shrubland (2)
FP = patch of *Araucaria* forest (2)
F = *Araucaria* forest (10)
PP = Pinus plantation (2)
B = bog-like soil (1)

Figure 3: Location of soil profiles and sampling design (orthophoto: courtesy of the University of Applied Forest Sciences, Rottenburg, modified).

Outside the reserve Pró-Mata are situated the *Araucaria* forest soil F3, two soils in the managed pastureland (P1, P2) and two in pine plantations of *Pinus taeda* and *elliottii* (PP1, PP2), which were established on grassland 15 years ago without soil cultivation. In the reserve are located eight soils under not managed grassland without (G1-3) and with shrubs (GS1-GS5). Two sites are under shrubland (S1, S2) which is characterized by shrubs and pioneer trees whereas gramineous species are less dominant. In Araucaria forests (F) are located eleven soils, whereas two of them are in patches of *Araucaria* forest (FP1, FP2) which are surrounded by grassland. In a small basin is located a water-saturated bog-like soil (B).

For investigation of vegetation history by $^{13}C/^{12}C$ isotopic signatures and radiocarbon ages have been selected thirteen soils covering the whole range of soils and vegetation types which is shown by the larger sample of the 27 soils (Figure 3). The bulk materials from the thirteen soils were separated by density fractionation into light fractions and heavy organo-mineral fractions. From these soils were selected eight soils (Oa and Ah horizons) to characterise the chemical composition of soil organic matter by ^{13}C NMR spectroscopy, lignin analyses (CuO oxidation) and soil lightness measurement. For this purpose, their heavy organo-mineral fractions were grouped according to the $^{13}C/^{12}C$ isotopic signature (see chapter 5.1.2). The isotopic composition of lignin-derived phenols (GC/C-IRMS) was determined for *Andropogon lateralis* which is the principal gramineous species of the grasslands at Pró-Mata (Bertoletti and Teixeira, 1995) and for two C_4-derived heavy organo-mineral fractions from a grassland soil (G1) covered with *A. lateralis*. It was shown before, that grasses and C_4-derived heavy organo-mineral fractions show markedly lower variation in the carbon isotopic signal compared to trees and heavy fractions with C_3 signature. Thus, more samples were analysed for the C_3 counterpart including the needles of the C_3 conifer *Araucaria angustifolia* and two organic surface layers (comprising Oi and Oe horizons) in C_3 Araucaria forest. Heavy organo-mineral fractions with C_3 signature were analysed from one pedon in a patch of Araucaria forest within grassland (FP2), from two pedons deep inside the Araucaria forest (F6, F10) and one shrubland soil (S1).

Organic surface layers (Oi and Oe horizons) were collected as mixed samples with a 0.2 m x 0.2 m rack at eight spots in regular distances adjacent to each soil profile, except for grassland without marked surface litter accumulation. All samples were oven-dried at 40° C, soil samples passed through a 2 mm sieve, organic surface layer and plant samples finely ground in a rotor beater mill. In addition, aliquots of all soil and organic surface layer samples were oven-dried at 105° C to determine the water content for the correction of mass balanced parameters to oven dry soil values. All samples were stored and transported in plastic bags.

For ^{13}C NMR spectroscopy, analyses of lignin (CuO oxidation) and $^{13}C/^{12}C$ isotopic signature different tissues of several plant species with the most frequent occurrence at sites with soil profiles in grassland, *Araucaria* forest and shrubland were sampled (Table 2). Three grass-mixture samples were collected by cutting all grasses within a 0.2 m x 0.2 m rack at three places adjacent to three grassland profiles.

2.3 Characterisation of bulk soils

All analytical determinations, except for bulk density, were made on material < 2 mm. For particle size analysis organic matter was oxidized with H_2O_2 (30 %). Afterwards the sample was dispersed with a solution of 200 ml of 0.025 M $Na_4P_2O_7$ solution and 200 ml of H_2O and shaken for 16 hours, followed by wet sieving for determination of the fractions 2000 – 630 µm, 630 – 200 µm and 200 - 63 µm. The residue was washed and freeze-dried. For dispersion 40 ml of 0.025 M $Na_4P_2O_7$ solution and 40 ml of H_2O was added to an aliquot of the freeze-dried sample (3 – 4 g) and the suspension was treated by ultrasound for about 3 minutes (75 J ml^{-1}) (Branson Sonifier). Afterwards the fractions 63 – 20 µm, 20 - 6.3 µm, 6.3 – 2 µm and < 2 µm were determined using the X-ray attenuation method (Sedigraph 5100, Micromeritics).
Total carbon (C_{tot}) and nitrogen (N_{tot}) were determined by combustion (Elementar Vario EL). As all soils were carbonate-free the measured C is completely organic. Carbon stocks (C_S) of each horizon were calculated by using the following equation:

$$C_S\ (\text{kg C m}^{-2}) = OC \times BD \times T \times (100\text{-}S/100) \times 10^{-2} \qquad \text{Equation 1}$$

where OC is the organic carbon content (g kg^{-1}), BD the bulk density (kg dm^{-3}), T the thickness (cm) and S the content of rock fragments (> 2 mm) of the soil horizon (vol-%). The contents of rock fragments were estimated optically in the soil profiles.
Soil pH was measured in water (pH H_2O) and in 1 M KCl (pH KCl) at a soil : solution ratio of 1 : 2.5. Phosphate retention was determined according to Blakemore et al. (1987) as described by Van Reeuwijk (2002) and the P concentrations were measured photometrically (Photometer Spectronic 601). Three analyses of Al, Fe and Si fractions were conducted: with dithionite-citrate-bicarbonate (DCB: Al_d, Fe_d, Si_d) according to Mehra and Jackson (1960), with oxalate (Al_o, Fe_o, Si_o) using the method of Schwertmann (1964) and with pyrophosphate (Al_p, Fe_p, Si_p) as described by Van Reeuwijk (2002), which is based on Blakemore et al. (1987) and USDA (1972). Superfloc was added to avoid flocculation in the pyrophosphate

extracts. The Al, Fe and Si concentrations were measured with an ICP-OES (Varian Vario-Pro). The melanic index was determined according to Van Reeuwijk (2002), who modified the method of Honna et al. (1988). The samples were shaken with a 0.5 M NaOH solution and the absorbances of the extracts were measured photometrically (Photometer Spectronic 601) at 450 and 520 nm wavelength. The ratio (450 nm / 520 nm) is the melanic index.

For cation exchange capacity (CEC) and exchangeable cations several procedures had to be done. The exchangeable base cations were removed with 1 M NH_4OAc at pH 7 (USDA, 2004), the sample was then washed with isopropanol (ethanol which has been often used in the past removed some adsorbed NH_4^+ ions from the exchange sites and therefore underestimated the potential CEC) and after that rinsed with 1 M KCl. In the leachate the NH_4^+ ions were measured (Segmented Flow Analyzer) to calculate the potential CEC. Al and H were determined in a different aliquot by the method of Bertsch and Bloom (1996) with 1 M KCl. All cation concentrations were measured with an ICP-OES (Varian Vario-Pro). Mineralogy was assessed on the clay fractions from two topsoil and two subsoil horizons by X-ray diffraction (XRD) after Moore and Reynolds (1989). The samples were preliminary treated with dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960) to remove Fe oxides. XRD was performed on random powder samples and on oriented samples (Co-Kα; Philips diffractometer PW1830) after saturation with Ca^{2+} and glycerol (room temperature) and K^+ (room temperature and stepwise heated to 560° C).

2.4 Density and particle-size fractionation

An aliquot of 10 g from the bulk soil (< 2 mm) was saturated with a Na polytungstate solution (1.6 g cm^{-3}), gently shaken, allowed to settle for 2 hours and then centrifuged to separate the free light fraction (LF) from the fraction with a density > 1.6 g cm^{-3}. The LF fraction was washed with deionized water on a 20 µm mesh sieve. The heavy fraction was centrifuged several times with deionized water until the electrical conductivity had dropped to < 2 µS cm^{-1}. All fractions were freeze-dried.

Selected heavy organo-mineral fractions were fractionated according to particle-size after separation of the light fractions by density fractionation. The heavy fractions (30 g) were suspended with deionised water and then dispersed by ultrasound (Branson Sonifier 250). After sonification, the suspension was separated by wet sieving into sand (63-2000 µm) and silt (20 - 63 µm) separates. The remaining finer particles were split up in a silt (2 – 20 µm) and clay fraction (< 2 µm) by gravity sedimentation, and were recovered from the suspensions by pressure filtration (cellulose nitrate, 0.45 µm). The sand fraction was dried by 40° C and all silt and clay fractions were freeze dried.

Pre-tests with gradual increases of energy inputs showed that 1200 J ml^{-1} had to be applied for complete dispersion of soil aggregates and to obtain similar particle-size distribution compared to texture analysis. The high aggregate stability is due to large contents of organic matter, Fe and Al oxides and the predominance of Al-humus-complexes (see chapter 3). However, bulk soils and particle-size separates showed similar $^{13}C/^{12}C$ isotopic signatures for samples treated with 1200 J ml^{-1} (Table 13, appendices). In addition, one clay fraction (FP2 Bw1) which was analysed for ^{14}C content shows a similar radiocarbon age with 7960 yr BP (37.1 %, percent modern carbon) compared to the bulk soil (8005 yr BP, 36.9 %, percent modern carbon). Thus, the carbon isotopic signatures of mineral-associated fractions provide no complementary information for vegetation origin of soil organic matter. ^{13}C NMR spectroscopy revealed that particle-size separates show no significant differences in the chemical composition relative to bulk soils (Table 14, appendices). Only the proportions of aromatic carbon are higher in the 2 – 20 µm fractions relative to other fractions or bulk soils. The results may indicate that the homogeneous composition of the mineral-associated fractions is typical for these soils, most of them with andic properties which was also detected for other Andosols (Baldock et al.,1992). On the other hand, it can not be excluded that the high energy inputs for dispersion of soil aggregates produced an artificial particle-size distribution with fractions showing similar characteristics. Therefore, the particle-size fractionation of bulk soils was not continued.

2.5 Treatment with hydrofluoric acid (HF)

Soil minerals from selected heavy organo-mineral fractions were removed by shaking approximately 10 g soil for 2 h with 50 ml of 10 % (w/w) hydrofluoric acid (HF) as described by Schmidt et al. (1997). After centrifugation for 10 min at 3000 rpm the supernatant was removed and the residue again shaken with HF. This procedure was repeated five times. Afterwards, the samples were washed five times with distilled water to remove residual HF and freeze dried. The losses of organic carbon (mass-%) and changes in C/N ratios by HF treatment were calculated with the amount of dry matter and the measured C and N contents before and after the treatment. Alterations of SOM by HF treatment were determined by comparing the chemical composition of SOM before and after HF treatment. The OC loss (mass-%) upon HF treatment (hydrofluoric acid) was 17 - 20 % in the heavy organo-mineral fractions of humus-rich A horizons of grassland soils. In *Araucaria* forest topsoils and lower horizons OC losses were larger (53 – 56 %). However, despite of different OC losses HF treatment caused no consistent alterations in the distribution of carbon functional groups suggesting that no preferential loss of specific carbon groups occurred. This is confirmed by comparing the C/N ratios before and after HF treatment with values for the R factor (R_f) of 0.9 – 1.0. Only the *Araucaria* forest topsoil sample (F6 Ah2) exceed with 1.4 the range of R factors (1.00 ± 0.20) which is considered to indicate only minor changes of C or N (Schmidt et al., 1997). In samples with SOC/Fe_d ratios < 1 may occur quantification problems of ^{13}C NMR spectra because of the presence of paramagnetic compounds (Arshad et al., 1988; Preston et al., 1994). The resolution of ^{13}C NMR spectra of Oa and A horizons is high due to the large OC content and all have SOC/Fe_d ratios > 1 (Table 1). Thus, they were analyzed by ^{13}C NMR spectroscopy without previous HF treatment.

2.6 Carbon isotope signals and chemical characterisation of soil organic matter

2.6.1 $^{13}C/^{12}C$ isotopic signature

$\delta^{13}C$ values were measured for plant tissues, organic surface layers (comprising Oi and Oe horizons) and soil material which includes Oa horizons and mineral soils according to the horizon definitions of FAO (2006). The soil material was fractionated by density in order to separate the heavy organo-mineral fraction from the litter- and/or root-derived free light fraction (LF). The ^{13}C contents of the organo-mineral soil fractions, LF, organic surface layers and plant samples were measured using a CHN auto-analyser (CHN NA 1500, Carlo Elba), coupled to an isotope ratio mass spectrometer (VG Sira 10) (Girardin and Mariotti, 1991), at the Laboratoire de Biogéochimie et Ecologie des Milieux Continentaux (BioEMCo), INRA-CNRS-Univ. in Thiverval-Grignon (France). The laboratory reference was calibrated against the Vienna Pee Dee Belemnite (V-PDB) international standard. The carbon isotope ratios are calculated in δ-notation on a per mil basis (parts per thousand, ‰), which is defined as the $^{13}C/^{12}C$ ratio of the sample relative to the international Vienna Pee Dee Belemnite (V-PDB) standard:

$$\delta^{13}C\ (‰) = \left(\frac{(^{13}C/^{12}C)_{sample}}{(^{13}C/^{12}C)_{V\text{-}PDB}} - 1 \right) \times 1000 \qquad \text{Equation 2}$$

Analytical precision for isotope measurements was ± 0.3 ‰.

The proportion of organic carbon derived from C_3 and C_4 plant sources was estimated using a frequently applied mass balance equation (Boutton, 1996; Boutton et al., 1998; Gill and Burke, 1999; Jessup et al., 2003; Biedenbender et al., 2004; Chiang et al., 2004):

$$\delta^{13}C_{meas} = x\,(\delta^{13}C_4) + (\delta^{13}C_3)\,(1 - x) \qquad \text{Equation 3}$$

where $\delta^{13}C_{meas}$ is the measured $\delta^{13}C$ value, $\delta^{13}C_4$ is the $\delta^{13}C$ value for C_4 vegetation, $\delta^{13}C_3$ is the $\delta^{13}C$ value for C_3 vegetation, x is the proportion of C from C_4 plant sources and (1 - x) is the proportion of C derived from C_3 plants.

For running this equation two input parameters, the $\delta^{13}C$ values of C_4 and C_3 vegetation, have to be determined or estimated. Plants with C_3 photosynthesis have $\delta^{13}C$ values ranging from -32 ‰ to -22 ‰ (mean ca. -27 ‰), whereas values for C_4 plants range from -21 ‰ to -9 ‰ with an average of ca. -13 ‰ (Smith and Epstein, 1971; Raven et al., 1981; Salisbury and Ross, 1985; Tieszen and Archer, 1990; Boutton, 1991; O`Leary, 1993). The analysis of the ^{13}C contents showed mean $\delta^{13}C$ values for C_4 gramineous species of -12.7 ‰, for C_3 shrubs of -29.0 ‰, for C_3 deciduous trees of -31.8 ‰ and for the C_3 conifer *Araucaria angustifolia* of -24.9 ‰ (Table 2).

Because of the heterogenous mixed *Araucaria* forest with varying abundances of *Araucaria angustifolia*, the maximum deviation for the $\delta^{13}C$ value of *Araucaria* forest floors amounts to 2.3 ‰ with a mean of -28.8 ‰ (n = 5, S.D. ± 0.9 ‰). *Araucaria angustifolia* was preferentially harvested in the last century and consequently occurred more frequently before. Therefore, the $\delta^{13}C$ value of -27.2 ‰ was used for the calculation, which represents the value of the *Araucaria* forest floor from site F6 with the highest abundance of *Araucaria angustifolia*. As $\delta^{13}C$ value of the C_4 vegetation was applied -13.8 ‰, which is the mean $\delta^{13}C$ value of the free light fraction (LF) in 0 – 20 cm depth of grassland soils without shrubs.

Assuming that ^{13}C enrichment or depletion with soil depth without vegetation change occur in both, grassland and forest soils, the amounts of soil C derived from *Araucaria* forest (C_3) and grassland (C_4) were calculated for the *Araucaria* forest soils by applying the same input parameters as in equation 3 in combination with a grassland reference soil. The latter was calculated as the mean of the $\delta^{13}C$ values of the grassland soil without shrubs G1 and the pine plantation soil PP2, because both soils show the lowest influence of shrubs as indicated by their $\delta^{13}C$ values. The amounts of soil C derived from *Araucaria* forest (C_F) were calculated using the following equation (Balesdent and Mariotti, 1996):

$$C_F = [(\delta^{13}C_{F\text{-soil}} - \delta^{13}C_{G\text{-ref}}) / (\delta^{13}C_{F\text{-litter}} - \delta^{13}C_{G\text{-litter}})] \times C_S \qquad \text{Equation 4}$$

where $\delta^{13}C_{F\text{-soil}}$ is the stable carbon isotope value from the respective *Araucaria* forest soil, $\delta^{13}C_{G\text{-ref}}$ is the stable carbon isotope value from the grassland reference soil, $\delta^{13}C_{F\text{-litter}}$ is the stable carbon isotope value of *Araucaria* forest litter (-27.2 ‰), $\delta^{13}C_{G\text{-litter}}$ is the stable carbon isotope value of grassland residues (-13.8 ‰) and C_S is the SOC stock of the respective *Araucaria* forest soil. The amounts of soil C derived from grassland (C_G) result from $C_G = C_S - C_F$.

2.6.2 Radiocarbon ages

The AMS ^{14}C measurements of selected organo-mineral soil fractions were obtained from the Leibniz-Labor in Kiel (Germany). The analyses have a precision of about 0.3 pMC (percent modern carbon) or 20 - 45 yr BP for standard sized samples containing 1 mg C (Nadeau et al., 1998). The ^{14}C concentrations were calculated from the measured $^{14}C/^{12}C$ ratio of the sample compared to 95 % of the NIST (National Institute of Standards and Technology) oxalic acid standard (Stuiver and Polach, 1977). Both were corrected for isotopic fractionation by using the simultaneously measured $^{13}C/^{12}C$ ratio. Results are expressed in percent modern carbon (pMC; 100 pMC = 1950 AD) (Stuiver and Polach, 1977) and in converted “calibrated age” (yr BP) according to Stuiver et al. (1998).

2.6.3 Solid-state CPMAS ^{13}C NMR spectroscopy

Selected plant, organic surface layer, free light and organo-mineral fraction (without prior HF-treatment) samples were analyzed by solid-state ^{13}C CPMAS NMR spectroscopy (Bruker DSX 200 NMR spectrometer). The cross-polarization magic angle spinning (CPMAS) technique (Schaefer & Stejskal, 1976) with a spinning speed of 6.8 kHz and a contact time of 1ms was applied. A ramped ^{1}H-pulse starting at 100 % power and decreasing until 50 % was used during contact time to avoid Hartmann-Hahn mismatches (Peersen *et al*., 1993). The pulse delays were 300 ms (organo-mineral fractions), 800 ms (organic surface layers, free light fractions) and 2000 ms (plants). In dependence of the signal-to-noise ratio a line boardening between 50 and 100 Hz was used prior to Fourier transformation. The chemical shifts of ^{13}C were referred to external tetramethylsilane (= 0 ppm). For quantification, the spectrum was divided into four major chemical shift regions according to Knicker & Lüdemann, 1995 (0 to 45 ppm alkyl-C, 45 to 110 ppm O-alkyl-C, 110 to 160 aromatic C, 160 to 220 ppm carboxyl-C) which were integrated. The occurrence of spinning side bands due to insufficient averaging of the chemical shift anisotropy at the used spinning speed was considered by adding their intensities to that of the parent signal (Knicker & Lüdemann, 1995; Knicker *et al*., 2005). The content of aromatic carbon (g kg^{-1}) in the heavy organo-mineral fractions was calculated as follows: (proportion of aromatic carbon (%) × organic carbon content (g kg^{-1})) / 100 (%).

2.6.4 Lignin-derived phenols (CuO oxidation)

Lignin analysis by cupric oxide (CuO) oxidation (Hedges & Ertel, 1982) was carried out for selected plant, organic surface layer and organo-mineral fraction samples according to the modified method of Kögel & Bochter (1985). Briefly, the samples (50 mg for plants and organic surface layers, 500 mg for organo-mineral fractions) were oxidized with 250 mg CuO and 2 M NaOH at 172° C under N_2 for 2h. Afterwards, a standard containing ethylvanillin was added to assess the recovery of lignin products, which was usually in the range of 60 – 70 %. The solution was adjusted to pH 1.8 – 2.2 and left over night for humic acid precipitation. Thereafter, the lignin-derived phenols were purified by eluting through a C18 column and derivatized by adding BSTFA (N, O-Bis (trimethylsilyl) trifluoro-acetamide). The silylated lignin monomers were separated on a HP 6890 gas chromatograph equipped with a SGE BPX-5 column (50 m length, 0.25 mm inner diameter, 0.32 µm coating) and detected by flame ionization detector (GC/FID). The GC oven temperature was kept at 100° C for 2 min, then heated to 172° C at 8° C/min, to 184° C at 4°C/min and to 300° C at a rate of 10° C/min. The samples were injected in split mode (1:10). Phenol concentrations were calculated with the internal standard phenylacetic acid. The results are given as mean values obtained from at least two replications. CuO oxidation products are composed of vanillyl (V)-units (vanillin, acetovanillone, vanillic acids), syringyl (S)-units (syringaldehyde, acetosyringone, syringic acid) and cinnamyl (C)-units (ferulic and p-coumaric acids). The sum of V-, S- and C-type phenols (VSC) expressed as mg VSC g^{-1} SOC or mg VSC g^{-1} plant OC is used to estimate the amount of lignin. In addition, the ratio acid:aldehyde (ac:al) was calculated for S- and V-type phenols and used as indicators of the degree of microbial alteration of lignin (Kögel, 1986).

2.6.5 Lignin isotopic analyses

The $^{13}C/^{12}C$ isotopic signature of the lignin-derived CuO oxidation products of selected plants, organic surface layers and heavy organo-mineral fractions was determined by compound specific isotope analysis (Goñi and Eglinton, 1996) at the Laboratoire de Biogéochimie et Ecologie des Milieux Continentaux (BioEMCo), INRA-CNRS-Univ. in Thiverval-Grignon (France). Samples were measured on a GC HP5890 coupled via a combustion interface to an Isochrom III isotope ratio mass spectrometer (IRMS) (Micromass-GVI Optima). A volume of 0.3 µl was injected in splitless mode. The same temperature program was used as for the quantification of lignins (GC/FID) and the CuO procedure was repeated 2-3 times (50 mg for plants and organic surface layers, 500 mg for organo-mineral fractions) as described above. The respective C18 column eluates were combined in order to obtain a concentration of each phenol in the extract higher than 2 nmol C/µl, which represents the detection limit of the GC/C-IRMS. Each composite sample was analyzed three times by GC/C-IRMS. The ^{13}C content of silylated phenol monomers were corrected for carbon addition during derivatization using BSTFA. In dependence of the phenol, derivatization introduced three to six carbon atoms with their distinct ^{13}C contents influencing the ^{13}C content of the phenol. Therefore, the $\delta\ ^{13}C$ values were corrected using the ^{13}C content of the derivatizing agent as described in Dignac et al. (2005). The mean $\delta\ ^{13}C$ values for V-, S-, and C-type lignin were calculated by weighting the ^{13}C contents of each monomer with its relative contribution to the corresponding lignin type. These values were used in combination with the concentrations of V, S and C to calculate the $\delta\ ^{13}C$ values of the total analyzable lignin VSC.

2.7 Soil lightness (L-value)

Soil lightness values of dried and ground heavy fractions are presented according to the CIE 1976 (L* a* b*) colour space system (CIE, 1978) and measured with a Chroma-meter (Minolta, CR-300). This method is described in detail by Torrent & Barron (1993) and allows to visualize the lightness of soils from L = 0 for absolute black to L = 100 for absolute white. After each sample the system was calibrated using a standard white plate and results are given as arithmetic means of four replicates.

2.8 Statistics

For comparison of mean values between groups of heavy organo-mineral fractions with C_4 and C_3 signature the conditions of normality were tested by the Shapiro-Wilk test. If values were not normally distributed (soil lightness value, melanic index) the nonparametric Mann-Whitney U-Test was applied to identify significant differences. The Students t-test was used for normally distributed values (aromatic C in %, C/N ratio, ratio of (alkyl C)/(O/N-alkyl C), $\delta\ ^{13}C$ value). Significant differences were identified at a confidence level of $p < 0.05$. For determination of significance of contrast between the regression models of Lvalue and aromatic C (g kg^{-1}) for heavy fractions with C_4 and C_3 signature was used the test for homogeneity of slopes (Rencher & Schaalje, 2008). All statistical analyses were conducted using SPSS Version 15.0 (Statistical Package for the Social Sciences, 2006).

3 THE MOSAIC OF NONALLOPHANIC ANDOSOLS, UMBRISOLS AND CAMBISOLS

3.1 Results

3.1.1 Morphological, physical and mineralogical properties

As shown in tables 1 and 2 (appendices) most pedons have deep and dark topsoils (10 YR 2/1 or 10 YR 2/0), high clay contents (50 – 65 %) and all have low bulk densities (topsoils: 0.3 – 0.8 kg dm^{-3}, subsoils: 0.6 – 1.3 kg dm^{-3}). Munsell colours reveal black grassland and dark brown forest topsoils. Depending on the inclination and the relative position within the relief (Table 1, appendices) different types of horizon sequences developed. Soils with A-C sequence and shallow depth (25 – 32 cm) are located on hilltops or upper slopes (G3, GS1, PP1, F5). On lower to middle slopes and in basins as well as on large plateaus deeper soils up to 160 cm depth with A-C and A-B-C sequences are found.

All soils but one (F9) in *Araucaria* forest and the two pedons in patches of *Araucaria* forest get darker with increasing topsoil depth and become black like grassland topsoils. The two shrubland (S1, S2) and four *Araucaria* forest soils (F6, F7, F8, F10), predominantly located on middle slopes, have buried A horizons, which are darker than the overlying ones and which indicate severe erosive processes in the past (Figure 4). We neither observed evidence of cutanic features nor of illuviation of clay, Fe or organic matter in the field. Furthermore no thixotropy was detected. However, macroscopically visible charcoal was found in six soils with *Araucaria* forest (F1-3, F6-8), four grassland (P1, GS2, GS4-5) and both shrubland pedons (S1, S2) (Table 1, appendices). In forest soils the charcoal pieces were mainly located in surface horizons, while they were found in deeper horizons in the grassland soils. In soils with shrubland vegetation charcoal was distributed among the whole pedon.

The XRD results of clay fractions from two topsoil (Ah2 of G2, Ah2 of GS1) and two subsoil (Bw of G1, 3Bw of GS2) horizons by random powder analyses indicate a crystalline mineralogy with quartz, kaolinite, secondary chlorite and some gibbsite. A small peak at 33.2 nm showed traces of feldspars. No illites, vermiculites or smectites were detected. The layer silicates of the clay fraction contained 52 – 64 % kaolinite and 36 – 48 % secondary chlorite calculated by semi-quantitative determination after glycerol solvation. Both were detected to be well-developed. We neither found large differences in the clay-mineral composition between the four analyzed samples nor between the upper layers (A horizons) and subsoils (B horizons). Only in some deeper subsoils, where XRD was not undertaken, can be assumed some 2:1 clay minerals indicated by relatively high CEC_b values combined with low OC contents.

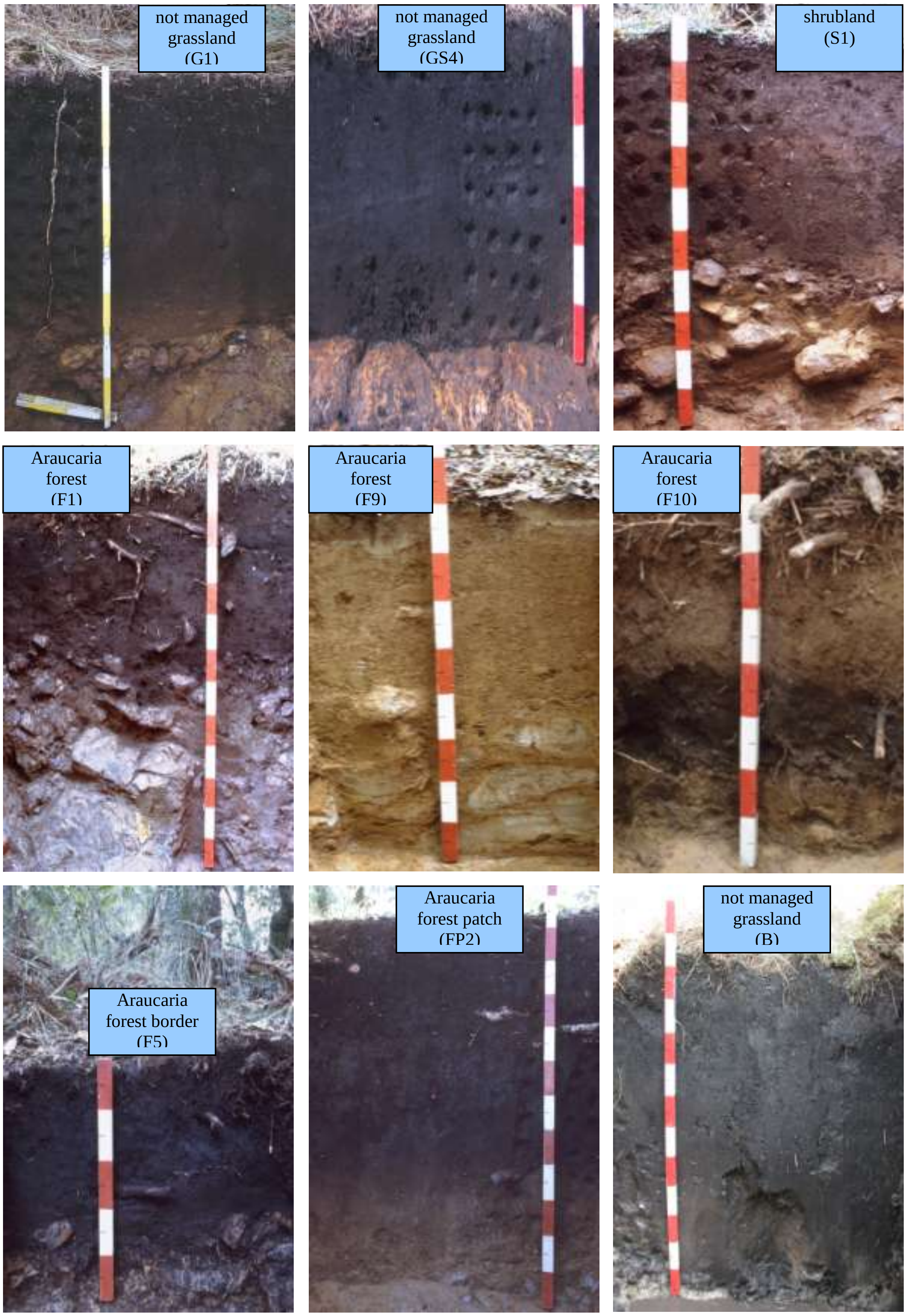


Figure 4: Soils of Pró-Mata with different vegetation cover.

3.1.2 Chemical properties

The characteristics of cation exchange of selected pedons are presented in Table 2 and the other chemical properties are shown in Table 1 (appendices). The codes of the pedons refer to the vegetation type and are explained in Figure 4. Most soil properties are related to the large organic carbon (OC) contents. The total nitrogen content (N_{tot}) has a high linear correlation with the OC content and bulk density as well as the potential cation exchange capacity (bufferd at pH 7) are also strongly related to the OC content (Figure 5).

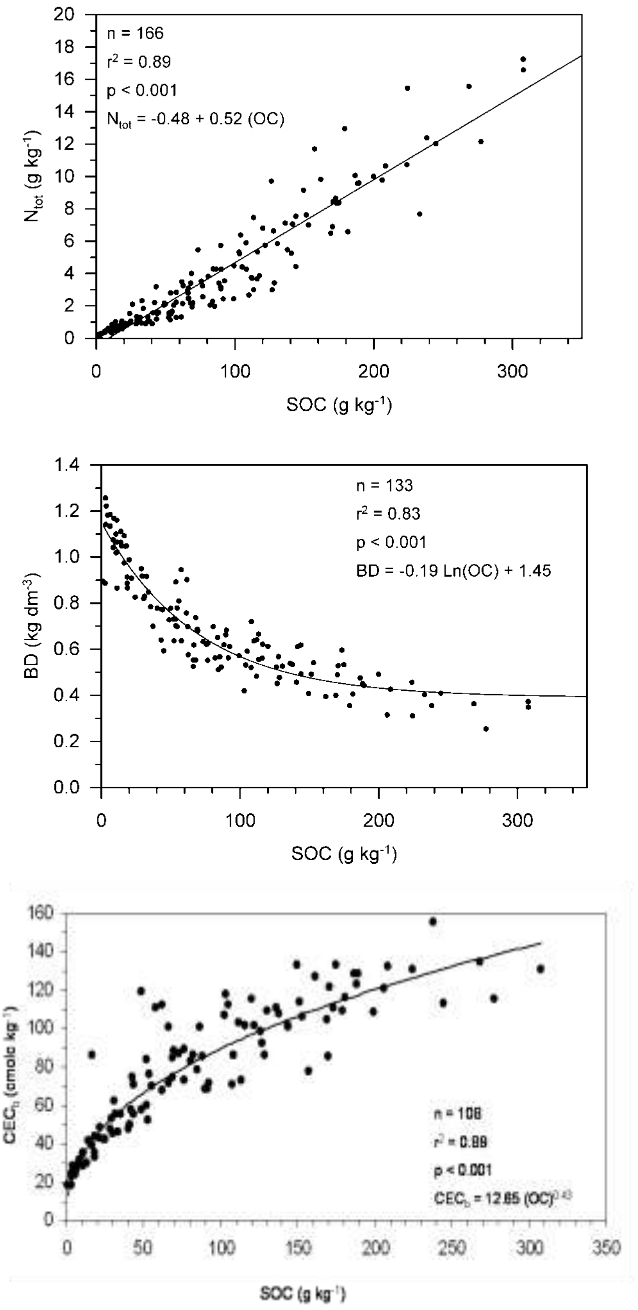


Figure 5: Relationships of SOC (g kg^{-1}) with N_{tot} (g kg^{-1}), BD (kg dm^{-3}) and CEC_b (cmolc kg^{-1}).

The lowest and highest OC contents of the uppermost horizons (Oa or Ah) are with forest vegetation 61.7 – 307.8 g kg^{-1}. With the exception of the buried horizons they decrease almost regularly with depth. The weighted averages of OC in the top 50 cm (OC_{wa50}) comprising Oa and mineral horizons and excluding Oi and Oe horizons show a wide variation for grassland (G, GS and P) and forest soils (F) with 70 – 177 and 30 – 178 g kg^{-1}, respectively. Both shrubland pedons (S1, S2) have relatively low OC_{wa50} with 80 and 96 g kg^{-1}, the two soils in forest patches (FP1, FP2) contain 126 and 175 g kg^{-1} and the bog-like soil (B) 155 g kg^{-1}. It should be noted that the four soils with thicknesses ≤ 32 cm have relatively high weighted averages of OC with 128 (PP1), 148 (G3), 153 (GS1) and 178 g kg^{-1} (F5). The C : N ratios of the topsoil horizons increase with depth and vary between 13 and 47.

Almost all soil samples have pH (H_2O) 4 – 5 and pH (KCl) 3.5 – 4.5. Values of ΔpH (pH H_2O - pH KCl) mostly vary from 0.4 – 0.9. The moderate to strong acidity is in accordance with very small concentrations of exchangeable bases (Ca: 0.1 – 2.8 cmolc kg^{-1}, K: 0.1 – 0.9 cmolc kg^{-1}, Mg: 0.1 – 2.6 cmolc kg^{-1}, Na: 0.1 – 0.5 cmolc kg^{-1}). The values for the sum of exchangeable bases (SEB) are low, and in the uppermost horizons (Oa or Ah) (0.6 – 5.7 cmolc kg^{-1}) they are higher than in the lower ones (0.1 – 1.1 cmolc kg^{-1}) because of the liberation of bases by the mineralization of organic matter. Consequently the effective cation exchange capacity measured at field pH (CEC_{eff} = sum of KCl-extractable Al and H, and SEB) is very low (2.9 – 19.8 cmolc kg^{-1}) and dominated by KCl-extractable Al, as indicated by the Al/CEC_{eff} ratios of 0.55 – 0.94 in the uppermost horizons (Oa or Ah) and 0.83 – 0.97 in the lower horizons. Compared with that, the potential CEC (CEC_b) values are much higher (18.3 – 155.2 cmolc kg^{-1}) and closely related to the OC content. Only in deep subsoils relatively high CEC_b values are found despite having low OC contents (e.g. Bw4 and Bw5 of P1 and Bw2 to Cw of PP2).

Phosphate retention ranges from 34.7 % to 99.5 %. It is > 82 % in the uppermost horizons (Oa or Ah) of grassland (G, GS, P) and shrubland (S), whereas in uppermost horizons of forest soils (F, FP) a variation of 50 to 87 % is noticed.

The values of Al fractions (Al_o, Al_d and Al_p) are lowest in the uppermost horizons. Then they increase with soil depth, which is particularly strong for Al_p, and decrease again in the lower subsoil horizons. Most uppermost horizons have Al_d > Al_p and Al_o, whereas most lower top- and subsoil horizons show the following relationships: $Al_p > Al_d > Al_o$. Only three soils (GS2, PP2, B), which are located in basins, and a few subsoil horizons of other pedons have $Al_o > Al_d$. The concentration of KCl extractable Al (0.02 – 0.13 %) is low in relation to Al_p, Al_d and Al_o.

For Fe, the extractions with pyrophosphate (p), dithionite-citrate-bicarbonate (d) and acid oxalate (o) result for most soils in the following relationships: $Fe_d > Fe_p > Fe_o$. The uppermost horizons contain the lowest values for all fractions. Most soils show both, increasing values for Fe_p and Fe_o as well as higher Fe_p/Fe_o ratios with increasing soil depth. In contrast, the Fe_d value is not related to soil depth. The Fe_o/Fe_d ratios regularly decrease with increasing soil depth, except of some soils with buried horizons. Topsoils of *Araucaria* forest have clearly lower Fe_o and Al_o concentrations as well as lower Fe_o/Fe_d ratios than those of the grassland soils. All soils have very low concentrations of Si_o (< 0.4 %) and Si_d (< 0.6 %), whereas values of Si_p (< 3.5 %) were higher (data not shown).

The melanic index (MI) reflects the vegetation type from which the SOM originates and melanic indexes increases with decreasing $\delta^{13}C$ values (Figure 6). SOM with MI < 1.7 shows melanic characteristics and is typically formed under grassland, whereas MI $\geq$ 1.7 indicates fulvic characteristics and forest derived SOM. Both reflect highly humified organic matter, but the melanic characteristics differ from the fulvic ones by a lower ratio of fulvic acids to humic acids (Honna et al., 1988).

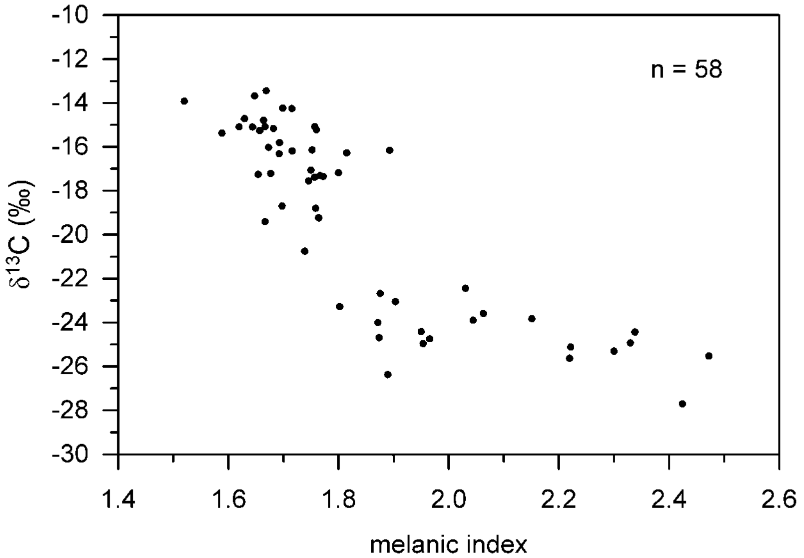


Figure 6: Relationship between $\delta\ ^{13}C$ values (‰) and melanic indexes (MI).

In the uppermost horizons (Oa or Ah) of all 27 soils the following MI indexes are found (Table 1, appendices): grassland and pine plantation: 1.5 – 1.8, *Araucaria* forest and patches: 1.9 – 2.6, shrubland: 2.0 - 2.2. Some grassland topsoil horizons show slightly higher MI values than the typical grassland value of < 1.7, which results from the input of shrub roots. The *Araucaria* forest site F5 on the forest border as well as the soils in patches of *Araucaria* forest (FP1, FP2) show decreasing melanic indexes with increasing soil depth. In soils with buried A horizons the MI is markedly lower in the first (F6, F7, F8, F10, S1) or second (S2) buried horizon (buried soils were only found in *Araucaria* forest and shrubland) compared to the overlying soils.

3.2 Discussion

3.2.1 Soil classification

All soils were classified according to the second edition of the World Reference Base for Soil Resources (WRB) (IUSS Working Group WRB, 2006). The identified diagnostic horizons and properties are listed in Table 1 (appendices). Table 3 shows the soil groups with ranges of phosphate retentions, Al_o + 0.5 Fe_o values and organic carbon contents of uppermost (Oa or Ah) and lower topsoil horizons and of the uppermost buried horizons. 21 of the 27 soils have andic properties in at least some layer. In 15 of them the andic properties reach the required thickness and start within the required depth for Andosols (see Introduction). In seven Andosols covered with grassland, shrubland and Pinus plantation the andic properties start directly at the soil surface without a litter layer (G2, G3) or below a litter layer (Oi and Oe horizons) (GS1, GS4, S1, S2, PP2).

Table 3: Ranges of phosphate retentions (P_{ret}), Al_o + 0.5 Fe_o values and organic carbon (OC) contents (values rounded) of uppermost (Oa or Ah) and lower topsoil horizons as well as uppermost buried horizons from Andosols, Umbrisols and Cambisols grouped according to the vegetation type.

	upper topsoil horizons			lower topsoil horizons			buried horizons			
	P_{ret} (%)	Al_o+ 0.5 Fe_o (%)	OC (g kg^{-1})	P_{ret} (%)	Al_o+ 0.5 Fe_o (%)	OC (g kg^{-1})	P_{ret} (%)	Al_o+ 0.5 Fe_o (%)	OC (g kg^{-1})	profiles
15 Andosols										
6 x grassland (G2, G3, GS1, GS2, GS4, PP2)	92 - 97	2.1 - 2.3	173 - 269	94 - 99	2.2 - 3.5	52 - 208	-	-	-	-
7 x *Araucaria* forest (F1, F2, F4, F5, F6, F8, FP2)	67 - 87	1.1 - 1.7	81 - 308	84 - 99	1.6 - 3.2	58 - 233	93 - 98	2.5 - 3.1	45 - 67	F6, F8
2 x shrubland (S1, S2)	87 - 93	2.0 - 3.2	108 - 141	87 - 97	2.2 - 4.4	77 - 128	94 - 97	2.6 - 3.4	49 - 84	S1, S2
11 Umbrisols										
6 x grassland (G1, GS3, GS5, P1, P2, PP1)	83 - 94	1.4 - 1.9	112 - 188	84 - 98	1.5 - 2.5	40 - 137	-	-	-	-
4 x *Araucaria* forest (F3, F7, F10, FP1)	54 - 85	0.8 - 1.7	62 - 224	71 - 96	2.0 - 2.4	116 - 141	95 - 97	2.4 - 2.9	41 - 84	F7, F10
1 x bog-like soil (B)	71	0.9	281	36 - 78	0.3 - 1.0	99 - 173	-	-	-	-
1 Cambisol										
Araucaria forest (F9)	50	1.0	90	-	-	-	-	-	-	-

In the grassland Andosol GS2 the andic properties start below an Oa horizon which fulfills all the criteria of andic properties except the maximum OC content. The other seven Andosols are under *Araucaria* forest (F1, F2, F5, F6, F8, F10, FP2). Above the andic properties they all have Oa and/or Ah horizons with lower $Al_o + 0.5\ Fe_o$ values (1.0 – 1.9 %), six of them having also lower phosphate retentions (66 – 84 %).

The melanic index (MI) was used to differentiate melanic from fulvic characteristics (see Table 1, appendices). Both reflect highly humified organic matter, but the melanic characteristics differ from the fulvic ones by a lower ratio of fulvic acids to humic acids and by the presence of a higher amount of A-type humic acids. Melanic characteristics are typically formed under grassland and fulvic under forest (Honna et al. 1988). The melanic horizon (IUSS Working Group WRB, 2006) requires in addition to a $MI < 1.7$ Munsell values and chromas, moist, of 2 or less. For the fulvic horizon it is sufficient to have a $MI \geq 1.7$ or a chroma or value of more than 2. Moreover, the melanic and fulvic horizons require a weighted average of 6 % or more organic carbon (OC) and 4 % or more OC in all parts as well as a cumulative thickness of 30 cm or more with less than 10 cm of non-melanic or non-fulvic material in between, respectively, and, of course, the presence of andic properties throughout. Following these criteria, three Andosols have a melanic horizon (GS4, FP2, PP2) and seven have fulvic horizons (G3, S1, S2, F1, F2, F6, F8). The remaining five Andosols have too low thicknesses for a fulvic horizon (F5, GS1), alternating MI values (G2, GS2) or too low OC contents (F10). Moreover, all Andosols are qualified as aluandic (IUSS Working Group WRB, 2006) due to low oxalate extractable Si ($Si_o < 0.6$ %) and high ratios of pyrophosphate extractable to oxalate extractable Al ($Al_p/Al_o \geq 0.5$). For each soil, lists of all applying prefix and suffix qualifiers according to WRB are given in Table 1 (appendices).

Eleven soils are classified as Umbrisols having an umbric horizon with an OC content ≥ 0.6 %, a base saturation < 50 %, a Munsell chroma ≤ 3 and value ≤ 3 when moist as well as a value ≤ 5 when dry, well developed structures with mostly granular or subangular blocky aggregates and a sufficient thickness. Six of them have andic properties for a certain depth range (G1, GS5, P2, FP1, F4, F7) starting in forest soils at greater depth than in grassland soils. Five are missing andic properties throughout (GS3, P1, F3, PP1, B), all failing the required concentrations of Al and Fe in acid oxalate. The water-saturated bog-like soil B, situated in a small basin, additionally fails the required phosphate retention and shows very small concentrations of oxalate, dithionite-citrate-bicarbonate and pyrophosphate extractable Fe and Al. On the other hand, every Andosol in our area has an umbric horizon. If the definition of Andosols were restricted to soils from recent volcanic materials all the Andosols presented here would key out as Umbrisols.

The soils of the area do not have spodic horizons. Some A horizons which belong to a second geological stratum (buried soils or not) have Al_o + 0.5 Fe_o contents which are more than the double of what is observed in an overlying horizon (F2, F3, F7, F10). But this is an effect of sedimentation and not of podzolization. Overlapping characteristics of Andosols and Podzols are well-known in the literature (Alexander et al., 1993; Aran et al., 2001; Bäumler et al., 2005).

The remaining soil F9 is a Cambisol having a cambic horizon from 8 to 58 cm and failing the acid oxalate and the phosphate retention requirements of andic properties throughout. F9 is characterized by the absence of a dark-coloured thick topsoil and very small values of Al_o + 0.5 Fe_o.

Figure 7 shows that phosphate retention is strongly related to the Al_o + 0.5 Fe_o value (R^2 = 0.79, $p < 0.001$, n = 164). Moreover it points out the higher phosphate retentions of grassland uppermost horizons (Oa or Ah) compared to those of Araucaria forest and that buried horizons of *Araucaria* forest and shrubland soils meet the andic criteria.

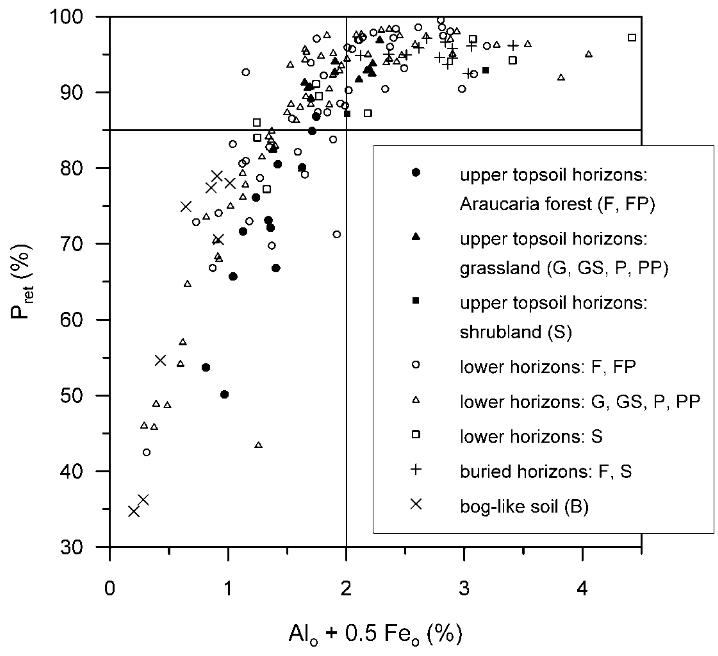


Figure 7: Relationship between phosphate retention (%) and Al_o+0.5 Fe_o (%).

3.2.2 Soil forming processes and the origin of andic properties

The soils of Pró-Mata originate from acid to intermediate rhyodacite and developed under a highland climate with high rainfalls. The intense status of weathering is reflected by high contents of clay dominated by kaolinite and chloritized 2:1 minerals as well as by the absence of primary silicate minerals. The climate led to small concentrations of exchangeable bases and high Al saturations, which all agree with the low pH. Several soil properties as high potential CEC and low bulk densities are strongly related to the high content of organic matter. Thus, a key process for the development of the andic properties is the accumulation of organic matter. Taking into account the originally high content of weatherable minerals in rhyodacite and the high weathering status, it can be concluded that high amounts of Al had been released, which then interacted with the organic phase leading to a stabilization of organic matter. The inhibition of humus mineralization by formation of organo-metallic complexes, particularly of Al and Fe with organic compounds, is well documented (Broadbent et al., 1964; Martin et al., 1966; Blaser & Klemmedson, 1987; Oades, 1988).

Phosphate retention is highly correlated to the amount of non-crystalline Al and to a lower degree also to non-crystalline Fe oxides (e. g. ferrihydrite), which are determined by acid oxalate extraction (o). Oxalate extraction estimates the amount of total non-crystalline Fe (Schwertmann, 1964) and Al, including Fe and Al bonded to humus, Al in allophane and imogolite, as well as Al and Fe in non-crystalline hydroxides and oxyhydroxides (Wada, 1977; Wada, 1980; Mizota & Wada, 1980). Most topsoils with $Al_o + 0.5\ Fe_o \geq 1.6$ % have phosphate retentions ≥ 85 % which indicates that other forms of active Al and Fe than those which are extractable by oxalate treatment are contributing also to the high phosphate retention. Pyrophosphate is an even more effective extractant of Al and Fe bound to humus but much less effective for the other forms (Wada, 1977; Higahsi & Shinagawa, 1981; Mizota and van Reeuwijk, 1989). Pyrophosphate extractable Al and Fe values exceeding oxalate-extractable Al and Fe values have been reported several times for nonallophanic Andosols (Wada et al., 1986; Bäumler & Zech, 1994; Egashira et al., 1997). Therefore Al_p/Al_o ratios are frequently used to estimate the relative proportions of the different kinds of active Al. The high Al_p/Al_o ratios (1 - 2) of most topsoils in Pró-Mata can be interpreted as evidence of the predominance of Al-humus complexes rather than of short range order minerals, which would lead to much lower Al_p/Al_o ratios of 0.1 – 0.4 (Nanzyo et al., 1993). In nonallophanic Andosols with pH (H_2O) below 4.9 the ratio of Al_p/Al_d is mostly greater than 0.9 (Shoji & Fuiwara, 1984) because of the stable complexes Al^{3+} ions form with soil organic matter (Shoji et al., 1982), which is coincident to the strongly acid soils with high Al_p/Al_d ratios (> 1). Additionally, hydroxyl-Al-organic complexes as well as ill-defined alumosilicate complexes, from which some Al is also extracted by pyrophoshate, can develop depending on the concentrations of humic substances (Huang, 1991). The presence of Al phases similar to hydroxyl-Al in soils, where intense weathering caused depletion of silica, is also reported by Wada and Wada (1976). Formation and stability of allophanes and imogolites is limited to pH (H_2O) > 4.9 (Shoji & Fujiwara, 1984) or, as stated by Wada (1989), from 5 to 7. Shoji et al. (1985) found that in nonallophanic Andosols with clay fractions dominated by chloritized 2:1 minerals, Al_o consists largely or wholly of Al complexed with humus. On the other hand, it is reported that pyrophosphate may release not only Al bonded in humus complexes but also some Al from mineral compounds (Higashi et al., 1981). Kaiser and Zech (1996) indicated that pyrophosphate due to alkaline dissolution may extract some Al from Al hydroxide phases and peptized Al hydroxides associated with organic matter. It cannot be excluded that in Pró-Mata even some Al from gibbsite may be extracted by pyrophosphate. Additionally, high Fe_p/Fe_o ratios (0.9 – 1.6) of most topsoils in Pró-Mata suggest that Fe may also be present to some extent in metal-humus complexes. But as Fe seldom forms complexes with humus, it cannot be excluded that pyrophosphate disperses also some poorly crystalline or even finely divided crystalline Fe oxides (Jeanroy & Guillet, 1981).

Dithionite-citrate-bicarbonate (DCB) also extracts various forms of Al and Fe in soils, such as from humus complexes, allophane-like constituents and hydrous oxides (Wada, 1977). Contrary to the other extractants, the latter may be to a greater extent in crystalline forms. The stronger increase of pyrophosphate extractable Al and Fe compared to dithionite extractable Al and Fe from the upper topsoil horizons to the horizons below with lower OC contents (Table 1, appendices) reflects the low complexing ability of litter and young humus for Al and Fe, which increases with time or humification and therefore with depth as stated by Wada and Higashi (1976). That in many soils the Al_o and Fe_o values are highest in the upper horizons is due to the inhibitory effect of organic compounds on the crystallization of minerals (Schwertmann, 1966; Shoji & Ono, 1978; Huang, 1991). This is especially the case for grassland soils which will be discussed later. In BA or B horizons with low OC contents the Al_p and Fe_p values decline stronger than those of the other Al and Fe species but there is no clear relation between the concentrations of Al_p and OC contents ($R^2 = 0.20$, $p < 0.001$, $n = 164$) as shown by Figure 8. Thus, the type of strongly humified substances rather than the amount of organic matter determines interactions between humus and different forms of active Al and Fe. Shoji and Ono (1978) showed that phosphate retention of nonallophanic Andosols with clay fractions dominated by chloritized 2:1 minerals is closely related to Al_d. The results from this study indicate that the relation of P retention is strongest with both, Al_o ($R^2 = 0.82$, $p < 0.001$, $n = 164$) and Al_d ($R^2 = 0.78$, $p < 0.001$, $n = 164$), and slightly less strong with Al_p ($R^2 = 0.71$, $p < 0.001$, $n = 164$) (Figure 8). For Fe the relation of P retention ($p < 0.001$, $n = 164$) is strongest with Fe_p ($R^2 = 0.54$), followed by Fe_o ($R^2 = 0.46$) and is lowest with Fe_d ($R^2 = 0.21$).

Almost all horizons of the soils show low contents of Si_d and only traces of Si_o, confirming the absence of allopohane and imogolite (Shoji et al., 1985). In contrast, Si_p values were considerably higher suggesting that some Si released by weathering is bound to humus, too.

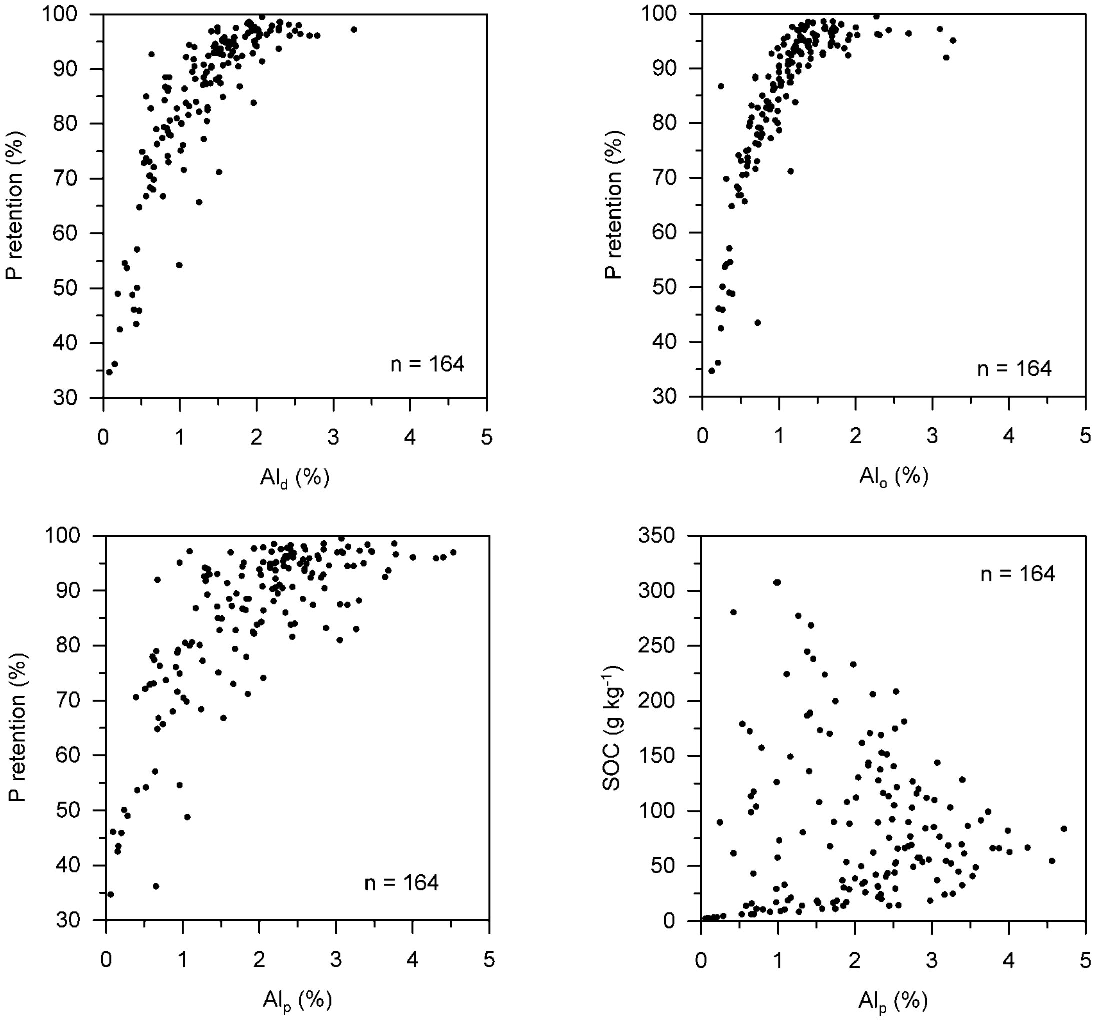


Figure 8: Relationships of phosphate retention (%) and SOC (g kg^{-1}) with Al_d (%), Al_o (%) and Al_p (%).

The topsoil horizons under *Araucaria* forest, where the organic matter is mainly derived from trees, do not exhibit andic properties. Generally, they have clearly lower Fe_o and/or Al_o concentrations, lower Fe_o/Fe_d ratios, and lower phosphate retentions than the upper topsoil horizons of the grassland soils. But the Fe_d concentrations are in the same range. This indicates that under forest crystallization of Fe (and Al) oxides seems to be easier than under grassland. A better aeration of the forest soils may contribute to crystallization. Burgert (2001) studied the water potentials in Pró-Mata soils for 100 days. For a depth of 40 cm he compared forest and non-forested areas and found markedly lower values in the forest for the whole time. That may reflect an ongoing process of losing andic properties with forest spreading. The depth where the andic properties start depends on the age of forest invasion and goes along with two other alterations: The soil colour changes from black into dark brown and the melanic index rises. The two soils in patches of *Araucaria* forest (FP1, FP2) and two other at the border of the *Araucaria* forest (F4, F5) show up that changes at 10 – 15 cm from the soil surface, whereas the three other *Araucaria* forest soils have it at greater depth.

4 SOIL ORGANIC MATTER AS INDICATOR OF VEGETATION CHANGES

4.1 Results

4.1.1 $^{13}C/^{12}C$ isotopic signatures

All measured woody plants have $\delta^{13}C$ values characteristic of C_3 plants and all grasses are C_4 species (Table 4, appendices). The principal gramineous species of the grasslands at Pró-Mata is *Andropogon lateralis* (Bertoletti and Teixeira, 1995) with a $\delta^{13}C$ value of -12.3 ‰ (stems). This value corresponds well with the mean $\delta^{13}C$ value of grass samples for stems and roots (-12.7 ‰ ± 0.7 ‰, n = 8). Needle and wood tissues of *Araucaria angustifolia* have higher $\delta^{13}C$ values (-24.8 ‰ ± 1.2 ‰, n = 4) than leaf and wood tissues of deciduous trees (-31.8 ‰ ± 1.4 ‰, n = 21). The mean differences between leaf and wood tissues for deciduous trees and shrubs are small (0.2 - 0.4 ‰) compared to the differences between needles and wood for *Araucaria angustifolia* (2.0 ‰) and *Pinus taeda/elliottii* (3.2 ‰).

The organic surface layers (Oi and Oe horizons) of *Araucaria* forest, patches of *Araucaria* forest, shrubland and pine plantation have similar mean $\delta^{13}C$ values (-28.7 ‰ ± 0.7 ‰, n = 8), while those from grasslands with shrubs amount to -20.0 ‰ (Table 5, appendices).

Low free light fraction (LF) $\delta^{13}C$ values of soils in *Araucaria* forests and patches (-26.9 ± 0.8, n = 23) reflect the characteristic input of organic matter by C_3 trees (Figure 9). In *Araucaria* forest soils at the forest border and in patches (F5, FP1, FP2) the $\delta^{13}C$ values of the LF are 5.3 to 11.6 ‰ lower compared to those of the organo-mineral fractions for the whole depth range below the surface horizons. This confirms their development on grassland. The LF of the shrubland soil S1 has $\delta^{13}C$ values (-28.2 ‰ to -25.8 ‰) similar to those of the *Araucaria* forest soils indicating the below-ground input of organic matter from C_3 shrubs and/or trees. In grassland soils, the $\delta^{13}C$ values of LF fractions are 10.5 ‰ higher on average compared to those in Araucaria forest and shrubland soils.

The pedons of the *Araucaria* forest with $\delta^{13}C$ values of the organo-mineral fraction from -27.7 to -22.2 ‰ clearly differ from grassland soils with -18.7 to -14.3 ‰ (whole depth ranges from the Oa or Ah horizons to the subsoils; Figure 9). An exception is the soil at the forest border (F5) which shows strongly increasing $\delta^{13}C$ values from -24.4 to -17.4 ‰ with depth. The two soils in patches of *Araucaria* forest FP1 and FP2 have similar increases of -24.7 to -17.2 ‰ and -25.0 ‰ to -15.8 ‰ in the top 50 – 60 cm, respectively. All three match grassland $\delta^{13}C$ values in the subsoils. The two pedons in the pine plantation have $\delta^{13}C$ values (-16.4 to -13.5 ‰) similar to grassland soils in the whole solum below the organic surface layer (Oi and

Oe horizons). The high difference between the mean $\delta^{13}C$ value of *Araucaria* forest species and grasses (ca. 17 ‰) is maintained to a lower degree in the surface horizons (Oa and Ah1: 9.4 ‰) between soils in *Araucaria* forest (incl. patches) and grasslands with or without shrubs (incl. pine plantation soils). Below the surface horizons these differences become continuously smaller with increasing soil depth.

The *Araucaria* forest soils at the forest border and in patches (F5, FP1, FP2) show the highest increases of $\delta^{13}C$ values (4.2 to 5.3 ‰) between Oa horizon and the horizon below. For *Araucaria* forest soils which are located deeper inside the forest (F1, F6, F10), the increase of $\delta^{13}C$ values is less strong and their values range between -23.7 to -22.2 ‰ at 50 - 60 cm depth. Only F10 has a remarkable increase from the Bw horizon (-25.5 ‰) to the underlying buried 2Ahb horizon (-22.5 ‰). The $\delta^{13}C$ values of the organo-mineral fraction of the shrubland soil S1 vary in the same range (-25.6 to -23.5 ‰) as those of the *Araucaria* forest soils (F1, F6, F10) and also tend to become more positive with increasing soil depth.

Grassland soils differ strongly from all others in their organo-mineral fraction $\delta^{13}C$ values of the surface horizons (Oa and Ah1), and soils with shrubs have lower values (-18.7 to -17.2 ‰) than those without (-16.1 to -14.3 ‰). Further, one of the two grasslands with shrubs (GS4) shows much lower values in the LF (-24.0 to -19.2 ‰) than in the organo-mineral fraction (-18.7 to -14.7 ‰). G1 (grassland without shrubs) shows the highest organo-mineral fraction $\delta^{13}C$ values with -14.3 to -15.4 ‰ and only small variations with soil depth. The proportion of SOC derived from C_4 sources was calculated by mass balance (equation 3, see chapter 2.6.1) (Table 5, appendices) and is largest in pine plantation (> 81 %) and grassland (63 – 97 %) soils, and lowest in *Araucaria* forest (F1, F6, F10) with 0 – 38 % and shrubland (12 – 28 %). Both soils in *Araucaria* forest patches (FP1, FP2) and the soil at the forest border (F5) show the largest variation with 17 – 85 % SOC derived from C_4 sources. Generally, the contribution of C_4 sources is largest in the subsoil.

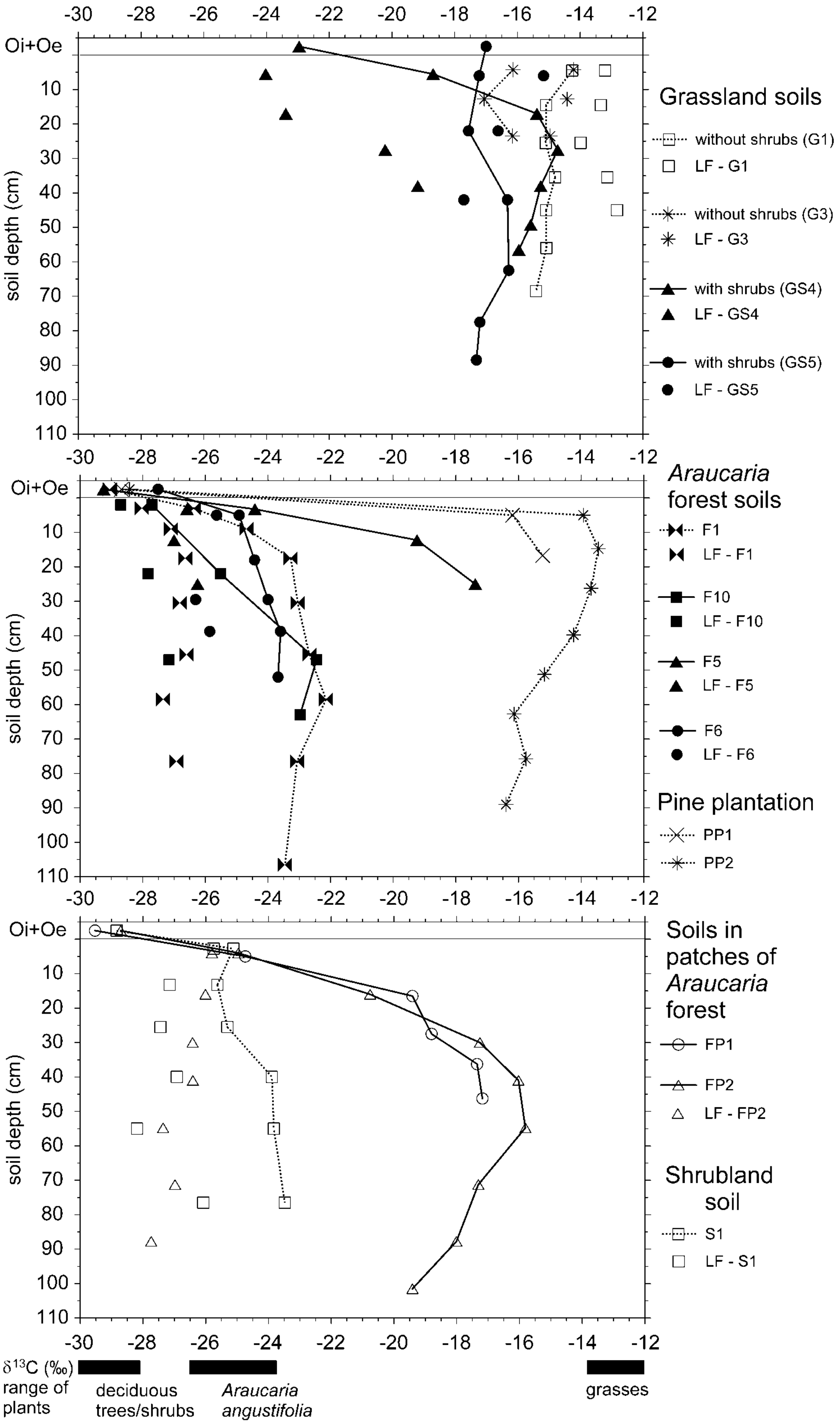


Figure 9: δ^{13}C values (‰) of organic surface layers (Oi+Oe), organo-mineral soil fractions and light fractions (LF) for 13 soils in grassland, *Araucaria* forest and *Araucaria* forest patches, Pine plantation and shrubland.

4.1.2 ^{14}C ages

All radiocarbon ages of surface horizons (Oa and Ah1) are younger than 1950 AD (> 100 % pMC; Table 5, appendices) indicating the dominance of bomb carbon and of rapidly cycling constituents (Trumbore et al., 1995). The ^{14}C error amounts to 20 – 45 yr BP for all samples. Below the surface horizons all soils show a consistent and strong increase of radiocarbon ages (Figure 10) which is strongly correlated with soil depth ($R^2 = 0.96$, $n = 23$, $p < 0.001$). The regression includes three radiocarbon data from a soil under grassland near the city of São Francisco de Paula from Behling et al. (2001) which is located more inland about 35 km from Pró-Mata. Contrary to all others, the *Araucaria* forest soil F1 shows only a slight increase with depth. It is found on a ridge and shows the youngest SOM radiocarbon ages throughout its depth compared to all other soils.

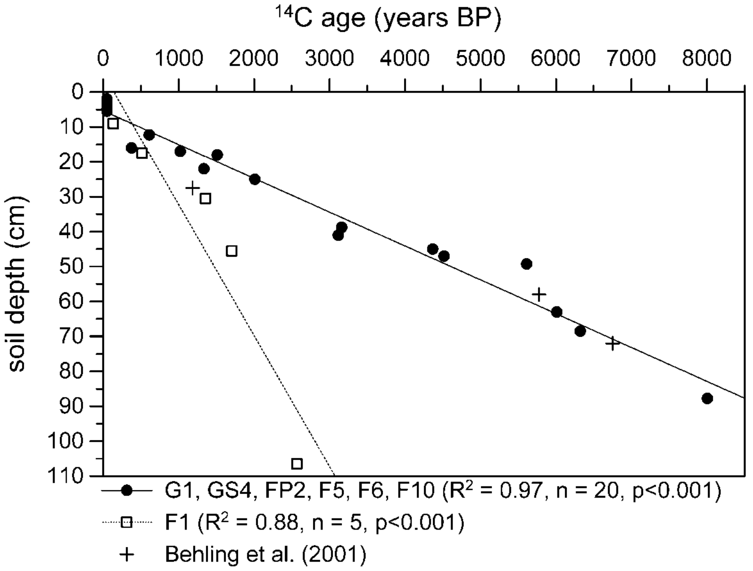


Figure 10: Depth profile of radiocarbon ages (years BP) including three radiocarbon values from a soil near the city of São Francisco de Paula analysed by Behling et al. (2001).

For the depth range of 7 – 24 cm radiocarbon values are available for five soils without buried horizons (Figure 11). SOM is clearly older in the grassland soil with shrubs GS4 (1020 yr BP, 11 – 23 cm) than in the *Araucaria* forest soils F1 (515 yr BP, 12 – 23 cm) and F5 (610 yr BP, 7 – 17 cm) and the forest patch soil FP2 (375 yr BP, 8 – 24 cm). The highest ^{14}C ages of SOM are found in the subsoils of grassland G1 with 6320 years BP (62 – 75 cm) and the patch of *Araucaria* forest FP2 with 8005 yr BP (79 – 96 cm), whereas the SOM of the *Araucaria* forest soil F1 in the 89 – 124 cm layer is only 2565 years BP old. There are two soils in the *Araucaria* forest with buried horizons (F6 and F10), which are characterized by relatively high ages, especially in the buried horizon. F6 has in the buried horizon (33 – 45 cm) with 3160 yr BP a radiocarbon age similar to that of FP2 in 36 – 46 cm depth (3115 yr BP) and from 10 – 26 cm with 1510 yr BP it is even older than GS4. F10 shows strongly increasing radiocarbon ages from the Bw1 (4 - 40 cm) to the buried 2Ahb (40 – 54 cm) from 1335 to 4515 yr BP.

4.2 Discussion

4.2.1 Grasslands and shrub encroachment

Soils in grasslands and pine plantations have $\delta^{13}C$ values (-18.7 to -13.5 ‰ – all horizons) near to those of C_4 grasses in the study area (-12.7 ‰ ± 0.7) and similar to those of soils in C_4 grasslands of the Brazilian Pantanal with -17.2 ± 0.6 ‰ (Victoria et al., 1995), in the Rio Grande Plains of southern Texas with -18 to -16 ‰ (Boutton et al., 1999), in C_4 grass-dominated ungrazed prairie in east-central Texas with -17 to -14 ‰ (Boutton et al., 1993), and they are comparable to the average $\delta^{13}C$ value for surface soils covered with C_4 grasslands and savannas throughout the world (-16.1 ± 2.2 ‰) as summarized by Victoria et al. (1995). The SOC is derived predominantly from C_4 grasses throughout the grassland (63 – 97 %) and pine plantation (> 81 %) soils, with some contribution of SOC from C_3 shrubs (Table 5, appendices). This indicates that, as far it is possible to trace back, *Araucaria* forest never existed at these sites or it was present for insufficient time periods to produce significant changes of soil $\delta^{13}C$ values. The lacking imprint from pine trees on grassland-derived SOC after 15 years of afforestation is not surprising because of low needle-shedding and slowly degradable litter as indicated by wide C:N ratios of 57 – 60.

$\delta^{13}C$ values of plant tissues remain relatively constant during the early stages of decomposition because the effects of fractionation with up to 2 ‰ are small (Nadelhoffer and Fry, 1988; Balesdent et al., 1993; Boutton, 1996; Boutton et al., 1998). Wedin et al. (1995) reported only small changes of $\delta^{13}C$ values for litter from four grasses (0.6 – 1.5 ‰). The grassland soil with shrubs GS5 shows a small difference of 0.2 ‰ between the organic surface layer (Oi and Oe) and the Ah1 horizon indicating a stable composition of grasses and shrubs, whereas in the grassland soil GS4 the large increase of 4.3 ‰ from the organic surface layer (Oi and Oe) to the Oa horizon reflects a more recent shrub encroachment. This is confirmed by the proportions of C_3-derived carbon by contents (Table 5, appendices) and by stocks (Figure 11). The proportions by stocks strongly decrease in GS4 from the Oa to the Ah1. In GS5 the C stocks remain almost constant from 0 – 32 cm. For PP2 and G1 they indicate permanent pure grass cover, whereas at G3 without shrubs past contributions from shrubs or other C_3 plants are shown.

Depletion of ^{13}C with soil depth in C_4 grassland ecosystems is reported by several studies (Volkoff and Cerri, 1987; Martin et al., 1990; Gill and Burke, 1999; Sanaiotti et al., 2002; Henderson et al., 2004; Krull et al., 2005). The grassland soil G1 without shrubs shows 1.1 ‰ depletion of ^{13}C from 0 – 75 cm depth (Figure 9) and in the pine plantation soil PP2 the depletion amounts to 3 ‰ from 19 – 96 cm. One explanation for this phenomenon is the accumulation of ^{13}C-depleted lipids and/or lignins due to their relative chemical stability, while ^{13}C-enriched compounds (sugars, amino acids, hemicelluloses and pectins) are preferentially decomposed during the initial stages of SOM decomposition (Deines, 1980; Benner et al., 1987; Wedin et al., 1995; Boutton, 1996). It has been shown that chars derived from C_4 grasses are significantly ^{13}C depleted relative to the original plant source (Krull et al., 2003). This can explain the decrease of $\delta^{13}C$ values in a short depth interval for the grassland soils with shrubs (GS4 and GS5) of 1.3 ‰ (34 – 61 cm) and 1.0 ‰ (73 – 95 cm), as macroscopically visible charcoal was found in the same depth ranges (Table 5, appendices). Different rooting patterns between C_4 grasses and C_3 shrubs and trees may contribute to the ^{13}C depletion in some subsoils because grass roots have generally < 10 % of root biomass below 50 cm, whereas shrubs and trees have > 40 % below 50 cm (Jackson et al., 1996). The LF below the surface horizon can be considered mainly as root material. In grassland soils without shrubs it is slightly higher than the organo-mineral fraction and in grassland soils with shrubs it shows decreasing (GS5) or significantly smaller (GS4) $\delta^{13}C$ values. This contributes to a ^{13}C depletion at greater soil depth. With respect to vegetation changes this also indicates a higher sensitivity of the LF fraction than the organo-mineral fraction, which is probably due to the more rapid rates of C-turnover of LF compared to mineral-associated fractions as reported by Yamashita et al. (2006). The decrease of $\delta^{13}C$ values (3.6 ‰) of the soil FP2 in a patch of *Araucaria* forest from 63 - 106 cm depth is probably also to some extent an effect of deeply rooting trees.

We found remains of old fences around the shrubland area with the soil S1 showing that this shrubland has developed on grassland which was used for pasture. This is reflected by the $\delta^{13}C$ values of S1 which are similar to *Araucaria* forest soils, but show some irregularities. The large difference between organic surface layer (Oi and Oe) and surface horizon (Ah1) of 3.7 ‰ indicates a vegetation change in recent times from grassland to shrubland. The slight decrease in the Ah2 and BAwh may reflect the forest which probably was cleared for pasture. However, 25 – 28 % proportions of C_4-derived SOC in the buried A horizon and below indicate that the *Araucaria* forest had established on grassland before.

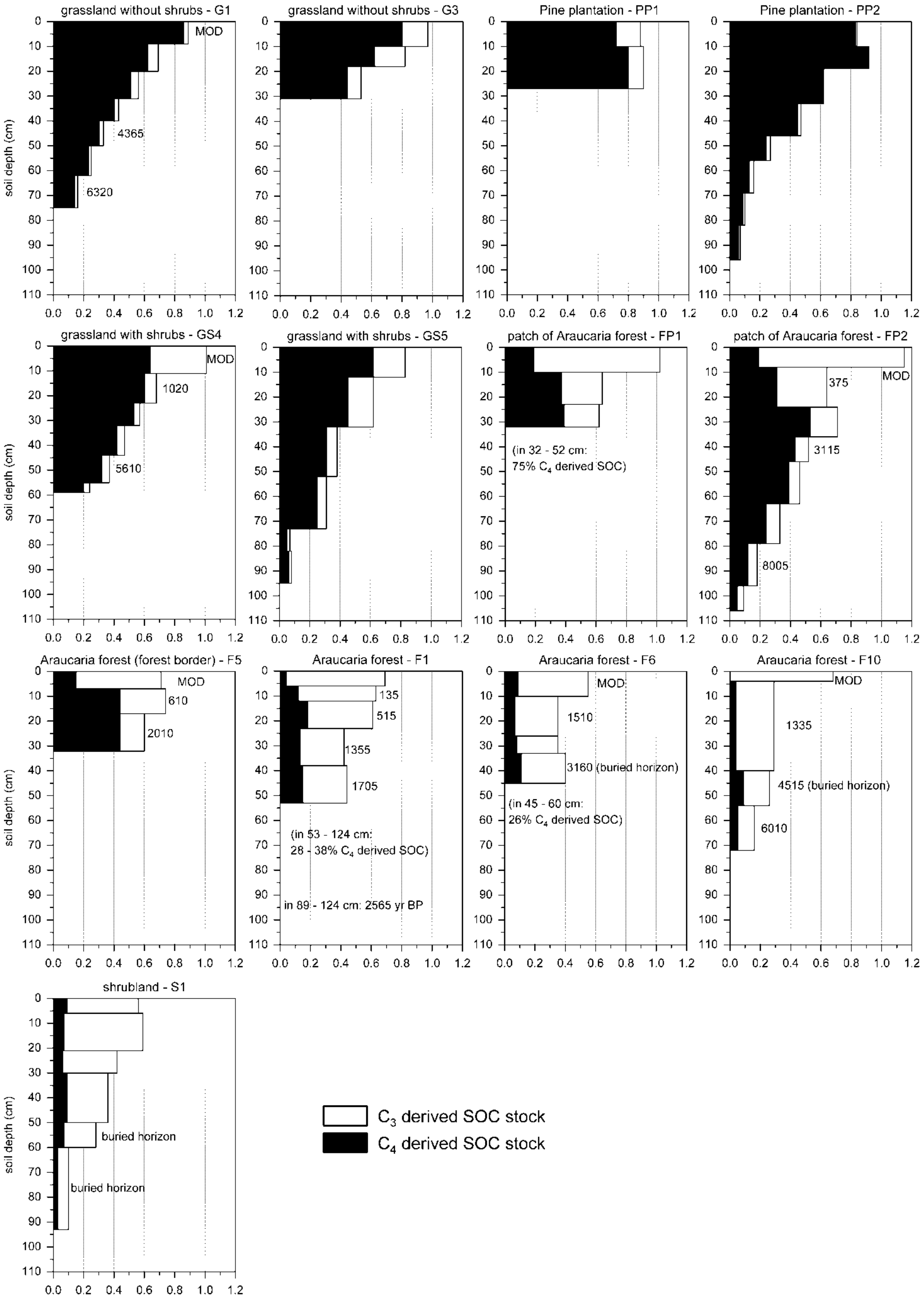


Figure 11: Depth distribution of C_4 and C_3 derived SOC stocks (kg m^{-2} cm^{-1}) calculated by mass balance (equation 3, see chapter 2.6.1). Numbers indicate radiocarbon ages expressed in years BP ± 20-45 BP (MOD = younger than 1950 AD).

4.2.2 Expansion of Araucaria forest on grassland

In soils with *Araucaria* forest, all recent organic input is completely C_3-derived as indicated by the low $\delta^{13}C$ values (Figure 9) for organic surface layers (-28.8 ‰ ± 0.9 ‰, n = 5) and LF (-26.9 ‰ ± 0.8 ‰, n =23). The enrichment of ^{13}C from the mean $\delta^{13}C$ value of leaves and wood of selected *Araucaria* forest species (-30.6 ‰) to the $\delta^{13}C$ values of litter layers amounts to 1.1 – 3.4 ‰ (Table 4, appendices). Thus, the organic surface layers reflect the varying composition of *Araucaria* forest, especially the alternating abundance of *Araucaria angustifolia* which has $\delta^{13}C$ values far higher than the other forest species. During the early stage of decomposition, changes of $\delta^{13}C$ values of woody plant litter are ≤ 0.7 ‰ (Boutton et al., 1998) which is confirmed by the organic surface layers from pine plantations with $\delta^{13}C$ values only 0.1 and 0.4 ‰ larger than those of pine needles.

The ^{13}C enrichments from the organic surface layers (Oi and Oe horizons) to the surface horizons (Oa or Ah) are clearly larger for the soils in *Araucaria* forest patches (FP1: 4.8 ‰, FP2: 3.8 ‰) and at the border of the *Araucaria* forest (F5: 4.8 ‰) than for F1 and F6 (2.7 and 2.5 ‰) which are deep inside the *Araucaria* forest (Figure 9 – no organic surface layers for F10). Further, these soils (FP1, FP2 and F5) have much higher proportions of C_4-derived SOC below the surface horizons (73 - 85 %; Table 5, appendices) and higher ^{13}C enrichments with soil depth (7.0 - 9.5 ‰) than those deep inside the forest (F1, F6 and F10) with increases of 4.2 ‰, 1.3 ‰ and 5.3 ‰, respectively. This indicates more recent forest expansion on grassland at the forest border (F5) and in patches (FP1, FP2). The continuously increasing proportions of C_4-derived SOC (6 - 38 %) with depth at F1 reflect the progressive replacement of old C_4 SOC by new C_3 SOC from the top downwards. In contrast, the rapid ^{13}C enrichment at F10 is attributed to the buried A horizon which still shows 35 % C_4-derived SOC indicating its origin from grassland vegetation. Because of the relatively high $\delta^{13}C$ value of the surface horizon, the soil F6 shows less sharp increases of $\delta^{13}C$ values with depth, but the proportions of C_4-derived SOC of 24 - 27 % in the buried horizons confirm their origin from grassland.

Generally, the increase of $\delta^{13}C$ values with depth is accompanied with soil darkening and decreasing melanic indexes in *Araucaria* forests and patches, which is also reported from other studies, where soils have lost within a relatively short period of time their black colour and melanic characteristics by spreading of deciduous forest on grassland (Golchin et al., 1997b; Higashi et al., 1999; Caner et al., 2003).

Thus, all *Araucaria* forest soils as well as the shrubland soil (S1) clearly show contributions of C_4-derived SOC in the subsoil indicating former grassland. Consequently, the soil-inherent process of ^{13}C depletion with depth in soils under grassland and pine plantation (1 - 3 ‰) should be still effective in *Araucaria* forest soils by reducing the ^{13}C enrichment originated from the former C_4 vegetation. All these processes can lead to errors in estimating the C_3 and C_4-derived SOC by the standard mass balance equation (equation 3, see chapter 2.6.1). Therefore, the amounts of SOC derived from *Araucaria* forest (C_3) and grassland (C_4) were calculated in the *Araucaria* forest soils (equation 4, see chapter 2.6.1). This mixing equation diminishes the effects of isotope variation during C decay (Balesdent and Mariotti, 1996) and shows increasing differences with soil depth for the proportions of C_4-derived SOC compared with the standard mass balance. In most *Araucaria* forest soils the proportions of C_4-derived SOC are 2 – 6 % (in the buried horizons of F10 and the shrubland soil S1 even 15 – 16 %) higher than those which were calculated with the standard mass balance confirming the expansion of *Araucaria* forest on grassland.

4.2.3 Timing of vegetation history

Although the specification of a precise soil age is impossible, the combination of radiocarbon dates with $\delta^{13}C$ values provides a chronology of vegetation changes (Scharpenseel and Becker-Heidmann, 1992; Hsieh, 1994). Therefore, the radiocarbon ages were related with the calculated amounts of SOC stocks derived from grassland (C_4) and *Araucaria* forest (C_3) according to equation 3 (see chapter 2.6.1).

The high proportions of C_4-derived SOC stocks in the grassland soils G1 (88 – 97 %) and GS4 (84 – 93 % below the surface horizon) supply evidence for the dominance of C_4 grasses since at least 5610 - 6320 yr BP (Figure 11). The oldest SOC (8005 yr BP) is found in a patch of *Araucaria* forest (FP2) in 79 – 96 cm depth with 69 % of C_4-derived SOC stock. Behling et al. (2001) suggested by pollen analyses from a core for the highland region of São Francisco de Paula (35 km away from Pró-Mata) that during this period (7500 – 4000 yr BP) grassland dominated the landscape, facilitated by a climate markedly drier than today with probably a 3 month dry season.

In the surface horizon (Oa) of GS4, the high ^{14}C concentration of 104 pMC (100 pMC = 1950 AD) and the low proportion of C_3-derived SOC stock (37 %) indicate that shrubs invaded this grassland site probably less than 50 years ago. This is in line with Martin et al. (1990) who reported that 52 – 70 % of SOC in the upper 10 cm turned over in 16 years after conversion of C_4 grasslands into savannas with C_3 trees.

Before at least 2000 and 3100 yr BP C_4 grasses also made up the major proportions of the vegetation at F5 and FP2 with 83 % (17 - 32 cm) and 73 % (36 - 46 cm) C_4-derived SOC stocks. SOC in surface-near horizons is clearly younger with 610 yr BP in F5 (7 - 17 cm) and 375 yr BP in FP2 (8 - 24 cm) and has higher C_3-derived SOC stocks with 59 % and 48 %, respectively. They are also younger than those from the grassland soil GS4 in comparable depths (11 - 23 cm: 1020 yr BP). Moreover, European settlers stabilized the grasslands by grazing and burning over the past 200 - 300 years (Rambo, 2000), and the forest was unable to further invade grasslands until its protection started in Pró-Mata in 1992. This indicates that forest invasion of F5 and FP2 started before 300 yr BP.

The lower C_4-derived SOC stocks in F1, F6 and F10 reflect an older establishment of forest on grassland compared to F5, FP1 and FP2. The *Araucaria* forest F1 is located on the upper slope of a ridge and has the youngest SOM radiocarbon ages throughout its depth compared to all other soils. Therefore, it can be assumed that this *Araucaria* forest developed on a truncated grassland soil, where after erosion of the topsoil again new grass-derived SOM was built up before the *Araucaria* forest invaded.

The *Araucaria* forest soils F6 and F10 have buried Ah horizons in the subsoils. Radiocarbon ages in the overlying parts are much lower than in the buried horizons. The ages of the latter are similar to those from G1 and FP2 at comparable depth ranges. The buried horizons have relatively higher proportions of C_4-derived SOC stocks than the overlying horizons. But even the latter have small proportions of C_4-derived SOC stocks indicating the establishment of grassland after the burial and/or the origin of the deposited material from soils with grassland cover. After the burial (directly or some time later) these sites were invaded by *Araucaria* forest as shown by the consistently large proportions of C_3-derived SOC stocks and the radiocarbon ages in the surface-near horizons of 1510 yr BP (F6, 10 - 26 cm) and 1335 yr BP (F10, 4 - 40 cm). If radiocarbon ages of the C_3 pools represent maximum ages, *Araucaria* forest invaded the grassland here after 1500 – 1300 yr BP. This rough estimation corresponds with the period of major forest expansion after about 1000 yr BP due to modern climatic conditions and high precipitation rates as reported by Behling et al. (2001). Further, the location deep inside the forest as well as the shorter distance to the steep brink of the highland support the assumed older ages of the *Araucaria* forest stands F6 and F10. It can be expected that the initial forest expansion started from the lowlands upwards to the highlands with increasing humidity and shorter dry periods.

Generally, the radicocarbon ages of soils at Pró-Mata are remarkably high which is emphasized by the comparison with the data compiled by Scharpenseel and Becker-Heidmann (1997). They reported mean radiocarbon ages in 100 cm depth of 16 Inceptisols (1160 yr BP), 9 Spodosols (2100 yr BP), 44 Vertisols (3650 yr BP), 13 Alfisols (4800 yr BP) and 47 Mollisols (5150 yr BP). The well base-saturated Mollisols as typical grassland soils show the highest radiocarbon ages. However, the here-presented Andosols and Umbrisols have still higher radiocarbon ages. This may is due to the large amounts of Al humus complexes which formed under strongly acid conditions because Al humus complexes are known to be particularly resistant to mineralization (Broadbent et al., 1964; Martin et al., 1966; Blaser and Klemmedson, 1987; Boudot et al., 1988; Oades, 1988). As the soils are high in both, organic matter and clay, the strong persistence of old C_4 pools in the *Araucaria* forest soils may also result from clay organic complexes. The old organic compounds do not easily exchange clay minerals with younger humus components (Scharpenseel and Becker-Heidmann, 1992).

4.2.4 Soil classification and vegetation pattern

The classification of 27 soils according to WRB (IUSS Working Group WRB, 2006) resulted in a mosaic of 15 Andosols, 11 Umbrisols and one Cambisol (Table 3). However, the chemical and physical analyses show that the soils differ in some properties not that much as their placement into different soil groups reflects. All have low bulk densities in the topsoil and with the exception of two (F9, B) all have high phosphate retentions at some depth.

The way the distribution of the Andosols and Umbrisols depends from the vegetation can only be understood by consideration of vegetation history. The melanic indexes (MI) depend directly from the vegetation. In the uppermost horizons (Oa or Ah) they have the following values (Table 1, appendices): grassland: 1.5 – 1.8, *Araucaria* forest: 1.9 – 2.6, shrubland: 2.0 – 2.2. In soils with buried A horizons the MI is lowest in the first (F6, F7, F8, F10, S1) or second (S2) buried horizon. (Buried soils were only found in *Araucaria* forest and shrubland and are all Andosols.) This is in agreement with the isotopic signature (Figure 6) and confirms that these buried soils have developed under grassland indicating the persistence of significant amount of grassland humus especially in the upper part of the buried soils. In the overlying soils predominantly tree-derived humus with higher MI values accumulated, and further down in the buried soils the remnants of old grassland humus decrease with depth and probably become outranged by recent input from tree roots. In these six Andosols the andic properties are always found in the buried soil. In the overlying soil it depends on the vegetation. While present in the two shrubland soils, under forest they are absent (F7) or present only in the layer directly overlying the buried soil (F6, F8, F10).

The *Araucaria* forest soil F5 lies on the forest border and shows like pedon FP2 in the patch of *Araucaria* forest the typical black colour of the grassland soils and decreasing melanic indexes with increasing soil depth, indicating that these forests recently invaded the grassland. It has been shown previously that, where deciduous forest spread onto grassland, the soils may lose in a relatively short period their black colour and their A-type humic acids (Golchin et al., 1997b; Higashi et al., 1999; Caner et al., 2003), which are typical for melanic characteristics (Honna et al., 1988). That the MI of some grassland soils is slightly higher than the typical grassland value of < 1.7 can be explained with the input of organic matter derived from shrubs. Also for the Andosol PP2 in the Pinus plantation the andic characteristics are related to the grassland which had been there before the afforestation 13 years ago. Obviously grassland favours in that environment the formation and permanence of andic properties.

5 ASSOCIATIONS BETWEEN SOIL ORGANIC MATTER COMPOSITION AND VEGETATION CHANGES

5.1 Results

5.1.1 Chemical composition of the above- and below-ground plant input

Solid-state CPMAS ^{13}C-NMR spectra from plant species are shown in Figure 12. Their intensity distributions are summarized in Table 6 (appendices). The spectra of all grass samples show comparable intensity distributions as reported for other C_4 grasses (Krull *et al.*, 2003; Dieckow *et al.*, 2005). They are characterized by high contributions of O-alkyl C (50 – 80 %) attributed to carbohydrate carbons in cellulose and hemicellulose. Their C2, C3, and C5 carbons cause resonances at 72 – 74 ppm, whereas the sharp signal at 105 ppm is characteristic for their anomeric C1 (Wilson *et al.*, 1983). The small shoulders at approximately 56 and 64 ppm indicate methoxyl C in lignin and hexose-C6 or pentose-C5, respectively (Wilson *et al.*, 1983) but can also be assigned to N-alkyl C as they occur in peptide structures (Knicker, 2000). Differences in the organic matter composition between plant species are detectable by the relative contributions of alkyl C. The C_4 grass *Andropogon lateralis* and both grass-mix samples have markedly lower alkyl C contents (8 – 12 %) than the leaves from the C_3 shrub *Baccharis uncinella* (30 %), those of the C_3 deciduous tree *Myrcia retorta* (16 %) and the needles from the C_3 conifer *Araucaria angustifolia* (23 %). In the alkyl C range, the signals between 29 – 32 ppm are typical for methylene C as they occur in fatty acids, suberin and cutin (Kögel-Knabner, 1997) but also for the amino acids. The signal at 21 ppm is attributed to terminal acetyl C.

In the aromatic C region the leaves from *Myrcia retorta* show resolved signals at 144 and 154 ppm which is often found for lignin from angiosperms (Gil & Pascoal Neto, 1999). These signals are also present in the spectra of the needles of the conifer *Araucaria angustifolia*. They can be attributed to C3 and C4 of the guaiacyl unit (144 ppm) and to C3 and C5 carbon of the syringyl unit at 154 ppm (Lüdemann and Nimz, 1973). On the other hand these split peaks are also characteristic for tannins and tannin-like structures (Lorenz *et al.*, 2000) and especially a signal around 145 ppm points to the contribution of tannins (Preston *et al.*, 1997). Other compounds that cause peaks in the aromatic C region (115, 126, 130 - 136) can be predominantly classified as lignin derived phenols and resonances at 172 ppm are attributed to carboxyl, amide and ester groups (Kögel-Knabner, 1997).

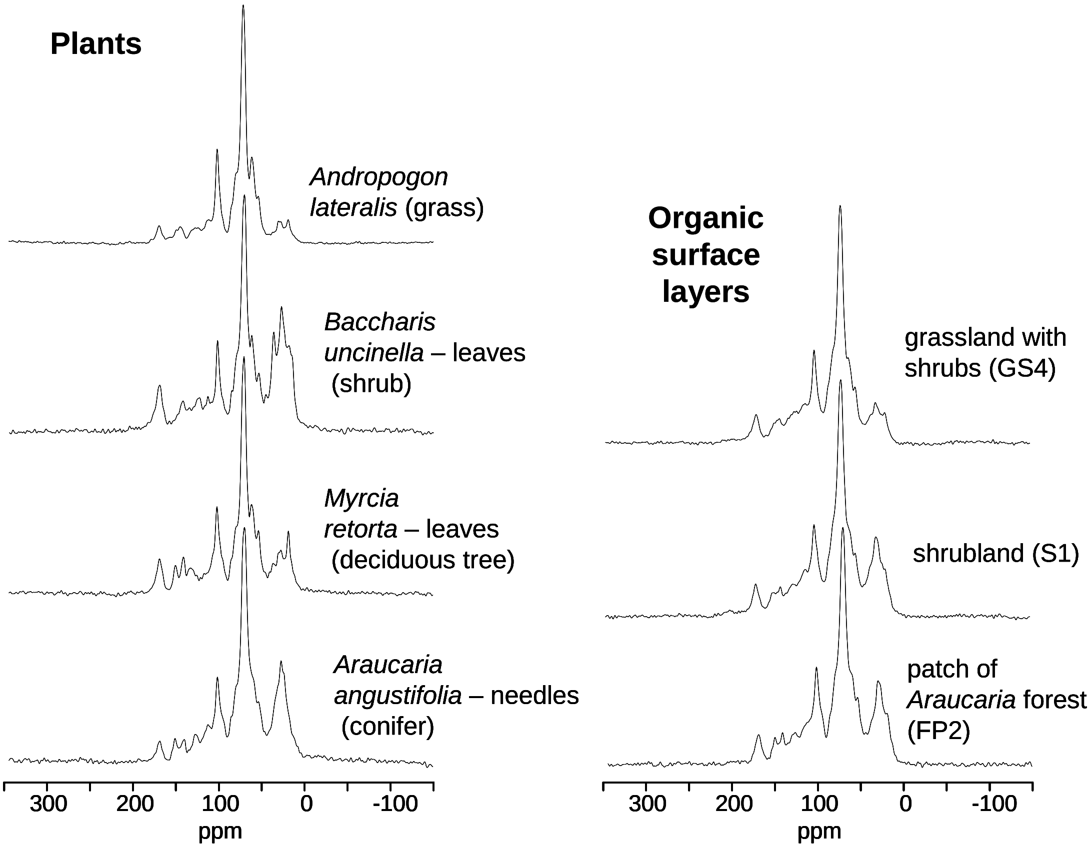


Figure 12: ^{13}C CPMAS NMR spectra from plant tissues and organic surface layers.

The proportions of the chemical shift regions of ^{13}C NMR spectroscopy for organic surface layers in *Araucaria* forest (Table 7, appendices) are in the range of those from tropical forests (Zech *et al.*, 1997) or temperate deciduous and coniferous forests. The main difference is that the needles from *Araucaria angustifolia* have relatively large proportions of alkyl C (23 %) compared to tree foliages and L-horizons (14 – 24 %) (Zech *et al.*, 1992; Baldock *et al.*, 1997; Rumpel *et al.*, 2002; Helfrich *et al.*, 2006). The spectra of the organic surface layers (Figure 12) show patterns which are comparable to those of the plant samples. In *Araucaria* forest (F-I, F-II, F-III) and shrubland (S) the spectra of the organic surface layers have similar intensity distributions (Table 7, appendices). They differ from the spectra of the organic surface layer of the grassland soil with shrubs (GS) by 7 – 11 % higher alkyl C and 6 – 11 % lower O/N-alkyl C proportions. Consequently, the (alkyl C)/(O/N-alkyl C) ratios are clearly larger for organic surface layers in *Araucaria* forest and shrubland than those from the grassland soil with shrubs. These (alkyl C)/(O/N-alkyl C) ratios are in the range recorded for the plant species as the three grass samples show lower ratios than the foliage of *Baccharis uncinella*, *Myrcia retorta* and *Araucaria angustifolia* (Table 6, appendices). The resolved signals at 144 and 154 ppm are still recognizable in the organic surface layers, but vanish in the spectra of the free light fraction (LF) of the *Araucaria* forest soils (spectra not shown). Similar to organic surface layers and plant samples, the (alkyl C)/(O/N-alkyl C) ratio is lower for LF from grassland soils (0.21 – 0.23) than those from *Araucaria* forest soils (0.42 – 0.54).

The yield of lignin-derived CuO oxidation products (mg VSC g^{-1} OC) and the proportions of vanillyl (V), syringyl (S) and cinnamyl (C) units differ between plant species (Table 6, appendices). Both grass samples show the largest contents of lignin-derived phenols which are dominated by C units as shown by the mean proportions of V, S and C units of 22, 28 and 50 %. In contrast, lignin from the conifer *Araucaria angustifolia* produces mainly V-type oxidation products (needle: 64 %, root: 87 %, wood: 96 %) and lignin from *Myrcia retorta* (leaves) is dominated by syringyl units (69 %). *Baccharis uncinella* (leaves) shows a more regular distributed lignin signature with proportions of V, S and C units of 24, 41 and 35 %. The organic surface layers in *Araucaria* forest show a large range of total lignin contents (12 – 33 mg VSC g^{-1} OC), whereas those in shrubland and grassland with shrubs have lignin contents of 21 and 23 mg VSC g^{-1} OC, respectively.

5.1.2 Chemical composition and soil lightness of heavy organo-mineral fractions

The heavy organo-mineral fractions from eight soils were grouped according to the $^{13}C/^{12}C$ isotopic signature as shown by Figure 13. The grassland soils G1 and GS4 (below the surface horizon) have consistently $\delta\ ^{13}C$ values typical for C_4 grasses. The soils at the forest border (F5) and in a patch of *Araucaria* forest (FP2) have strongly increasing $\delta\ ^{13}C$ values with soil depth. They match grassland $\delta\ ^{13}C$ values below 25 cm soil depth. These samples with high $\delta\ ^{13}C$ values from G1, GS4, F5 and FP2 represent the group with C_4 signature ($\delta\ ^{13}C$ value > -18 ‰, n = 13). All other *Araucaria* forest (F1, F6, F10) and shrubland (S1) soils clearly differ from grassland soils by lower $\delta\ ^{13}C$ values. They are the group with C_3 signature inclusive of the surface horizons of F5 and FP2 ($\delta\ ^{13}C$ value < -22 ‰, n = 13). Three heavy fractions from three different soils (GS4, F5, FP2) show intermediate $\delta\ ^{13}C$ values reflecting similar proportions of C_4- and C_3-derived organic matter. Therefore, they were outlined as C_4-C_3 transition ($\delta\ ^{13}C$ value of -18 to -22 ‰, n = 3).

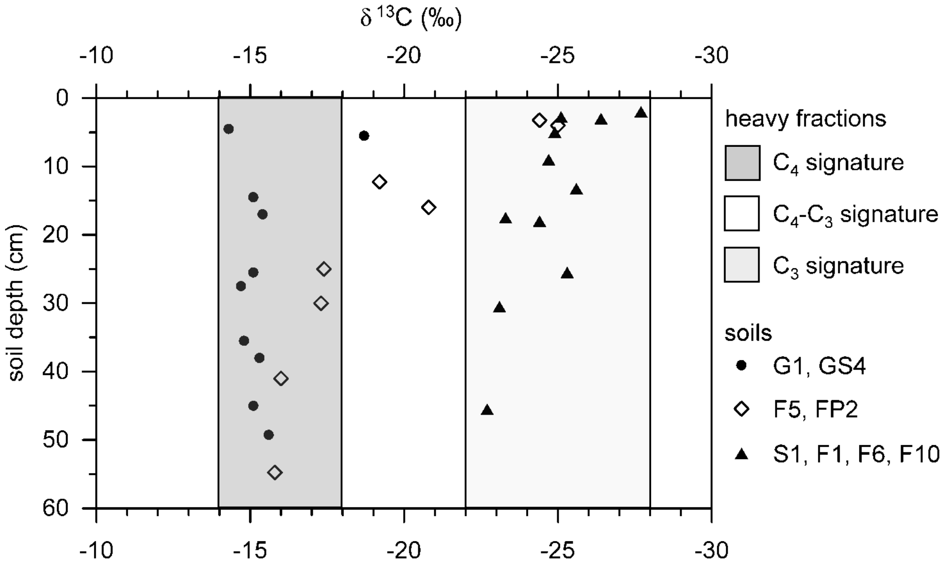


Figure 13: Grouping of heavy organo-mineral fractions according to the δ ^{13}C values: soils in grassland without (G1) and with shrubs (GS4), in a patch of Araucaria forest (FP2), at the Araucaria forest border (F5), in shrubland (S1) and deep inside the Araucaria forest (F1, F6, F10).

In spectra from heavy organo-mineral fractions the major signals are found at around 30, 72, 102, 128 and 172 ppm (Figure 14) as described for plant and organic surface layer samples. All surface horizons have markedly lower proportions of O-alkyl C associated with larger alkyl C and carboxyl C than the above-ground plant input (Table 7, appendices). Compared to grass samples and the organic surface layer from the grassland soil with shrubs (GS4) the signals at 56, 115 and around 145 ppm disappear in the spectra of the surface horizons of both grassland soils indicating degradation of lignin. In contrast, signals characteristic for lignin and/or tannin structures (56, 135 – 150 ppm) are still maintained in the spectra of the surface horizons of *Araucaria* forest (F1, F6, F10, FP2, F5) and shrubland (S1) soils.

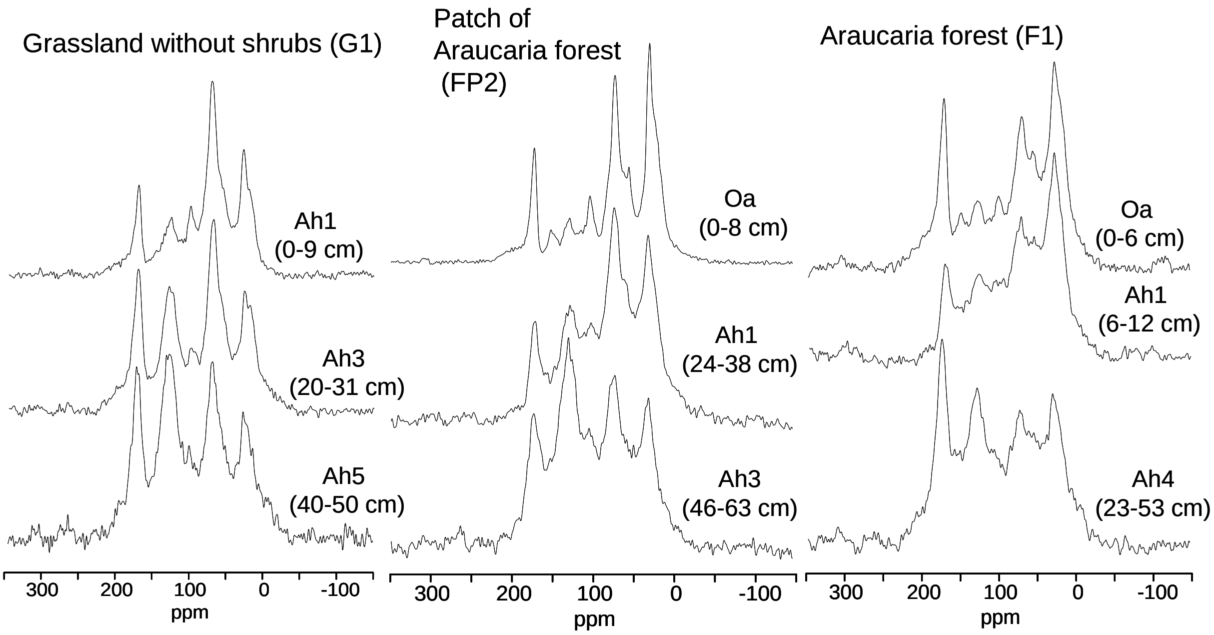


Figure 14: ^{13}C CPMAS NMR spectra of heavy organo-mineral fractions from soils in grassland without shrubs (G1), patch of Araucaria forest (FP2) and Araucaria forest (F1).

All soils show increasing C/N ratios and proportions of aromatic C with soil depth. This is particularly expressed for both grassland soils (G1, GS4) and the soil FP2 in a patch of *Araucaria* forest with up to 33 - 34 % aromatic C and C/N ratios of 40 – 43. The increase of aromatic C with soil depth is associated with decreasing O-alkyl and alkyl C contents, while carboxyl C shows irregular trends. Figure 15 reveals that heavy fractions of grassland soils with C4 signature generally have larger proportions of aromatic C as well as C/N ratios than those with dominating C3 signature formed by C3 trees or shrubs.

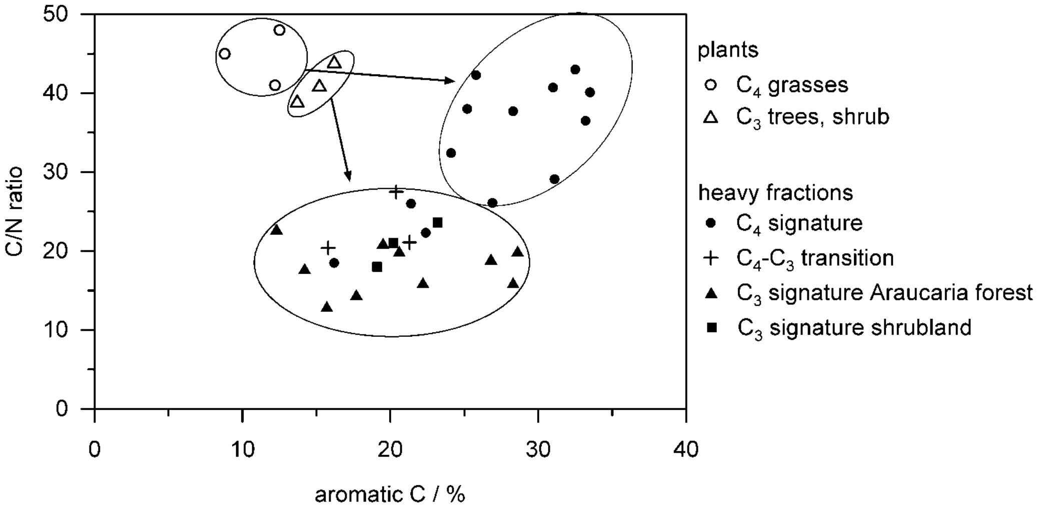


Figure 15: Relationship between the proportions of aromatic C (%) and C/N ratios for plants and heavy organo-mineral fractions.

In addition, organic matter with C_4 and C_3 signature shows different shifts of C/N ratios and proportions of aromatic C during the pathway from vegetation source to heavy fraction. There is a low decrease of C/N ratios and a strong increase of proportions of aromatic C from C_4 grasses to heavy fractions with C_4 signature. This is in contrast to the C_3 counterpart as C/N ratios strongly decrease and proportions of aromatic C slightly increase from trees and shrubs to heavy fractions.

Figure 16 shows that the calculated amounts of aromatic C (g kg^{-1}) determines the soil lightness values as latter decrease (become darker) with increasing aromatic C contents. The grouping according to the $^{13}C/^{12}C$ isotopic signature shows darker C_4- than C_3-derived heavy organo-mineral fractions at similar aromatic C content and there is no significant contrast between both regressions as revealed by the test of homogeneity of slopes (Table 8).

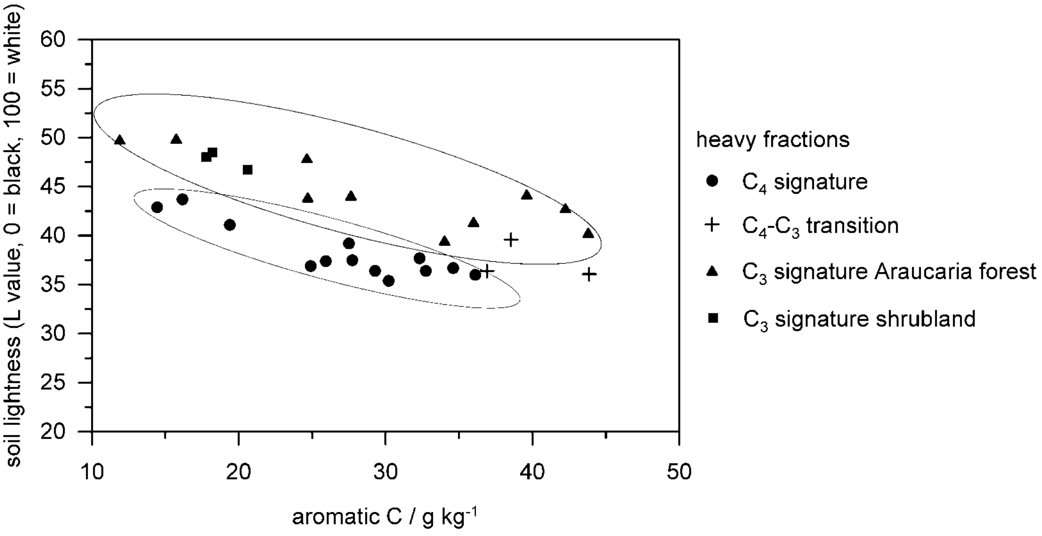


Figure 16: Relationship between concentrations of aromatic C (g kg^{-1}) and soil lightness values (L value, 0 = black, 100 = white) for heavy organo-mineral fractions.

The permanent grassland soil G1 without shrubs shows decreasing contents of O/N-alkyl and alkyl C with soil depth as well as (alkyl C)/(O/N-alkyl C) ratios of 0.5 in the whole solum. Shrub cover at the grassland soil GS4 cause larger alkyl C and lower O/N-alkyl C contents (each 5 %) in the surface horizon compared to G1. In the horizons below, the (alkyl C)/(O/N-alkyl C) ratio of GS4 decreases from 0.7 to 0.4 – 0.5. The surface horizons of *Araucaria* forest and shrubland soils also differ from those of G1 by larger (alkyl C)/(O/N-alkyl C) ratios (Table 7, appendices), whereas carboxyl and aromatic C contents vary independent from vegetation type. Below the surface horizon, the soils at the forest border (F5) and in the forest patch (FP2) have (alkyl C)/(O/N-alkyl C) ratios similar to G and GS. In contrast, the *Araucaria* forest soil F6 which is located deeper into the forest and the shrubland soil (S1) have (alkyl C)/(O/N-alkyl C) ratios of 0.7 – 0.8.

Table 8: Equations and test for homogeneity of slopes for the regression models of Lvalue and aromatic C (g kg^{-1}) for heavy fractions with C_4 and C_3 signature.

model	R^2	significance of overall fit	p-value for slope	95 % confidence interval of slope		standard errors on coefficients	significance of contrast between models
				lower bound	upper bound		
L $value_{C3}$ = -0.29aromatic C + 53.1	0.75	$p \leq 0.001$	$p \leq 0.001$	49.9	56.3	0.05	p = 0.875
L $value_{C4}$ = -0.35aromatic C + 47.7	0.79	$p \leq 0.001$	$p \leq 0.001$	44.4	51.0	0.05	

Figure 17 points out that the (alkyl C)/(O/N-alkyl C) ratios of grasses, light fractions and heavy fractions from C_4 grassland are smaller compared to source vegetation and heavy fractions from C_3 *Araucaria* forest and shrubland. Both, organic matter with C_3 and C_4 signature show increasing (alkyl C)/(O/N-alkyl C) ratios from source materials to the respective heavy fractions, whereas $\delta\ ^{13}C$ values move in the opposite directions as organic matter with C_3 signature shows ^{13}C enrichment and those with C_4 signature depletion of ^{13}C.

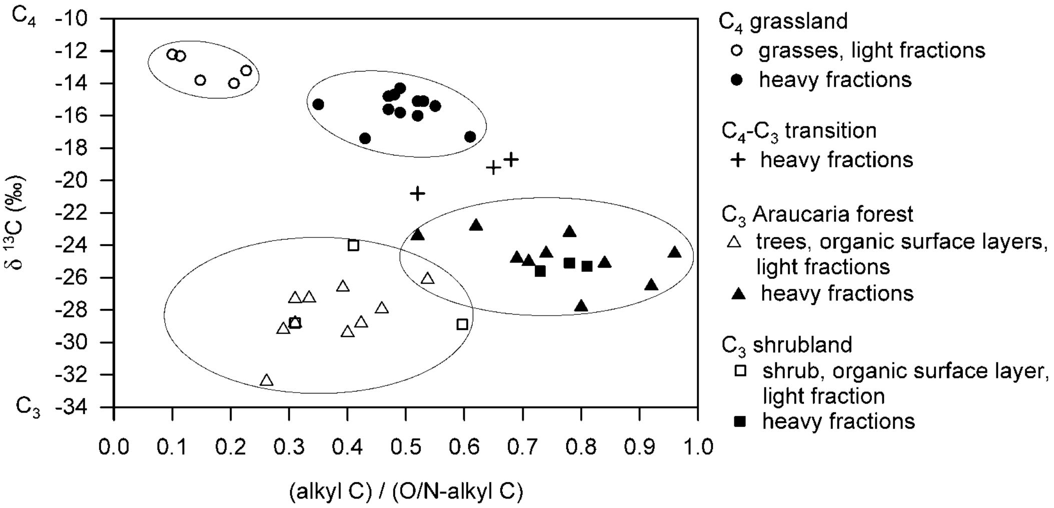


Figure 17: Relationship between (alkyl-C) / (O/N-alkyl C) ratios and $\delta\ ^{13}C$ values (‰) of heavy organo-mineral fractions, light fractions, organic surface layers and plants in grassland (C_4), Araucaria forest (C_3) and shrubland (C_3).

This is highlighted by mean values of vegetation sources and heavy fractions in Table 9. Latter also shows that the mean values of C/N ratio, aromatic C (%), soil lightness value, (alkyl C)/(O/N-alkyl C) ratio and δ ^{13}C value are significantly different between C_4- and C_3-derived groups of heavy fractions. The means of all parameters of the C_4-C_3 transition group are between those with C_4 and C_3 signature. This applies in particular for the δ ^{13}C value because means of C/N ratio and proportion of aromatic C (%) are close to the group with C_4 signature and mean values of soil lightness and ratio of (alkyl C)/(O/N-alkyl C) are more similar to the group with C_3 signature.

Table 9: Mean values (coefficient of variation) of proportions of aromatic C (%), C/N ratios, soil lightness values, (alkyl C) / (O/N-alkyl C) ratios, melanic indexes and δ ^{13}C values for vegetation sources and heavy organo-mineral fractions.

	source vegetation[2]		heavy organo-mineral fractions		
parameters[1]	C_4	C_3	C_4	C_4-C_3	C_3
aromatic C (%)	11.2 (18)	15.0 (8)	27.1 (19)	19.2 (15)	21 (25)
C/N ratio	45 (8)	41 (6)	33 (24)	23 (17)	19 (17)
soil lightness value	-	-	38 (7)	37 (5)	45 (10)
(alkyl C) / (O/N alkyl C) ratio	0.2 (35)	0.4 (28)	0.5 (13)	0.6 (14)	0.8 (15)
melanic index	-	-	1.66 (3)	1.73 (1)	2.08 (11)
δ^{13}C value (‰)	-13.1 (6)	-27.8 (8)	-15.5 (6)	-19.6 (6)	-24.8 (5)

1 significant differences amongst mean values of C_4- and C_3-derived heavy fractions at 0.05 probability level, coefficient of variation in brackets

2 C_4: grasses, light fractions; C_3: trees, shrubs, light fractions, organic surface layers

Most soils show low contents of lignin derived phenols (Table 7, appendices) with exception of the surface horizons of F6 and S1 with 5.8 and 4.7 mg VSC g^{-1} OC, respectively. The VSC contents of surface horizons are markedly lower than those of the respective organic surface layer, which is combined with strongly increasing ratios of $(ac/al)_V$ and $(ac/al)_S$. With increasing soil depth, the VSC contents slightly increase in most soils, whereas the ratios of $(ac/al)_V$ and $(ac/al)_S$ do not change consistently. The C_4 source materials clearly differ from C_3 sources in the distribution of V-, S- and C-units as shown by S/V and C/V ratios (Figure 18). This characteristic pattern is not found in the heavy organo-mineral fractions because all show similar S/V and C/V ratios independent from C_3 or C_4 origin.

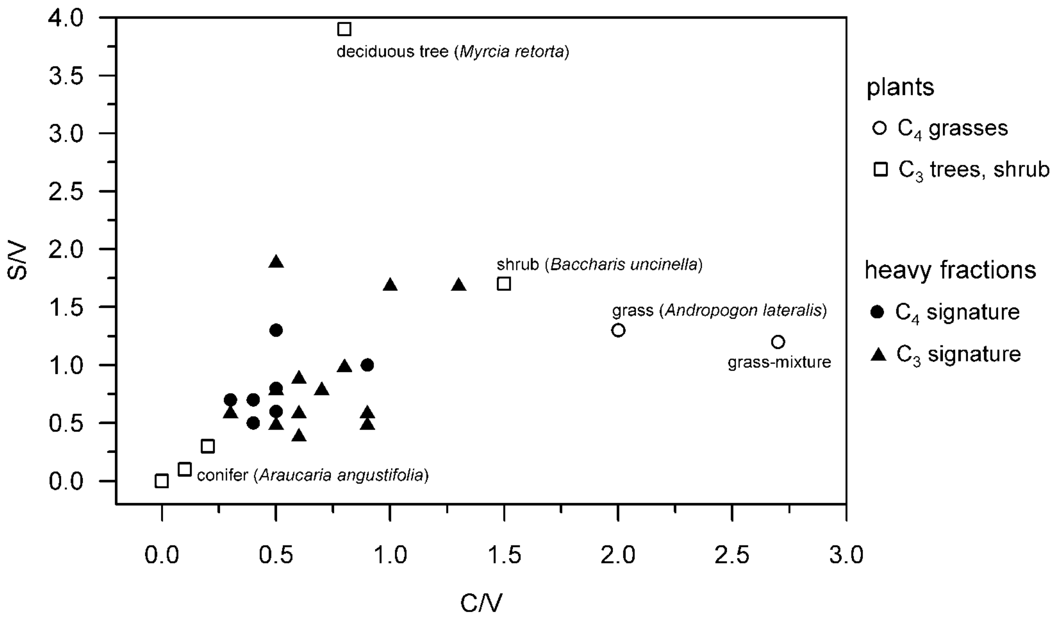


Figure 18: Plot of lignin-derived phenols expressed as syringyl to vanillyl ratios (S/V) and cinnamyl to vanillyl ratios (C/V) for plants and heavy organo-mineral fractions.

5.2 Discussion

5.2.1 Soil organic matter signatures in grassland with long-term fire history

In the surface horizons of the C_4 grassland soils (G1, GS4), the C distribution among spectral regions of ^{13}C NMR spectroscopy in the heavy organo-mineral fraction is similar compared to those from Ferralsols (Dalmolin *et al.*, 2006) and Acrisols (Dieckow *et al.*, 2005) with native subtropical grassland in southern Brazil. However, they differ with soil depth showing a strong increase of aromatic C (Table 7, appendices). With depth in a soil profile, variable trends were described for the amount of aromatic C (Zech *et al.*, 1992; Baldock *et al.*, 1997; Kögel-Knabner, 1997; Zech *et al.*, 1997; Helfrich *et al.*, 2006). The large proportions of aromatic C (29 – 34 %) with peaks at around 130 ppm in both grassland soils and in C_4-derived lower Ah horizons of the *Araucaria* forest (C_3) soils F1 and FP2 are associated with low contents of lignin-derived phenols. This indicates the contribution of charred grass residues to SOM resulting from a long fire history (Skjemstad *et al.*, 1996; Golchin *et al.*, 1997b; Schmidt *et al.*, 1999; Knicker *et al.*, 2005; Rumpel *et al.*, 2006).

In grassland soils, several factors may contribute to the larger proportion of charred material of lower horizons compared to those which are close to the surface. There has been no input of charred organic material into the grassland soils for 15 years due to the termination of burning in the reserve Pró-Mata. The predominant presence of charred material in subsoils as a result of bioturbation was detected by several studies (Glaser *et al*., 2000; Dieckow *et al*., 2005). The charred material may also have been lost due to the complete oxidation by subsequent fires (Ohlson & Tryterud, 2000; Czimczik *et al*., 2005; Knicker *et al*., 2006).

In mineral soils, C/N ratios typically decrease with soil depth due to increasing degree of decomposition, which has been documented for particle size and density fractions (Guggenberger *et al*., 1994; Helfrich *et al*., 2006). However, the soils investigated here have increasing C/N ratios with soil depth. The heavy fractions with predominantly C_4 signature derived from grassland with frequent burning generally show larger proportions of aromatic C and higher C/N ratios than those with C_3 signature which have formed under tree or shrub cover (Figure 15). The heavy fractions indicating C4-C3 transition and three others with C_4 signature show values which are in the range of those with C_3 signature because they belong to horizons close to the soil surface. Both grassland soils and the soil in a patch of *Araucaria* forest (FP2) have in deeper Ah horizons C/N ratios of up to 37 – 43 (Table 7, appendices) similar to those of grass samples (Figure 15). This result is consistent with the observation that charcoal carbon preserves the C/N ratio of the organic material from which it originates (Knicker *et al*., 1996; Almendros *et al*., 2003). Therefore, the uncommon increase of C/N ratios with soil depth could be mainly due to the contribution of increasing amounts of charred grass material. Chars derived from C_4 grasses are ^{13}C depleted relative to the fresh plant material (Krull *et al*., 2003). Thus, the increasing proportions of aromatic C with soil depth may contribute to ^{13}C depletion of permanent grassland soils (0.8 – 0.9 ‰).

Figure 16 shows that the soil lightness values decrease (become darker) with increasing aromatic C concentration (g kg^{-1}). A similar result was found by Spielvogel *et al*. (2004). Several studies observed that soils darken with increasing content of charred organic carbon or aromatic C contents (Schmidt *et al*., 1999; Schmid *et al*., 2001; Knicker *et al*., 2006). The results further indicate that grass-derived heavy fractions are darker than those with C_3 signature formed under *Araucaria* forest or shrubs with comparable aromatic C concentration (Figure 16). There is no significant contrast between the slopes of the two linear regressions obtained for heavy fractions with C_4 and C_3 signature (Table 8). However, the results showed neither evidences for a significant influence of soil texture, content of oxalate and dithionite soluble Fe and Al on soil lightness, nor that those factors cause the difference between C_4- and C_3-derived heavy fractions. Caner *et al*. (2003) showed that the darkest and most condensed humic acids were formed under grassland, whereas forest vegetation produced less dark organic matter and less condensed humic acids. These dark humic acids belong to the A-type category of Kumada (1983) and are considered to indicate charred organic matter (Shindo *et al*., 1986; Skjemstad *et al*., 1996; Golchin *et al*., 1997a). The melanic index (MI) can be used to differentiate between melanic (domination of A-type humic acids with MI < 1.7) and fulvic (lower degree of humification with MI ≥ 1.7) Andosols (Honna *et al*., 1988). Soil organic matter with C_4 signature has significantly lower melanic index values compared to those with C_3 signature (Table 3). The lower the melanic index, the darker the heavy fractions (Table 2). Kramer et al. (2004) used NaOH extraction on volcanic ash soils and found highly carboxylated humic-acid fractions with hydrogen-deficient condensed aromatic structures, which are characteristic for black carbon-like materials. The MI is determined by photometrically measurements after extraction with NaOH. Therefore, grass-derived heavy fractions are maybe darker than those with C_3 signature because of the presence of carboxylated humic acid fractions with condensed aromatic structures derived from charring processes. The carboxylation is essential for charred humic substances to be base-extractable which is likely a long-lasting process under natural conditions (Knicker, 2007) suggesting that their presence is not the result of recent burning.

5.2.2 Effects of forest expansion on grassland

The results show for plants, light fractions and organic surface layers (Figure 17) that organic matter derived from shrubs or trees (C_3) is composed of larger alkyl-C and smaller O/N-alkyl C proportions compared to grass-derived organic matter (C_4) which is in agreement with the results of other studies (Golchin *et al*., 1997a; Helfrich *et al*., 2006). Consequently, the mean (alkyl C)/(O/N-alkyl C) ratio is larger for organic matter derived from C_3 than C_4 vegetation sources (Table 3). When progressing from organic surface layers to heavy organo-mineral fractions of the surface horizons, the increase of (alkyl C)/(O/N-alkyl C) ratios and decrease of VSC contents as well as C/N ratios reflect the increasing extent of decomposition (Zech *et al*., 1992; Kögel-Knabner, 1993; Baldock *et al*., 1997; Nierop *et al*., 2001). In addition, the $(ac/al)_V$ und $(ac/al)_S$ ratios increase indicating strong lignin alteration during biodegradation (Kögel-Knabner, 1997). The difference in alkyl-C and O/N-alkyl C proportions between C_4- and C_3-derived plant materials is also found in the heavy organo-mineral fractions. The grassland soil without shrubs (G1) is characterised by low (alkyl C)/(O/N-alkyl C) ratios of 0.47 – 0.53 and high $\delta\ ^{13}C$ values of -15.1 to -14.3 ‰ throughout the solum. Surface horizons of *Araucaria* forest, shrubland and grassland with shrubs have lower $\delta\ ^{13}C$ values, and also 5

– 14 % more alkyl-C and comparably lower proportions of O/N-alkyl-C than G1 (Table 7, appendices). The large alkyl C content of surface horizons from grassland covered with shrubs (GS4, S1) results from the organic matter input by shrubs (*Baccharis uncinella,* leaves) which are rich in alkyl C (Table 6, appendices).

As *Araucaria* forest expansion and shrub encroachment on grassland occured in different time periods at the studied sites soils with present forest or shrub cover (C_3) show grassland (C_4) derived SOM in various depths as indicated by their $^{13}C/^{12}C$ isotopic signature (Figure 13). In soils with young shrub encroachment (GS4) and forest establishment at the forest border (F5) and in a patch of *Araucaria* forest (FP2), the heavy organo-mineral fractions show increasing $\delta\ ^{13}C$ values and decreasing (alkyl C)/(O/N-alkyl C) ratios with increasing soil depth. This reflects the replacement of C_4-derived SOC rich in O/N-alkyl C by C_3-derived SOC rich in alkyl C from the top downwards after succession of woody plants on grassland. In contrast, the *Araucaria* forest soils which are located deeper into the forest (F1, F6) and the shrubland soil S1 do not show these changes throughout the Ah horizons, indicating long-term existence of shrubs or trees. Both, organic matter with C_3 and C_4 signature show similar increases of (alkyl C)/(O/N-alkyl C) ratios to the respective heavy fractions (Table 9). Therefore, the characteristic difference in the alkyl C and O/N-alkyl C contents between C_4 grasses and C_3 trees or shrubs could be largely maintained during the processes of biodegradation and stabilisation in the heavy organo-mineral fractions. Their ratio of (alkyl C)/(O/N-alkyl C) points to previous vegetation as source for soil organic matter which is consistent with the $^{13}C/^{12}C$ isotopic signature (Figure 17). The results show that the preservation of components from earlier vegetation strongly influence the composition of SOM, hence the knowledge of past vegetation changes is essential for interpreting SOM composition and humification.

Grasses and the organic surface layer of the grassland soil with shrubs (GS4) show clearly higher proportions of cinnamyl phenols than tree and organic surface layer samples from the *Araucaria* forest (Table 6, appendices). Similar results were found by other studies (Hedges & Mann, 1979; Otto & Simpson, 2006) who also observed large proportions of vanillyl monomers for conifers and high proportions of syringyl units for deciduous trees. The *Araucaria* forest is composed of *Araucaria angustifolia* and deciduous trees with S/V ratios of 0.0 – 0.3 (needle, wood, root) and 3.9 (*Myrcia retorta,* leaf), respectively. Therefore, the organic surface layers in *Araucaria* forest show intermediate S/V ratios compared to those of trees (Table 7, appendices). They even cover the range of those from grasses and the organic surface layer from GS. The characteristic lignin patterns of plants are not shown by the heavy fractions as reflected by similar S/V and C/V ratios independent from C_3 or C_4 origin (Figure

18). Lignins of finer organo-mineral fractions may are strongly degraded, whereas fresh (root) litter deposits of sand-associated SOM resembles the lignin signature from organic surface layers (Kögel-Knabner & Ziegler, 1993; Guggenberger *et al*., 1994). Additionally, the plant-specific lignin signatures may disappear during decomposition as V units are more resistant than S units (Kirk *et al*., 1975; Kögel, 1986). The assumption that lignins of the heavy organo-mineral fractions are strongly modified by decomposition is in line with the VSC contents which are markedly lower compared to many other grassland or forest soils (Guggenberger *et al*., 1994; Amelung *et al*., 1999; Rumpel *et al*., 2002; Ganjegunte *et al*., 2005).

6 PRESERVATION OF LIGNIN IN HEAVY FRACTIONS

6.1 Results and Discussion

6.1.1 Isotopic signatures of plant tissues and organic surface layers

Lignin contents and $^{13}C/^{12}C$ isotopic signatures of lignin-derived phenols and total organic carbon (OC_{tot}) from plants and organic surface layers are presented in Table 10 (appendices). The needles of the conifer *Araucaria angustifolia* and the grass *Andropogon lateralis* have OC_{tot} δ ^{13}C values typical for C_3 and C_4 plants of -26.5 ‰ and -12.3 ‰. The organic surface layers in Araucaria forest (C_3), which is composed of *A. angustifolia* and deciduous trees, have tree-derived isotopic signatures (-27.4 ‰ and -29.0 ‰).

All plant tissues and organic surface layers yield lignin phenols expressed as VSC lignins with $^{13}C/^{12}C$ isotopic signatures (weighted by the contents of the single lignin phenols) that are lighter (3.7 - 6.2 ‰) than their respective OC_{tot} δ ^{13}C values (Figure 19). These findings are consistent with the heavier isotopic composition of most carbohydrates in plant tissues relative to lignin (4 - 7 ‰) or to whole-plant material (1 - 2 ‰) (Deines, 1980; Benner et al., 1987). Other studies reported similar values (2.0 - 7.0 ‰) for ^{13}C depletion of lignins compared to OC_{tot} of C_3 and C_4 plant tissues (Benner et al., 1987; Goñi and Eglinton, 1995; Wedin et al., 1995; Schweizer et al., 1999; Dignac et al., 2005). The ^{13}C depletion of lignins is attributed to kinetic isotope fractionation during the biosynthesis of the aromatic amino acids phenylalanine and tyrosine which are precursors of lignin (Sarkanen and Ludwig, 1971; Benner et al., 1987).

Both organic surface layers in Araucaria forest show higher degrees of ^{13}C depletion compared to plant samples, possibly due to lignin contributions from deciduous trees with larger extent of ^{13}C depletion. It is difficult to generalise the isotopic differences between nonwoody tissues from conifers, deciduous trees and grasses because there are few data available for comparison. Goñi and Eglinton (1995) also found the largest ^{13}C depletion of lignins relative to OC_{tot} for oak leaves compared to pine needles or grasses. The isotopic difference between VSC lignins of the C_4-grass *A. lateralis* and the C_3 conifer *A. angustifolia* (or organic surface layers) amounts to 13.5 ‰ (or 17.7 ‰) which is in agreement with the difference between OC_{tot} δ ^{13}C values of 14.2 ‰ (or 15.9 ‰). The distinct ^{13}C isotopic signatures of C_3 vs. C_4 plants enables to relate soil organic matter to plant sources for VSC lignins in accordance with OC_{tot}.

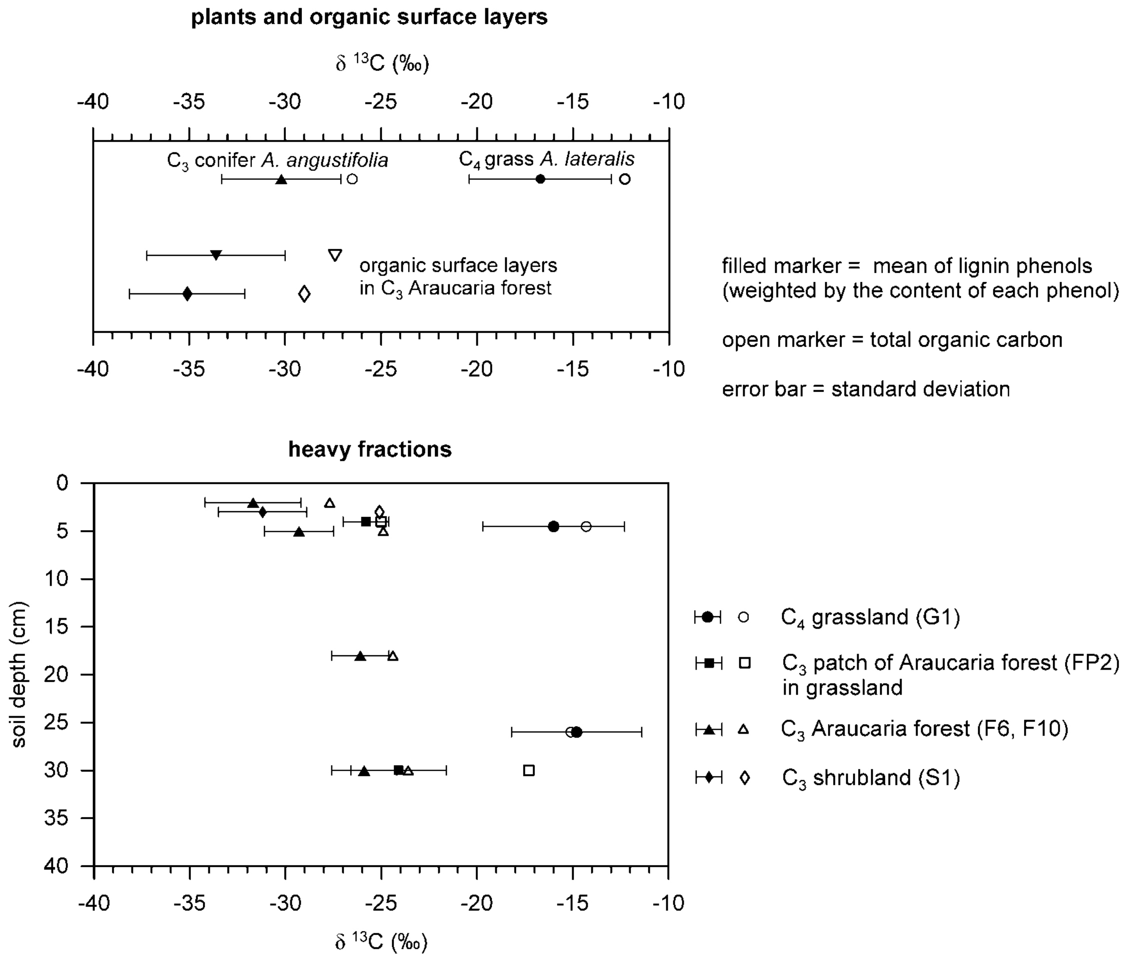


Figure 19: δ ^{13}C values (‰) of VSC lignins (weighted average of isotopic values is calculated by using the concentration of each phenol; standard deviation as error bar) and total organic carbon for C_3 *Araucaria angustifolia*, C_4 grass *Andropogon lateralis*, organic surface layers in C_3 Araucaria forest and heavy organo-mineral fractions.

6.1.2 Isotopic patterns in heavy organo-mineral fractions

δ^{13}C values of OC_{tot} in heavy organo-mineral fractions from the grassland (C_4) soil (G1) under *A. lateralis* are clearly higher than those from C_3 Araucaria forest and shrubland soils (Table 10, appendices). Only the heavy fraction of the lower horizon in the patch of Araucaria forest (FP2 Ah1) shows a ^{13}C/^{12}C isotopic signature which is close to that of grass-derived soil organic matter. Heavy fractions have VSC lignin contents which are about 14 times lower in average compared to plants and organic surface layers. The differences in ^{13}C abundance of VSC lignins between C_4- and C_3-derived heavy fractions (12.3 ‰) are similar to those of OC_{tot} (10.4 ‰). Consequently, VSC lignins and OC_{tot} of heavy fractions show similar trends of $\delta^{13}C$ values with increasing soil depth (Figure 19) and the isotopic signatures of both, mineral-associated lignins and OC_{tot} of heavy fractions consistently indicate vegetation origin. In all plant tissues, organic surface layers and C_3-derived heavy fractions the highest $\delta\ ^{13}C$ values were found for cinnamic phenols (p-coumaric and ferulic acids). $^{13}C/^{12}C$ isotopic signatures of lignin-derived phenols in natural soils are only reported for maize (C_4) and wheat (C_3) lignins from an agricultural field experiment (Dignac et al., 2005; Bahri et al., 2006). These studies and those of marine sediments (Goñi and Eglinton, 1996) also revealed that cinnamic phenols are ^{13}C enriched compared to vanillyl (V) or syringyl (S) units and sometimes OC_{tot}. The heavier isotopic composition of C-type units is attributed to different biosynthetic origin compared to that of the other phenols or to their more direct pathway of incorporation into the lignin polymer of the growing plant tissue as the degree of ^{13}C depletion generally increases with the number of enzymatic steps required for biosynthesis (O`Leary, 1981; Goñi and Eglinton, 1996).

In contrast, C_4-derived heavy fractions show another pattern of ^{13}C contribution to V, S and C units (V > C > S). V units, partly also C units, have higher $\delta\ ^{13}C$ values relative to $OC_{tot,}$ which even results in a slightly higher $\delta\ ^{13}C$ value for VSC lignins in the heavy fraction of the Ah3 horizon from the grassland soil (Figure 20). In most C_3-derived heavy fractions the structural units of lignin are ^{13}C depleted relative to OC_{tot}. Only the humus-rich Oa horizon from the soil FP2 shows homogeneous isotopic signatures for V-, S- and C-type phenols as well as OC_{tot} indicating C_3 origin (Figure 20). In this soil, which was sampled in a patch of Araucaria forest, the forest established more recently on grassland compared to other Araucaria forest topsoils with dominating C_3-derived SOC stocks (see chapter 4). The Ah1 horizon which is about 20 cm deep shows C_3 origin of lignins and C_4-derived OC_{tot} indicating non-lignin components of the heavy fraction derived under grassland. Thus, grass lignins must be largely decomposed and replaced by lignins from trees which may point to higher turnover rates of lignins compared to total SOC. Similar results were obtained for agricultural soils (Dignac et al., 2005).

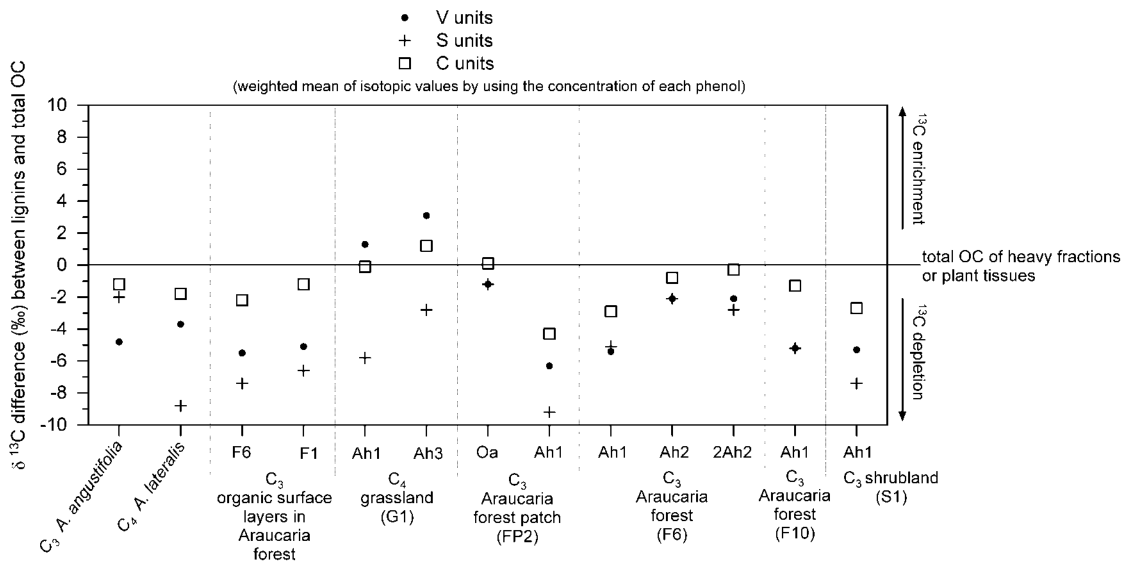


Figure 20: $^{13}C/^{12}C$ isotopic difference (‰) between total organic carbon and vanillyl (V), syringyl (S) and cinnamyl (C) lignin units (weighted average is calculated by using the concentration of each phenol) for *Araucaria angustifolia* (C_3 conifer), *Andropogon lateralis* (C_4 grass), organic surface layers in Araucaria forest and heavy organo-mineral fractions with C_4- and C_3-signature.

6.1.3 From plant litter to SOM: shifts of isotopic signatures in grassland and forest soils

Grassland soils (C_4) show ^{13}C depletion in the decay continuum from plant litter to heavy fractions of the upper mineral soil and with soil depth (see chapter 4). For samples which were analysed for isotopic signatures of lignin the OC_{tot} δ ^{13}C values show ^{13}C enrichment (3.6 ‰) of C_3- and depletion (2.4 ‰) of C_4-derived heavy fractions relative to aboveground plant litter (Table 11). There are several mechanisms of isotopic shifts which may induce the prevailing ^{13}C enrichment for C_3 forest, whereas depletion of ^{13}C dominates in C_4 grasslands. VSC lignins of heavy fractions show higher δ ^{13}C values than those of plants or organic surface layers and the ^{13}C enrichment is larger for C_3- (5.2 ‰) than C_4- (1.3 ‰) derived heavy fractions (Table 11). Bahri et al. (2008) detected depletion of ^{13}C for maize lignin phenols during decomposition by laboratory incubation. This unusual observation was explained by the preferential degradation of root versus shoot derived lignins. Another study detected ^{13}C enrichment (about 2 - 5 ‰) of maize and wheat lignins from roots relative to lignins from leaves (Bahri et al., 2006). For OC_{tot} was found that roots are enriched in ^{13}C relative to leaves and C_3 trees show also larger enrichment (mean of 3.6 ‰) than C_4 grasses (mean of 1.1 ‰). It was shown for C_4 and C_3 grasses that root lignin fractions are in average 1.1 ‰ enriched relative to the respective aboveground lignin fractions (Wedin et al., 1995).

Thus, lignins of heavy fractions may be isotopically heavier either due to differences in the ^{13}C contents between lignins of above- and belowground plant inputs or isotopic fractionation during microbial decomposition (Hobbie and Werner, 2004).

Table 11: Mean $\delta\,^{13}$C values (‰) of vanillyl (V), syringyl (S) and cinnamyl (C) units of lignin and total organic carbon as well as proportions of alkyl C and O-/N-alkyl C from plant sources and heavy organo-mineral fractions.

	mean ^{13}C/^{12}C isotopic signature*					
C$_4$ signature	V	S	C	VSC	total OC	O-/N-alkyl C[c]
plant source[a]	-16.0	-21.1	-14.1	-16.7	-12.3	75.6
heavy fraction	-12.5	-18.9	-14.1	-15.4	-14.7	40.7
difference[b]	3.5	2.2	0.0	1.3	-2.4	-34.9
C$_3$ signature						
plant source[a]	-32.8	-33.0	-29.2	-33.0	-27.6	59.4
heavy fraction	-28.0	-28.7	-25.7	-27.7	-24.0	39.7
difference[b]	4.9	4.2	3.4	5.2	3.6	-19.7

* weighted by the contents of the individual lignin-derived phenols
V = vanillyl units, S = syringyl units, C = cinnamyl units
[a] C$_4$: A. lateralis, C$_3$: mean of A. angustifolia and both organic surface layers
[b] ^{13}C enrichment (+) or depletion (-) from plant to soil organic matter
[c] mean proportions (%) as determined by ^{13}C NMR spectroscopy (data from Dümig et al., 2008c)

Heavy fractions with C$_3$ signature and tree roots show similar OC$_{tot}$ ^{13}C enrichments relative to leaves suggesting that the isotopic difference between above- and belowground plant inputs is the primary driver of ^{13}C enrichment between plant litter and the upper mineral forest soil. It also implies, that lignin of heavy fractions is mainly derived from root material and lignins of aboveground plant litter are largely decomposed in the decay continuum from organic surface layer to the upper mineral soil. This is in agreement with the observations of higher decomposition rates for leaves compared to roots in soils (Bertrand et al., 2006) and that plant lignin contents of roots are about two times larger than those of shoots (Rasse et al., 2005). It may also explain the absence of aboveground plant-specific distributions of vanillyl (V), syringyl (S) and cinnamyl (C) lignin units in heavy fractions as related to different origin (see chapter 5).

In subtropical highland soils, the VSC lignin contents of heavy fractions are low compared to temperate agricultural (Guggenberger et al., 1994; Kiem and Kögel-Knabner, 2003) or forest soils (Guggenberger et al., 1994; Rumpel and Kögel-Knabner, 2002) as well as temperate and semiarid grassland soils (Heim and Schmidt, 2007; Ganjegunte *et al.*, 2005).

This is may be due to favorouble climatic conditions for degradation of soil organic matter.

Lignin is a high molecular weight, three-dimensional macromolecule and plant-residue lignin inputs to soils are large as lignins are the second most abundant compound of vascular-plant tiussues after cellulose (Crawford, 1981). However, lignin is not extractable as intact polymer from soils. CuO oxidation or any other molecular method based on the chemical release of lignin monomers does not completely depolymerize lignin, but only phenolic monomers and dimers are released from the lignin polymer (Hedges and Ertel, 1982). Thus, CuO oxidation most probably underestimates the lignin content of heavy fractions and therefore lignins could contribute to ^{13}C depletion in grassland soils as they are ^{13}C depleted relative to OC_{tot}. It is difficult to estimate the extent of ^{13}C depletion due to lignins as lipids can be even more depleted in ^{13}C relative to OC_{tot}. Plants with different photosynthetic pathways show varying ^{13}C depletion of lipids relative to OC_{tot} and lipids of C_4 grasses are more depleted (7 - 9 ‰) compared to those from C_3 woody plants (2.5 to 5.5 ‰) (Collister et al., 1994, Chikaraishi and Naraoka, 2001). This may contribute to the dominant ^{13}C depletion in grassland soils just as the different flux pattern of ^{13}C enriched carbohydrates when comparing the contents of O/N-alkyl C from plant sources and heavy fractions as determined by ^{13}C NMR spectroscopy. As shown in Table 11, the percent loss of carbohydrates is about 15 % higher for C_4 compared to C_3.

7 CONCLUSIONS

For the first time, Andosols were detected in South America outside the volcanic rim of the Andes. The studied 27 soils are 15 Andosols, 11 Umbrisols and one Cambisol. Six Umbrisols show also andic properties but just miss the thickness or depth requirements for Andosols. The other five miss the requirements for Al and Fe concentrations in acid oxalate. But only one Umbrisol and the Cambisol fail the phosphate retention criterion of the andic propterties and all soils have low bulk densities at some depth. The andic properties belong to the nonallophanic (aluandic) type and result mainly from Al and Fe humus complexes, but probably also from interactions of humus with poorly crystalline active Al and Fe phases. The development of these andic properties is due to the high release of Al and Fe by intense weathering of rhyodacite and the accumulation of organic matter favoured by the formation of organo-metallic complexes under strong acid conditions with high rainfalls. Andic properties are predominantly found in upper and intermediate depths of grassland soils and in buried and other subsoil horizons under *Araucari*a forest, but not in recent forest topsoils. This indicates that the andic properties have evolved under grassland vegetation. *Araucaria* forest invading the grasslands promotes the crystallization of Al and Fe oxides which characterizes an ongoing process of losing andic properties. The results indicate that the invasion of shrubs and the expansion of *Araucaria* forest into grasslands is not controlled by the presence or absence of andic properties.

The combination of δ^{13}C values and radiocarbon ages give evidence that current grassland areas in and around Pró-Mata are not the result of forest clearings in recent times, but represent relics at least from the early and mid Holocene period (6000 – 8000 yr BP). They were stabilized in the Holocene probably due to a grassland favouring climate drier than today and during the last 200 - 300 years by grazing and burning of grasslands. The C_3- and C_4-derived SOC stocks clearly reflect a chronosequence of expansion of *Araucaria* forest on grassland which started after 1500 - 1300 yr BP. Small patches of *Araucaria* forest and forest at the border to the grassland are markedly younger than sites deep inside the forest stands. Grassland soils lose from the top downwards their typically black colours and melanic characteristics after the establishment of forest or after shrub encroachment as evidenced by the close relationship between melanic indexes and δ^{13}C values. The results also confirm a natural ^{13}C depletion with depth in grassland soils. In the *Araucaria* forest soils this counteracts the enrichment of ^{13}C in the subsoil due to old grassland SOC. Consequently, this has to be considered for the assessment to which amount ^{13}C enrichment in forest subsoils is due to remaining old C_4-derived SOC or a result of soil-inherent processes. Further, the exceptionally old SOM is typical for the soils of the region which mostly have andic properties at some depth and are classified as Andosols and Umbrisols.

The use of ^{13}C NMR spectroscopy, lignin analyses and measurement of soil lightness on groupings of heavy organo-mineral fractions according to the $^{13}C/^{12}C$ isotopic signature reveals changes in the chemical composition of soil organic matter (SOM) after encroachment of woody plants (C_3) into frequently burned grasslands (C_4). The heavy fractions with C_4 signature from grassland soils and grass-derived lower Ah horizons of present *Araucaria* forest (C_3) soils show the presence of charred grass residues as shown by large proportions of aromatic C, but low contents of lignin-derived phenols. The increasing amounts of charred grass material with soil depth results in the uncommon increase of C/N ratios which are similar to those of grass samples in deeper Ah horizons. Thus, the burning of grasslands have led to the differentiation of C_3- and C_4-derived SOM because heavy fractions from unburned Araucaria forest and shrubland soils have lower proportions of aromatic C, lower C/N ratios and are less dark compared to those with C_4 signature. The aboveground plant-specific distributions of vanillyl (V), syringyl (S) and cinnamyl (C) units of lignin-derived phenols are not found in heavy fractions. This suggests that VSC units are not applicable as biomarker for plant origin in these soils. The characteristic difference in the proportions of alkyl C and O/N-alkyl C between C_3 trees or shrubs and C_4 grasses is also detectable in heavy fractions. This is shown by consistent changes of the (alkyl C)/(O/N-alkyl C) ratio and the $^{13}C/^{12}C$ isotopic signature with soil depth indicating that the ratio of (alkyl C)/(O/N-alkyl C) of heavy fractions is associated with the C_4 and C_3 vegetation origin. This study demonstrates that the knowledge of vegetation cover and their changes in the past is necessary to interpret SOM composition due to the possible preservation of organic matter components from earlier vegetation and land use.

Compound-specific $^{13}C/^{12}C$ isotopic signatures of lignins from heavy organo-mineral fractions reveal differences between C_4 grassland and C_3 Araucaria forest soils which are consistent with those of total organic carbon. Similar to the isotopic differences between roots and leaves for total organic carbon, lignins of heavy fractions show higher $\delta\ ^{13}C$ values compared to lignins of aboveground plant inputs. Therefore, lignins of heavy fractions could be mainly derived from root material and lignins of aboveground plant litter may largely be decomposed in the decay continuum from organic surface layer to the upper mineral soil. For C_3 Araucaria forest, the extent of ^{13}C enrichment is markedly larger compared to C_4 grasslands when comparing roots with leaves and lignins from heavy fractions with those of aboveground plant inputs which may result in the prevailing ^{13}C enrichment. Lignins of plant tissues and heavy fractions are ^{13}C depleted relative to total organic carbon which contributes to the dominant ^{13}C depletion of C_4 grassland soils. The results emphasise the importance of root litter for the formation of soil organic matter.

This study revealed that the formation and permanence of nonallophanic Andosols is related to grass vegetation, whereas Araucaria forest establishment results in the development of Umbrisols and the loss of andic properties. The findings of this investigation are important contributions for a better understanding of vegetation history in the southern Brazilian highlands. This was achieved by characterising soil organic matter, especially by the combined evaluation of the chemical composition and the carbon isotope signatures.

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9 APPENDICES

LIST OF APPENDICES

Table 1: Soil physical and chemical properties and classification: soils of not managed grasslands without (G) or with shrubs (GS).

Soil	Horizon [1]	Depth	Munsell colour		BD	OC	C / N	pH	pH	P_{ret}	Fe_o	Al_o	Fe_d	Al_d	Fe_p	Al_p	$Al_o + 0.5$	Fe_o /	Fe_p /	Fe_p /	Alo/	Al_p /	Al_p /	MI	u/	f/	a	RSG	pref.	suff.
		(cm)	(moist)	(dry)	(g cm^{-3})	(g kg^{-1})	ratio	(H_2O)	(KCl)	(%)	(%)						Fe_o (%)	Fe_d	Fe_d	Fe_o	Ald	Al_d	Al_o		c	m			qualifiers	qualifiers
G1	Ah1	0 - 9	10 YR 2/0	10 YR 2/0	0.48	186.6	18.5	4.6	3.7	94.2	1.2	1.3	2.7	1.8	1.4	1.4	1.91	0.5	0.5	1.1	0.7	0.7	1.1	1.72	u			UM	Endoleptic	Hyperhumic
middle	Ah2	9 - 20	10 YR 2/0	10 YR 2/0	0.53	130.5	22.3	4.5	4.0	97.7	1.3	1.4	3.2	2.1	1.9	2.0	2.09	0.4	0.6	1.4	0.7	1.0	1.4	1.67	u		a			Hyperdystric
slope	Ah3	20 - 31	10 YR 2/0	10 YR 2/1	0.61	92.5	26.1	4.6	4.0	97.8	1.4	1.4	3.2	2.0	2.1	2.5	2.13	0.4	0.7	1.5	0.7	1.2	1.7	1.64	u		a			Pachic
7%	Ah4	31 - 40	10 YR 2/0	10 YR 2/1	0.70	62.3	29.1	4.6	4.0	94.9	1.0	1.3	3.5	1.7	2.0	2.2	1.79	0.3	0.6	2.0	0.7	1.3	1.7	1.66	u					Laxic
	Ah5	40 - 50	10 YR 2/0	10 YR 2/2	0.77	43.5	36.5	4.8	4.0	95.8	1.0	1.2	4.0	1.7	2.1	2.4	1.65	0.2	0.5	2.1	0.7	1.5	2.1	1.62	u					Clayic
	BAwh	50 - 62	10 YR 2/1	10 YR 3/2	0.83	31.2	28.4	4.5	4.0	93.7	1.0	1.0	3.8	1.6	2.1	2.3	1.53	0.3	0.6	2.1	0.6	1.4	2.2	1.76	u					
	Bw	62 - 75	10 YR 2.5/2	10 YR 5/4	0.91	18.6	20.0	4.7	4.1	89.5	1.0	1.1	3.6	1.2	1.7	1.8	1.66	0.3	0.5	1.6	1.0	1.5	1.5							
G2	Ah1	0 - 13	10 YR 2/0	10 YR 2/0	0.60	173.4	20.8	4.6	3.9	93.1	1.8	1.3	3.0	1.6	1.2	1.5	2.19	0.6	0.4	0.7	0.8	1.0	1.2	1.67	u		a	AN	Aluandic	Hyperdystric
middle	Ah2	13 - 25	10 YR 2/0	10 YR 2/1	0.72	108.2	25.3	4.7	4.1	95.1	1.6	1.4	3.4	1.6	1.4	1.9	2.18	0.5	0.4	0.9	0.9	1.2	1.3	1.67	u		a		Endoleptic	Clayic
slope	Ah3	25 - 36	10 YR 2/0	10 YR 2/1	0.68	69.7	31.8	4.6	4.1	94.5	1.7	1.5	3.1	1.5	2.1	3.4	2.36	0.5	0.7	1.3	1.0	2.2	2.2	1.76	u		a		Umbric	
10%	AChw	36 - 41	10 YR 2/0	10 YR 2/2	0.81	55.8	27.4	4.7	4.2	93.0	1.2	1.3	3.3	1.5	1.8	3.0	1.94	0.4	0.5	1.5	0.9	2.0	2.2		u					
	CAwh	41 - 55	10 YR 2/2	2.5 Y 4/4	nd	31.7	24.6	4.9	4.3	90.6	1.1	1.3	4.1	1.5	1.6	2.3	1.86	0.3	0.4	1.4	0.9	1.6	1.7		u					
G3	Ah1	0 - 10	10 YR 2/0	10 YR 2/1	0.49	199.8	20.0	4.7	4.0	97.0	1.9	1.3	3.0	2.1	1.7	1.7	2.28	0.6	0.6	0.9	0.6	0.8	1.3	1.75	u	f	a	AN	Aluandic	Hyperdystric
crest	Ah2	10 - 18	10 YR 2/0	10 YR 2/1	0.54	152.9	21.9	4.8	4.1	98.5	1.8	1.5	3.8	2.5	2.2	2.3	2.36	0.5	0.6	1.2	0.6	0.9	1.6	1.75	u	f	a		Fulvic	Clayic
2%	Ah3	18 - 31	10 YR 2/0	10 YR 2/2	0.48	111.8	29.8	4.8	4.1	96.4	2.1	1.5	4.1	2.2	2.5	2.9	2.58	0.5	0.6	1.2	0.7	1.4	1.9	1.89	u	f	a		Epileptic	
																													Umbric	
GS1	Oi/Oe	3-0				444.6	30.0	5.1	4.5																			AN	Aluandic	Hyperdystric
crest	Ah1	0 - 7	10 YR 2/0	10 YR 2/1	0.44	189.3	19.7	4.6	3.8	93.9	1.5	1.5	2.8	1.7	1.5	1.4	2.22	0.5	0.5	1.0	0.9	0.8	1.0	1.70	u		a		Epileptic	Clayic
1%	Ah2	7 - 18	10 YR 2/0	10 YR 2/1	0.49	151.4	19.9	4.8	4.1	97.6	1.5	1.7	3.1	2.1	1.8	2.4	2.45	0.5	0.6	1.2	0.8	1.2	1.4	1.70	u		a		Umbric	
	AChw	18 - 25	10 YR 2/0	10 YR 2/1	nd	121.7	21.2	4.5	4.1	98.3	1.5	1.5	3.9	2.0	2.0	2.5	2.30	0.4	0.5	1.3	0.8	1.3	1.7		u					
GS2	Oi/Oe	4 - 0				450.2	32.7	4.8	3.9																			AN	Aluandic	Hyperdystric
lower	Oa1	0 - 12	10 YR 2/0	10 YR 2/0	0.36	268.6	17.3	3.8	3.7	91.8	1.1	1.5	1.2	1.3	1.0	1.4	2.11	1.0	0.8	0.9	1.2	1.1	0.9	1.47					Folic	Epiclayic
slope	Oa2	12 - 24	10 YR 2/0	10 YR 2/0	0.43	208.4	19.6	4.7	4.0	96.3	1.6	2.5	2.2	2.3	1.4	2.5	3.27	0.7	0.6	0.9	1.1	1.1	1.0	1.60	u		a		Umbric	
12%	Ah1	24 - 36	10 YR 2/0	10 YR 2/1	0.53	174.8	20.9	4.7	4.3	96.4	1.4	2.8	2.6	2.7	1.3	2.5	3.54	0.5	0.5	0.9	1.0	0.9	0.9	1.62	u		a			
	2ABhw	36 - 51	10 YR 2/1	10 YR 3/3	0.63	73.4	13.4	4.7	4.6	95.1	1.2	3.5	2.6	2.1	0.6	1.0	4.05	0.5	0.2	0.5	1.7	0.5	0.3	1.97	u		a			
	2BAwh1	51 - 63	10 YR 2/2	10 YR 3/3	0.64	43.1	13.5	4.7	4.6	92.0	1.1	3.2	2.7	1.8	0.3	0.7	3.82	0.4	0.1	0.3	1.8	0.4	0.2	2.04	u		a			
	3BAwh2	63 - 71	10 YR 2/2	10 YR 4/2	0.85	33.9	18.4	4.6	4.1	84.3	0.6	1.0	1.7	0.8	1.0	2.1	1.34	0.4	0.6	1.5	1.2	2.5	2.0	1.99	u					
	3Bw	71 - 98	2.5 Y 4/4	2.5 Y 6/4	1.10	10.5	18.0	4.5	3.8	48.8	0.2	0.4	1.4	0.4	0.5	1.1	0.49	0.1	0.3	2.9	1.0	2.8	2.7		c					
GS3	Oi/Oe	2 - 0				450.3	46.0	4.4	3.7																			UM	Endoleptic	Hyperhumic
crest	Ah1	0 - 8	10 YR 2/1	10 YR 2/1	0.64	112.2	30.3	4.8	3.9	82.5	0.9	0.9	3.5	1.4	1.8	2.0	1.38	0.3	0.5	1.9	0.6	1.4	2.2	1.81	u					Hyperdystric
7%	Ah2	8 - 19	10 YR 2/1	10 YR 2/2	0.66	89.7	28.4	4.9	4.1	88.1	1.1	1.1	4.1	1.4	2.0	2.3	1.61	0.3	0.5	1.9	0.8	1.6	2.1	1.71	u					Pachic
	Ah3	19 - 27	10 YR 2/1	10 YR 2/2	0.74	68.0	31.2	4.9	4.2	88.5	1.0	0.9	4.7	1.4	2.2	2.7	1.70	0.2	0.5	2.2	0.7	1.9	2.8	1.72	u					Laxic
	Ah4	27 - 41	10 YR 2/1	10 YR 2/2	0.78	54.7	32.7	4.7	4.1	87.5	0.8	0.7	3.7	0.9	2.2	3.2	1.50	0.2	0.6	2.7	0.8	3.5	4.3	1.78	u					
	ABhw	41 - 54	10 YR 2/2	10 YR 3/3	0.92	32.6	34.4	4.8	4.1	83.0	0.4	0.6	3.4	0.6	2.4	3.4	1.40	0.1	0.7	5.8	1.1	5.8	5.5		u					
	Bw1	54 - 65	7.5 YR 3/4	10 YR 5/3	1.05	17.3	28.6	5.5	4.3	77.9	0.8	0.7	3.7	0.9	1.6	1.9	1.15	0.2	0.4	1.9	0.8	2.1	2.6		c					
	Bw2	65 - 75	7.5 YR 3/2	7.5 YR 6/2	1.02	10.6	26.8	4.7	4.2	73.7	0.4	0.6	3.4	0.6	0.7	0.8	0.82	0.1	0.2	1.6	1.1	1.4	1.3		c					
GS4	Oi/Oe	2 - 0				451.3	47.3	4.8	4.1																			AN	Aluandic	Hyperdystric
lower	Oa	0 - 11	10 YR 2/0	10 YR 2/0	0.41	244.7	20.4	4.7	3.7	92.6	1.7	1.4	2.5	1.7	1.5	1.4	2.22	0.7	0.6	0.9	0.8	0.8	1.0	1.70			a		Melanic	Clayic
slope	Ah1	11 - 23	10 YR 2/0	10 YR 2/0	0.40	169.0	26.0	4.7	3.9	97.1	2.0	1.9	3.3	2.5	2.2	2.3	2.88	0.6	0.7	1.1	0.8	0.9	1.2	1.59	u	m	a		Folic	
1.5 %	Ah2	23 - 32	10 YR 2/0	10 YR 2/1	0.45	126.7	42.3	4.6	4.0	98.1	2.0	1.9	3.8	2.6	2.2	2.7	2.94	0.5	0.6	1.1	0.7	1.1	1.4	1.63	u	m	a		Endoleptic	
	Ah3	32 - 44	10 YR 2/0	10 YR 2/1	0.57	85.3	43.0	4.7	4.2	97.5	1.7	1.8	2.7	1.8	2.4	3.0	2.68	0.6	0.9	1.4	1.0	1.6	1.7	1.66	u	m	a		Umbric	
	Ah4	44 - 55	10 YR 2/0	10 YR 3/2	0.73	52.2	40.7	4.6	4.2	97.6	1.2	1.2	3.3	1.6	2.0	2.5	1.84	0.4	0.6	1.7	0.8	1.6	2.0		u					
	Bw	55 - 59	10 YR 2/2	10 YR 4/2	0.82	30.5	27.5	4.7	4.3	94.4	1.1	1.1	3.2	1.2	1.5	1.9	1.65	0.3	0.5	1.4	0.9	1.6	1.7		u					
GS5	Ah1	0 - 12	10 YR 2/0	10 YR 2/1	0.49	170.2	24.7	4.4	3.8	91.4	0.9	1.2	3.0	2.2	1.5	1.7	1.65	0.3	0.5	1.6	0.5	0.8	1.4	1.68	u			UM	Endoleptic	Hyperhumic
lower	Ah2	12 - 32	10 YR 2/0	10 YR 2/2	0.56	113.4	37.8	4.6	4.0	94.5	1.1	1.4	4.1	2.1	1.8	2.4	2.01	0.3	0.5	1.6	0.7	1.2	1.7	1.75	u		a			Hyperdystric
slope	Ah3	32 - 52	10 YR 2/0	10 YR 2.5/2	0.73	53.3	46.9	4.6	4.1	90.7	1.0	1.2	4.1	1.6	1.9	2.5	1.67	0.2	0.5	1.9	0.7	1.6	2.2	1.69	u					Pachic
16%	Ah4	52 - 73	10 YR 2/1	10 YR 3/2	0.78	40.3	45.2	4.6	4.2	95.4	1.1	1.1	4.3	1.6	2.0	2.4	1.66	0.3	0.5	1.8	0.7	1.5	2.2	1.81	u					Laxic
	BAwh	73 - 82	10 YR 3/4	10 YR 5/4	0.87	18.8	32.6	4.7	4.3	80.0	1.2	1.0	3.7	1.1	1.0	1.1	1.62	0.3	0.3	0.8	1.0	1.1	1.1		c					Clayic
	Bw	82 - 95	10 YR 4/3	10 YR 6/3	0.87	11.2	32.8	4.5	4.1	76.3	0.8	0.7	3.2	0.7	0.7	0.7	1.13	0.3	0.2	0.9	1.0	1.0	1.0		c					

Table 1, continued: soils of pastureland (P), shrubland (S) and patches of *Araucaria* forest (FP).

Soil	Horizon[1]	Depth (cm)	Munsell colour (moist)	Munsell colour (dry)	BD ($g\ cm^{-3}$)	OC ($g\ kg^{-1}$)	C / N ratio	pH (H_2O)	pH (KCl)	P_{ret} (%)	Fe_o (%)	Al_o	Fe_d	Al_d	Fe_p	Al_p	$Al_o + 0.5\ Fe_o$ (%)	Fe_o / Fe_d	Fe_p / Fe_d	Fe_p / Fe_o	Alo/ Ald	Al_p / Al_d	Al_p / Al_o	MI	u/ c	f/ m	a	RSG	pref. qualifiers	suff. qualifiers
P1	Ah1	0 - 13	10 YR 2/0	10 YR 2/1	0.54	136.2	19.1	4.9	3.9	89.3	1.3	1.1	2.4	1.4	1.6	1.4	1.70	0.5	0.7	1.3	0.7	1.0	1.3	1.63	u			UM	Haplic	Hyperhumic
middle	Ah2	13 - 28	10 YR 2/0	10 YR 2/1	0.62	88.4	25.9	4.7	4.0	88.5	1.3	1.2	2.7	1.4	1.8	1.9	1.86	0.5	0.7	1.4	0.9	1.4	1.6	1.62	u					Hyperdystric
slope	ABhw	28 - 40	10 YR 2/0	10 YR 2/2	0.77	44.0	28.7	4.5	4.1	83.8	0.9	0.9	3.1	1.1	2.2	2.5	1.36	0.3	0.7	2.4	0.8	2.2	2.8	1.70	u					Pachic
6%	BAwh	40 - 48	10 YR 2/1	10 YR 3/2	0.92	29.4	27.3	4.3	3.9	81.6	0.9	0.8	3.6	1.2	2.1	2.5	1.29	0.3	0.6	2.2	0.7	2.2	3.1		u					Laxic
	Bw1	48 - 60	10 YR 3/3	10 YR 5/4	1.05	18.1	20.2	4.7	4.2	85.0	1.1	0.8	3.3	0.6	1.6	1.5	1.37	0.3	0.5	1.5	1.4	2.6	1.9		u					Clayic
	Bw2	60 - 80	10 YR 3/4	10 YR 5/4	1.06	14.0	13.6	4.6	4.1	86.7	nd	nd	2.9	0.8	1.7	1.8	nd	nd	0.6	nd	nd	2.2	nd		c					
	Bw3	80 - 100	10 YR 3/4	10 YR 6/4	1.02	11.3	13.2	4.6	4.1	79.4	1.0	0.6	3.1	0.8	1.7	1.7	1.12	0.3	0.5	1.7	0.8	2.1	2.8		c					
	Bw4	100 - 118	10 YR 4/4	10 YR 6/4	1.08	8.4	13.9	4.7	3.9	68.0	0.9	0.5	3.1	0.7	1.2	0.9	0.92	0.3	0.4	1.4	0.7	1.3	1.9		c					
	Bw5	118 - 146	10 YR 4/4	10 YR 6/4	1.04	8.5	14.2	4.5	4.0	68.4	0.9	0.5	2.8	0.6	1.3	1.3	0.91	0.3	0.4	1.4	0.7	2.0	2.8		c					
	2Bgw1	146 - 190	10 YR 4/4	10 YR 6/4	1.13	6.2	17.0	4.6	3.8	54.2	0.6	0.3	3.6	1.0	0.6	0.5	0.60	0.2	0.2	1.1	0.3	0.5	1.7		c					
	2Bgw2	190 - 224	10 YR 4/6	10 YR 6/4	1.22	3.6	11.5	4.7	3.9	45.9	0.2	0.3	3.2	0.5	0.1	0.2	0.37	0.1	0.0	0.6	0.5	0.4	0.8		c					
	2Bgw3	224 - 274	10 YR 4/6	10 YR 6/4	1.14	3.2	11.3	4.7	3.9	43.5	1.0	0.7	2.9	0.4	0.1	0.2	1.26	0.4	0.0	0.1	1.7	0.4	0.2		c					
	2Bgw4	274 - 287	10 YR 4/6	10 YR 6/4	1.26	3.0	11.1	4.6	3.9	46.1	0.2	0.2	2.7	0.4	0.0	0.1	0.29	0.1	0.0	0.1	0.5	0.2	0.4		c					
	3Bg	287 - 310+	10 YR 6/4	10 YR 8/2	0.89	1.1	8.1	4.6	3.9																					
P2	Ah1	0 - 12	10 YR 2/0	10 YR 2/0	0.45	188.2	19.7	4.5	3.8	92.8	1.4	1.2	2.3	1.6	1.5	1.4	1.90	0.6	0.7	1.1	0.7	0.9	1.2	1.63	u			UM	Endoleptic	Hyperhumic
crest	Ah2	12 - 23	10 YR 2/0	10 YR 2/0	0.53	137.7	25.1	4.6	4.0	95.0	1.8	1.6	3.2	1.8	1.8	2.3	2.47	0.6	0.6	1.0	0.9	1.3	1.5	1.68	u		a			Hyperdystric
1.5%	Ah3	23 - 34	10 YR 2/0	10 YR 2/0	0.63	76.8	29.9	4.5	4.0	93.6	1.4	1.3	3.6	1.6	2.0	2.7	1.96	0.4	0.5	1.4	0.8	1.7	2.2	1.68	u					Pachic
	ABhw	34 - 41	10 YR 2/0	10 YR 2/1	0.70	53.7	35.7	4.7	4.1	92.4	1.4	1.2	3.4	1.4	2.0	2.9	1.89	0.4	0.6	1.5	0.8	2.1	2.4		u					Laxic
	BAwh	41 - 47	10 YR 2/0	10 YR 3/2	0.78	35.5	39.5	4.4	4.1	86.4	1.2	1.0	3.3	1.1	1.7	2.1	1.58	0.4	0.5	1.4	0.9	1.9	2.2		u					Clayic
	Bw	47 - 55	10 YR 2/2	10 YR 5/3	0.89	18.6	27.5	4.6	4.0	75.1	0.8	0.6	6.0	1.0	1.5	1.5	1.02	0.1	0.2	1.9	0.6	1.4	2.5		u					
S1	Oi/Oe	3 - 0				474.0	41.4	5.8	5.3																			AN	Aluandic	Hyperdystric
crest	Ah1	0 - 6	10 YR 2/1	10 YR 3/2	0.52	108.0	18.3	4.4	3.9	87.1	2.1	1.0	5.1	1.4	2.6	1.5	2.01	0.4	0.5	1.3	0.7	1.1	1.6	2.22	u	f	a		Fulvic	Clayic
3%	Ah2	6 - 21	10 YR 2/2	10 YR 3/3	0.68	90.1	21.1	4.4	3.9	87.2	2.2	1.1	5.1	1.4	2.8	1.7	2.18	0.4	0.5	1.2	0.8	1.2	1.6	2.22	u	f	a		Endoleptic	
	Ah3	21 - 30	10 YR 2/2	10 YR 3/2	0.55	76.6	23.6	4.5	4.1	97.0	2.7	1.7	6.1	2.2	3.7	3.1	3.07	0.4	0.6	1.4	0.8	1.4	1.8	2.30	u	f	a		Umbric	
	2Ahb	30 - 50	10 YR 2/1	10 YR 3/2	0.55	66.3	27.1	4.4	4.2	93.7	1.9	1.9	4.8	2.4	3.2	3.8	2.86	0.4	0.7	1.7	0.8	1.6	2.0	2.04	u	f	a			
	2ABhwb	50 - 60	10 YR 2/2	10 YR 3/3	0.73	48.8	23.8	4.5	4.1	97.1	1.9	1.7	5.1	2.1	2.8	3.6	2.68	0.4	0.6	1.5	0.8	1.7	2.1	2.15	u	f	a			
	2Bwb	60 - 93	10 YR 3/4	10 YR 5/4	0.83	24.4	24.5	4.5	4.2	91.1	1.1	1.2	6.4	1.7	2.5	2.3	1.74	0.2	0.4	2.4	0.7	1.4	1.9	2.50	c					
S2	Oi/Oe	3 - 0				490.7	32.7	5.4	4.5																			AN	Aluandic	Hyperdystric
middle	Ah1	0 - 10	10 YR 2/0	10 YR 2/2	0.61	141.4	20.0	4.8	3.9	92.9	3.0	1.7	4.9	2.1	3.1	2.2	3.18	0.6	0.6	1.0	0.8	1.0	1.3	1.99	u	f	a		Fulvic	
slope	Ah2	10 - 20	10 YR 2/0	10 YR 2/2	0.57	127.8	19.3	4.9	4.1	94.2	3.0	1.9	5.2	2.1	2.9	2.3	3.41	0.6	0.6	1.0	0.9	1.1	1.2	1.92	u	f	a		Umbric	
8%	BAwh	20 - 28	10 YR 2/0	10 YR 2.5/2	0.57	99.3	22.1	5.0	4.3	97.2	2.1	3.3	4.9	3.5	2.7	3.7	4.42	0.4	0.6	1.3	0.9	1.1	1.1	2.00	u	f	a			
	2Ahb	28 - 35	10 YR 2/0	10 YR 2/1	0.65	83.8	36.7	5.0	4.2	96.1	1.9	2.5	4.5	2.9	3.2	4.7	3.41	0.4	0.7	1.7	0.9	1.6	1.9	1.77	u	f	a			
	3BAwhb	35 - 47	10 YR 2/0	10 YR 2/2	0.70	54.6	33.6	4.9	4.3	95.9	1.6	1.8	4.2	2.2	3.1	4.6	2.61	0.4	0.7	1.9	0.8	2.1	2.5	1.74	u	f	a			
	3BCwb1	47 - 68	10 YR 3/4	10 YR 6/4	0.99	20.1	25.6	4.8	4.3	89.5	0.9	1.3	4.4	1.4	1.3	2.3	1.77	0.2	0.3	1.4	0.9	1.7	1.8	1.93	c					
	3BCwb2	68 - 83	10 YR 3/4	10 YR 6/4	1.11	14.0	17.6	4.9	4.2	86.0	0.6	1.0	3.1	0.9	1.5	2.4	1.24	0.2	0.5	2.6	1.1	2.8	2.5	2.80	c					
	4BCwb3	83 - 97	10 YR 3/4	10 YR 5/4	1.05	14.5	19.6	5.0	4.1	84.0	0.7	0.9	4.9	1.3	1.5	2.6	1.25	0.2	0.3	2.1	0.7	2.0	2.9		c					
	4BCwb4	97 - 107	10 YR 4/4	10 YR 6/4	nd	14.0	20.3	4.9	4.3	77.2	0.8	0.9	5.5	1.4	0.9	1.3	1.33	0.1	0.2	1.2	0.7	1.0	1.4		c					
FP1	Oi/Oe	4 - 0				500.0	39.2	5.1	4.3																			UM	Folic	Hyperhumic
middle	Oa	0 - 10	10 YR 2/1	10 YR 2/2	0.46	223.9	20.9	3.9	3.4	84.9	1.1	1.2	2.8	1.7	1.5	1.6	1.71	0.4	0.5	1.4	0.7	1.0	1.4	1.97					Endoleptic	Hyperdystric
slope	Ah1	10 - 23	10 YR 2/0	10 YR 2/0	0.46	140.7	26.8	4.5	3.9	96.0	1.6	1.6	3.7	2.2	2.1	2.5	2.37	0.4	0.6	1.3	0.7	1.2	1.6	1.67	u		a			Laxic
12%	Ah2	23 - 32	10 YR 2/0	10 YR 2/1	0.56	115.9	31.6	4.7	4.0	95.9	1.3	1.3	4.8	2.0	2.1	2.8	2.01	0.3	0.4	1.6	0.7	1.4	2.1	1.76	u		a			
	AChw	32 - 42	10 YR 2/0	10 YR 2/2	nd	89.8	29.3	4.8	4.1	95.7	1.4	1.4	4.3	1.8	2.1	2.7	2.05	0.3	0.5	1.5	0.8	1.5	2.0	1.77	u					
	CAwh	42 - 51	10 YR 2/1	10 YR 3/2	nd	37.1	36.3	4.7	4.3	92.7	0.4	0.9	2.4	0.7	1.3	1.8	1.15	0.2	0.5	2.9	1.4	2.8	2.0	1.80	u					
FP2	Oi/Oe	3 - 0				512.3	38.9	4.7	4.1																			AN	Aluandic	Hyperdystric
middle	Oa1	0 - 8	10 YR 2/0	10 YR 2/2	0.37	307.7	17.8	3.5	3.1	76.1	0.9	0.8	1.6	1.1	1.0	1.0	1.24	0.6	0.6	1.1	0.7	0.9	1.2	1.95					Melanic	Clayic
slope	Oa2	8 - 24	10 YR 2/0	10 YR 2/0	0.32	206.0	21.1	4.2	3.8	97.9	1.7	1.4	3.0	2.4	2.1	2.2	2.23	0.5	0.7	1.2	0.6	0.9	1.6	1.74	u		a		Folic	
14%	Ah1	24 - 36	10 YR 2/0	10 YR 2/0	0.49	143.9	32.4	4.3	3.9	98.6	1.9	1.8	3.4	2.5	2.5	3.1	2.81	0.6	0.7	1.3	0.7	1.2	1.7	1.65	u	m	a		Umbric	
	Ah2	36 - 46	10 YR 2/0	10 YR 2/0	0.56	91.5	37.7	4.4	4.0	98.4	1.8	1.5	3.7	2.0	2.8	3.6	2.42	0.5	0.8	1.6	0.8	1.8	2.4	1.67	u	m	a			
	Ah3	46 - 63	10 YR 2/0	10 YR 2/0	0.56	82.1	40.1	4.3	4.0	98.6	1.9	1.7	3.9	2.0	2.9	4.0	2.61	0.5	0.8	1.6	0.8	2.0	2.4	1.69	u	m	a			
	BAwh	63 - 79	10 YR 2/0	10 YR 2/1	0.64	52.4	33.4	4.7	4.1	96.9	1.6	1.3	3.8	1.6	2.5	3.2	2.11	0.4	0.7	1.6	0.8	2.1	2.5	1.77	u		a			
	Bw1	79 - 96	10 YR 2/2	10 YR 5/4	0.91	21.7	27.5	4.7	4.1	92.2	1.5	1.0	3.6	1.1	1.8	2.3	1.81	0.4	0.5	1.2	0.9	2.0	2.2		u					
	Bw2	96- 106	10 YR 4/5	10 YR 6/4	1.16	11.2	23.3	4.9	4.1	82.8	1.0	0.9	4.4	1.0	1.3	1.7	1.35	0.2	0.3	1.3	0.9	1.7	2.0		c					

Table 1, continued: soils of *Araucaria* forest (F).

Soil	Horizon [1]	Depth (cm)	Munsell colour (moist)	Munsell colour (dry)	BD (g cm^{-3})	OC (g kg^{-1})	C / N ratio	pH (H_2O)	pH (KCl)	P_{ret} (%)	Fe_o (%)	Al_o	Fe_d	Al_d	Fe_p	Al_p	$Al_o + 0.5 Fe_o$ (%)	Fe_o / Fe_d	Fe_p / Fe_d	Fe_p / Fe_o	Alo/ Ald	Al_p / Al_d	Al_p / Al_o	MI	u/ c	f/ m	a	RSG	pref. qualifiers	suff. qualifiers
F1	Oi/Oe	7 - 0				457.3	28.1	5.3	3.6																			AN	Aluandic	Hyperdystric
upper	Oa	0 - 6	10 YR 2/0	10 YR 2/2	0.31	224.3	14.5	4.8	3.5	80.5	0.8	1.0	2.4	1.4	1.0	1.1	1.42	0.3	0.4	1.3	0.7	0.8	1.1	1.89					Fulvic	Epiclayic
slope	Ah1	6 - 13	10 YR 2/0	10 YR 2/2	0.40	161.8	16.5	4.5	3.6	83.8	1.2	1.3	3.9	2.1	1.7	2.1	1.89	0.3	0.4	1.4	0.6	1.0	1.6	1.87	u				Folic	
15%	2Ah2	13 - 23	10 YR 2/0	10 YR 2/1	0.41	149.4	16.3	4.5	3.9	97.2	1.4	1.7	3.1	2.2	1.0	1.2	2.40	0.4	0.3	0.8	0.8	0.5	0.7	1.80	u	f	a		Umbric	
	2Ah3	23 - 38	10 YR 2/1	10 YR 2/2	0.42	103.0	19.3	4.5	4.0	97.5	1.4	2.1	4.0	2.4	2.0	2.7	2.82	0.4	0.5	1.4	0.9	1.1	1.3	1.90	u	f	a			
	2Ah4	38 - 53	10 YR 2/1	10 YR 2.5/2	0.52	86.4	20.2	4.4	4.0	97.3	0.9	1.7	3.7	2.0	1.9	3.5	2.14	0.3	0.5	2.0	0.8	1.7	2.1	1.88	u	f	a			
	2CAwh	53 - 64	10 YR 2/1	10 YR 3/3	nd	68.7	17.1	4.6	4.1	97.1	0.7	1.4	3.7	2.1	1.6	3.2	1.75	0.2	0.4	2.2	0.7	1.5	2.3		u					
	2CBw1	64 - 89	7.5 YR 3/2	7.5 YR 5/2	nd	21.3	23.4	4.7	4.1	80.6	0.5	0.9	3.5	0.9	0.8	1.2	1.12	0.1	0.2	1.5	1.0	1.3	1.3		u					
	2CBw2	89 - 124	7.5 YR 3/4	7.5 YR 5.5/2	nd	13.9	28.7	4.4	4.0	72.9	0.3	0.6	3.6	0.5	0.4	0.6	0.73	0.1	0.1	1.3	1.1	1.1	1.0							
F2	Oi/Oe	6 - 0				452.4	28.6	4.7	3.8																			AN	Aluandic	Hyperdystric
crest	Ah1	0 - 6	10 YR 2/0	10 YR 2/2	0.36	179.0	13.8	4.3	3.4	72.1	1.5	0.6	2.6	0.7	1.3	0.5	1.36	0.6	0.5	0.8	0.9	0.8	0.9	1.94	u				Fulvic	Epiclayic
3%	Ah2	6 - 11	10 YR 2/0	10 YR 2/2	0.52	126.2	13.0	4.3	3.5	79.2	1.7	0.8	3.3	0.9	1.9	1.0	1.65	0.5	0.6	1.1	0.9	1.1	1.3	1.92	u				Endoleptic	
	2Ah3	11 - 35	10 YR 2/0	10 YR 2/2	0.61	120.1	17.7	4.4	3.8	92.4	2.1	2.0	3.8	1.9	2.5	2.8	3.08	0.6	0.7	1.2	1.1	1.5	1.4	1.95	u	f	a		Umbric	
	2Ah4	35 - 55	10 YR 2/0	10 YR 2.5/2	nd	103.2	19.8	4.5	4.0	99.5	0.8	2.4	3.0	2.2	1.3	3.2	2.80	0.3	0.4	1.6	1.1	1.5	1.4	1.98	u	f	a			
F3	Oi/Oe	4 - 0				499.1	46.8	5.8	5.1																			UM	Endoleptic	Hyperhumic
upper	Ah1	0 - 10	10 YR 2/2	10 YR 4/2	0.90	61.7	17.7	4.8	4.1	53.7	1.0	0.3	3.1	0.3	0.8	0.4	0.81	0.3	0.3	0.8	0.9	1.3	1.4	2.16	u					Hyperdystric
slope	AChw	10 - 28	10 YR 2/1	10 YR 3/2	0.89	53.7	19.1	4.8	4.1	86.5	1.1	1.0	3.3	0.9	1.4	1.9	1.54	0.3	0.4	1.2	1.1	2.1	2.0	2.11	u					Pachic
20%	2CAwh	28 - 51	10 YR 2/1	10 YR 3/2	nd	65.9	22.5	4.9	4.3	96.9	0.6	1.8	2.3	1.5	1.0	2.6	2.10	0.3	0.4	1.6	1.2	1.7	1.4	2.00	u					
F4	Oi/Oe	5 - 0				503.9	39.9	4.9	4.3																			UM	Folic	Hyperhumic
middle	Oa1	0 - 5	10 YR 2/0	10 YR 2/2	0.35	307.8	18.6	3.7	3.1	71.6	0.8	0.7	1.8	1.1	1.1	1.0	1.13	0.4	0.6	1.4	0.7	0.9	1.4	1.85						Hyperdystric
slope	Oa2	5 - 20	10 YR 2/0	10 YR 2/1	0.40	233.1	30.4	3.9	3.4	71.2	1.4	1.2	2.7	1.6	1.8	2.0	1.92	0.5	0.7	1.3	0.8	1.2	1.6	1.81						Pachic
3%	Ah1	20 - 44	10 YR 2/0	10 YR 2/1	0.64	110.0	41.2	4.6	3.8	90.5	1.7	1.5	4.3	1.9	2.5	3.0	2.33	0.4	0.6	1.5	0.8	1.6	2.1	1.68	u		a			Laxic
	Ah2	44 - 60	10 YR 2/0	10 YR 2/2	0.76	61.3	46.4	4.4	3.9	88.2	1.5	1.3	3.8	1.2	2.6	3.4	1.99	0.4	0.7	1.8	1.0	2.7	2.7	1.76	u					
	Ah3	60 - 71	10 YR 2/0	10 YR 2/2	0.95	57.6	44.8	4.4	4.0	87.4	1.3	1.2	4.6	1.5	2.5	2.8	1.84	0.3	0.5	1.9	0.8	1.9	2.4	1.79	u					
	AChw	71 - 83	10 YR 2/1	10 YR 3/2	nd	38.6	37.0	4.4	4.0	82.2	1.2	1.0	4.3	1.3	1.8	2.0	1.59	0.3	0.4	1.6	0.8	1.5	2.0		u					
	2Bw1	83 - 108	10 YR 3/4	10 YR 5/4	1.09	16.5	27.1	4.8	4.0	73.0	0.9	0.7	3.6	0.9	1.4	1.7	1.18	0.2	0.4	1.6	0.8	2.0	2.4		c					
	2Bw2	108 - 135	10 YR 3/4	10 YR 6/4	1.06	11.2	21.6	4.6	4.0	66.8	0.7	0.5	4.0	0.8	1.3	1.6	0.87	0.2	0.3	1.9	0.6	2.0	3.1		c					
	2Cw	135 - 158	10 YR 6/3	10 YR 7/2	0.89	2.7	20.4	4.6	4.1	42.5	0.1	0.2	0.6	0.2	0.2	0.2	0.31	0.2	0.4	1.8	1.1	0.7	0.6							
F5	Oi/Oe	5 - 0				516.0	35.3	5.2	4.5																			AN	Aluandic	Hyperdystric
upper	Oa	0 - 7	10 YR 2/0	10 YR 2/1	0.25	277.2	22.8	4.2	3.5	86.8	1.3	1.1	3.0	1.9	1.6	1.3	1.75	0.4	0.5	1.2	0.6	0.7	1.1	1.95					Folic	Clayic
slope	Ah1	7 - 17	10 YR 2/0	10 YR 2/0	0.41	181.2	27.5	4.4	3.8	96.1	2.2	2.1	4.2	3.0	2.5	2.6	3.19	0.5	0.6	1.1	0.7	0.9	1.3	1.76	u		a		Epileptic	
5%	Ah2	17 - 32	10 YR 2/0	10 YR 2/0	0.48	128.4	37.5	4.6	4.1	98.0	1.9	1.9	4.2	2.7	3.0	3.4	2.88	0.4	0.7	1.6	0.7	1.2	1.7	1.76	u		a		Umbric	
F6	Oi/Oe	4 - 0				504.4	40.2	5.4	4.7																			AN	Aluandic	Hyperdystric
middle	Ah1	0 - 10	10 YR 2/1	10 YR 3/2	0.70	80.6	21.1	4.1	3.8	80.1	1.9	0.7	5.6	1.1	2.1	1.3	1.63	0.3	0.4	1.1	0.6	1.2	2.0	2.33	u				Fulvic	Epiclayic
slope	Ah2	10 - 26	10 YR 2/1	10 YR 3/2	0.64	57.7	20.3	4.3	4.1	93.2	2.3	1.3	4.9	1.8	3.2	2.8	2.49	0.5	0.6	1.4	0.7	1.6	2.2	2.34	u	f	a		Endoleptic	
13%	2Ahb1	26 - 33	10 YR 2/0	10 YR 3/2	0.58	62.7	19.3	4.6	4.2	96.6	2.1	1.8	4.3	2.0	3.4	4.0	2.84	0.5	0.8	1.6	0.9	2.0	2.3	1.87	u	f	a		Umbric	
	3Ahb2	33 - 45	10 YR 2/0	10 YR 3/2	0.62	66.7	27.1	4.8	4.3	96.1	1.8	2.1	4.6	2.6	2.8	4.2	3.06	0.4	0.6	1.5	0.8	1.6	2.0	2.06	u	f	a			
	3CAwhb	45 - 60	10 YR 2/2	2.5 Y 4/4	nd	49.2	22.6	4.7	4.2	94.9	1.5	1.8	3.8	1.8	2.0	2.8	2.51	0.4	0.5	1.4	1.0	1.5	1.6	2.18	u					
	3CBwb	60 - 76	10 YR 3/3	2.5 Y 6/2	nd	17.0	26.6	4.8	4.2	78.7	0.4	1.1	2.7	0.9	0.6	1.0	1.27	0.2	0.2	1.3	1.2	1.1	0.9							
F7	Oi/Oe	2 - 0				438.6	31.4	5.7	5.2																			UM	Epileptic	Hyperhumic
middle	Ah	0 - 8	10 YR 2/1	10 YR 3/3	0.67	113.3	15.2	4.1	3.5	73.1	1.6	0.5	2.8	0.6	1.5	0.6	1.34	0.6	0.5	0.9	0.8	1.0	1.3	2.39	u					Hyperdystric
slope	ABhw	8 - 21	10 YR 2/1	10 YR 3/3	0.55	68.1	20.0	4.2	3.8	88.5	2.5	0.7	4.3	0.9	2.9	1.7	1.95	0.6	0.7	1.2	0.8	1.9	2.3	2.05	u					Laxic
7%	2Ahb	21 - 28	10 YR 2/0	10 YR 2/2	0.51	84.3	19.6	4.2	3.9	95.8	2.7	1.5	5.1	1.8	3.2	2.9	2.90	0.5	0.6	1.2	0.9	1.6	1.9	1.76	u		a			
	2AChwb	28 - 35	10 YR 2/0	10 YR 3/2	nd	66.5	21.4	4.4	3.9	94.9	1.4	1.4	3.8	1.7	1.9	2.7	2.12	0.4	0.5	1.4	0.9	1.6	1.9	1.84	u		a			
	3ABhwb	35 - 42	10 YR 2/2	10 YR 5/3	0.78	49.9	23.6	4.5	4.2	93.9	0.9	1.3	3.0	1.5	1.4	2.1	1.70	0.3	0.5	1.6	0.8	1.4	1.7	2.20	u					

Table 1, continued: soils of *Araucaria* forest (F), Pinus plantation (PP) and the bog-like soil (B).

Soil	Horizon ^{1}	Depth	Munsell colour		BD	OC	C / N	pH	pH	P_{ret}	Fe_o	Al_o	Fe_d	Al_d	Fe_p	Al_p	$Al_o + 0.5$	Fe_o /	Fe_p /	Fe_p /	Alo/	Al_p /	Al_p /	MI	u/	f/	a	RSG	pref.	suff.
		(cm)	(moist)	(dry)	(g cm^{-3})	(g kg^{-1})	ratio	(H_2O)	(KCl)	(%)	(%)						Fe_o (%)	Fe_d	Fe_d	Fe_o	Ald	Al_d	Al_o		c	m			qualifiers	qualifiers
F8	Oi/Oe	3 - 0				413.8	30.8	5.9	5.4																			AN	Aluandic	Hyperdystric
middle	Ah1	0 - 16	10 YR 2/1	10 YR 3/2	0.53	104.0	16.3	4.2	3.7	66.8	1.8	0.5	3.2	0.6	1.9	0.7	1.41	0.6	0.6	1.1	0.8	1.2	1.4	2.09	u				Fulvic	
slope	Ah2	16 - 26	10 YR 2/1	10 YR 2/2	0.62	75.8	21.4	4.5	3.8	90.5	3.8	1.1	6.8	1.3	4.6	2.4	2.98	0.6	0.7	1.2	0.8	1.9	2.3	2.06	u	f	a		Endoleptic	
9%	2Ahb	26 - 36	10 YR 2/0	10 YR 2/2	0.53	66.2	23.6	4.8	4.0	92.5	2.7	1.7	5.2	1.8	3.7	3.9	3.03	0.5	0.7	1.4	0.9	2.2	2.3	1.87	u	f	a		Umbric	
	2BAwhb	36 - 49	10 YR 2/2	10 YR 3/3	0.59	44.9	28.1	4.9	4.1	94.5	2.2	1.8	4.6	1.8	2.7	3.3	2.90	0.5	0.6	1.2	1.0	1.9	1.9	2.18	u	f	a			
	2Bwb	49 - 63	10 YR 3/4	2.5 Y 4/4	0.70	37.2	28.1	4.7	4.2	94.6	2.0	1.8	4.0	1.5	2.4	3.1	2.79	0.5	0.6	1.2	1.2	2.0	1.7	2.45		f	a			
F9	Oi/Oe	3 - 0			nd	nd	nd	nd	nd																			CM	Endoleptic	Alumic
middle	Ah	0 - 5	10 YR 2/2	10 YR 3/3	nd	89.7	15.6	4.6	3.8	50.1	1.4	0.3	3.9	0.5	1.0	0.2	0.97	0.4	0.3	0.7	0.6	0.5	0.9	2.55						Hyperhumic
slope	Bw1	5 - 8	10 YR 4/3	10 YR 6/3	nd	33.0	14.2	4.8	4.1	69.8	2.1	0.3	6.2	0.7	1.8	1.1	1.37	0.3	0.3	0.9	0.5	1.6	3.4		c					Hyperdystric
1%	Bw2	8 - 18	10 YR 3/4	10 YR 5/3	nd	26.1	12.4	4.7	3.9	74.1	0.9	0.5	4.6	0.9	2.3	2.1	0.92	0.2	0.5	2.7	0.6	2.4	4.4		c					Laxic
	Bw3	18 - 36	10 YR 3/4	10 YR 4/3	nd	24.1	15.8	4.6	3.9	81.0	1.0	0.7	4.7	1.0	2.7	3.2	1.15	0.2	0.6	2.7	0.7	3.2	4.8		c					
	Bw4	36 - 55	7.5 YR 3/4	10 YR 5/4	nd	18.5	17.3	4.7	4.1	83.2	0.7	0.7	5.7	1.2	2.3	3.0	1.04	0.1	0.4	3.1	0.6	2.6	4.5		c					
F10	Oi/Oe	5 - 0			nd	nd	nd	nd	nd																			AN	Aluandic	Hyperdystric
middle	Ah	0 - 4	10 YR 2/1	10 YR 2/2	0.41	157.4	13.5	4.2	3.3	65.7	0.9	0.6	4.0	1.3	1.5	0.8	1.04	0.2	0.4	1.6	0.4	0.6	1.4	2.42	u				Endoleptic	Clayic
slope	Bw	4 - 40	10 YR 2/2	10 YR 3/3	0.68	42.1	19.1	4.6	4.0	90.3	2.0	1.0	4.7	1.5	3.2	2.3	2.02	0.4	0.7	1.6	0.7	1.5	2.2	2.47	u		a		Umbric	
2%	2Ahb	40 - 54	10 YR 2/1	10 YR 3/2	0.64	40.8	25.9	4.8	4.0	95.0	1.8	1.5	3.9	1.7	2.9	3.5	2.36	0.5	0.8	1.6	0.8	2.1	2.4	2.03	u		a			
	2Bwb	54 - 72	10 YR 3/4	10 YR 5/4	0.71	24.9	23.4	4.7	4.2	87.4	1.1	1.2	4.2	1.6	2.2	3.3	1.76	0.3	0.5	2.0	0.8	2.1	2.7	2.57	c					
PP1	Oi/Oe	7 - 0				465.0	60.3	4.2	3.3																			UM	Epileptic	Hyperhumic
upper	Ah1	0 - 10	7.5 YR 2/0	7.5 YR 2/0	0.62	143.8	19.1	4.3	3.7	90.8	1.0	1.2	2.9	1.4	1.7	2.2	1.69	0.3	0.6	1.8	0.9	1.6	1.8	1.72	u					Hyperdystric
slope	Ah2	10 - 27	7.5 YR 2/0	7.5 YR 2/0	0.62	116.2	21.8	5.5	4.0	95.2	1.1	1.4	4.5	2.1	1.9	2.4	1.89	0.2	0.4	1.7	0.6	1.1	1.7	1.76	u					Laxic
7%																														Clayic
PP2	Oi/Oe	10 - 0				441.7	57.1	4.0	3.0																			AN	Aluandic	Hyperdystric
lower	Oa	0 - 10	10 YR 2/0	10 YR 2/0	0.36	238.2	19.2	4.3	3.5	93.0	1.3	1.5	1.3	1.6	1.1	1.5	2.18	1.0	0.8	0.9	1.0	0.9	1.0	1.52		m	a		Melanic	Clayic
slope	Ah1	10 - 19	10 YR 2/0	10 YR 2/0	0.53	170.7	20.2	4.4	4.0	95.2	1.7	2.0	1.6	1.7	1.4	2.2	2.90	1.1	0.9	0.8	1.2	1.3	1.1	1.67	u	m	a		Folic	
5%	Ah2	19 - 33	10 YR 2/0	10 YR 2/0	0.59	105.1	23.8	4.3	4.0	94.1	1.3	1.8	1.9	1.5	1.4	2.5	2.43	0.7	0.7	1.0	1.2	1.7	1.4	1.65	u	m	a		Umbric	
	Ah3	33 - 46	10 YR 2/0	10 YR 2/0	0.69	69.1	35.5	4.4	4.0	94.0	1.8	1.5	2.2	1.3	2.0	2.7	2.34	0.8	0.9	1.1	1.2	2.2	1.9		u		a			
	BAwh	46 - 56	10 YR 2/0	10 YR 3/2	0.95	28.9	32.5	4.4	4.0	88.5	1.3	0.9	2.3	0.8	1.6	1.9	1.53	0.5	0.7	1.2	1.1	2.3	2.2		u					
	Bw1	56 - 69	10 YR 2/2	10 YR 5/3	0.97	16.4	21.9	4.5	4.0	82.8	1.3	0.7	2.4	0.6	1.4	1.5	1.38	0.5	0.6	1.1	1.2	2.4	2.1		u					
	Bw2	69 - 82	10 YR 4/3	10 YR 6/3	1.17	9.1	18.9	4.5	3.9	70.5	0.7	0.5	2.7	0.6	0.8	1.0	0.90	0.3	0.3	1.2	0.9	1.7	1.9		c					
	Bw3	82 - 96	10 YR 4/4	10 YR 6/3	1.19	6.3	14.3	4.3	3.8	64.8	0.5	0.4	2.2	0.5	0.5	0.7	0.66	0.2	0.2	0.9	0.8	1.4	1.8		c					
	Bw4	96 - 120	10 YR 4/4	10 YR 6/3	1.14	6.2	14.9	4.1	3.7	57.1	0.5	0.4	2.2	0.5	0.4	0.7	0.62	0.2	0.2	0.8	0.8	1.4	1.8		c					
	Cw	120 - 127	10 YR 5/2	10 YR 7/2	1.18	4.6	14.2	4.5	3.8	49.0	0.1	0.4	0.2	0.2	0.1	0.3	0.39	0.3	0.2	0.7	1.8	1.5	0.8							
B	H	10 - 0	10 YR 2/0	10 YR 2/0	nd	280.5	15.9	4.0	3.4	70.6	0.6	0.6	0.6	0.7	0.5	0.4	0.92	1.1	0.9	0.8	0.9	0.6	0.7	1.72				UM	Folic	Hyperhumic
bottom	Ahl1	0 - 11	10 YR 2/0	10 YR 2/0	nd	172.5	19.9	4.2	3.5	78.0	0.4	0.8	0.3	0.9	0.4	0.6	1.02	1.3	1.2	0.9	0.9	0.7	0.8	1.63	u					Hyperdystric
	Ahl2	11 - 21	10 YR 2/0	10 YR 2/0	nd	117.6	30.4	4.3	3.5	79.0	0.2	0.8	0.3	0.7	0.2	0.7	0.91	0.9	0.8	1.0	1.1	1.0	0.9	1.63	u					Pachic
	Ahl3	21 - 42	10 YR 2/0	10 YR 2/0	nd	99.0	40.6	4.3	3.8	77.4	0.1	0.8	0.1	0.8	0.1	0.7	0.86	0.9	0.9	1.0	1.0	0.8	0.8	1.56	u					Laxic
	Ahl4	42 - 61	10 YR 2/0	10 YR 3/1	nd	57.7	25.9	4.4	3.8	74.9	0.1	0.6	0.1	0.5	0.2	1.0	0.64	1.0	1.7	1.7	1.1	1.9	1.7	1.51	u					
	Ahl5	61 - 73	10 YR 2/0	10 YR 4/1	nd	29.2	21.9	4.5	3.8	54.6	0.1	0.4	0.1	0.3	0.2	1.0	0.43	0.9	1.4	1.5	1.3	3.5	2.7	1.53	u					
	Ahl6	73 - 92	10 YR 2.5/1	10 YR 5/1	nd	16.0	28.8	4.6	3.7	36.2	0.1	0.2	0.2	0.2	0.2	0.7	0.28	0.8	0.8	1.0	1.4	4.3	3.2	1.58	u					
	Br	92 - 112+	2.5 Y 6/2	10 YR 8/1	nd	2.2	9.0	4.7	3.7	34.7	0.2	0.1	0.2	0.1	0.1	0.1	0.20	1.0	0.4	0.4	1.5	0.7	0.5		c					

Soils: G = grassland without shrubs, GS = grassland with shrubs, P = pastureland, S = shrubland, FP = patch of Araucaria forest, F = Araucaria forest, PP = Pinus plantation, B = bog-like soil

1 horizon designation according to FAO (2006)

diagnostic horizons, diagnostic properties according to WRB (IUSS Working Group WRB, 2006):
u = umbric, c = cambic, f = fulvic, m = melanic, a = andic

RSG (Reference Soil Groups): AN = Andosol, UM = Umbrisol, CM = Cambisol

Table 2: Clay, silt and sand fractions, as well as cation exchange characteristics of mineral soil horizons from 18 profiles.

Soil	Horizon [a]	Depth (cm)	Clay (%)	Silt	Sand	CEC_b [b] (cmolc kg^{-1})	SEB [c] (cmolc kg^{-1})	Al [d] (cmolc kg^{-1})	CEC_{eff} [e] (cmolc kg^{-1})	Al/CEC_{eff}
G1	Ah1	0 - 9	69	27	4	128.3	1.6	8.6	10.2	0.84
	Ah2	9 - 20	68	26	5	109.0	0.7	8.1	8.8	0.92
	Ah3	20 - 31	67	27	6	71.2	0.4	6.7	7.1	0.95
	Ah4	31 - 40	66	27	7	67.7	0.3	6.4	6.7	0.95
	Ah5	40 - 50	67	25	8	70.5	0.3	5.6	5.9	0.95
	BAwh	50 - 62	65	26	9	62.0	0.3	5.8	6.1	0.95
	Bw	62 - 75	61	29	10	43.7	0.3	3.6	3.9	0.92
G2	Ah1	0 - 13	61	32	7	110.9	1.1	7.7	8.8	0.88
	Ah2	13 - 25	60	30	11	86.5	0.3	5.5	5.8	0.95
	Ah3	25 - 36	61	28	11	88.5	0.2	5.2	5.5	0.96
	AChw	36 - 41	58	27	15	69.9	0.2	3.6	3.8	0.95
	CAwh	41 - 55	57	25	18	55.2	0.2	2.7	2.9	0.93
G3	Ah1	0 - 10	62	34	4	108.4	4.2	6.8	11.1	0.61
	Ah2	10 - 18	63	31	6	105.9	0.7	6.1	6.8	0.89
	Ah3	18 - 31	63	28	8	102.8	0.6	5.3	5.9	0.90
GS1	Ah1	0 - 7	63	31	5	128.7	2.1	7.5	9.6	0.78
	Ah2	7 - 18	63	30	8	113.8	0.9	6.2	7.1	0.87
	AChw	18 - 25	57	31	12	101.5	0.6	5.1	5.7	0.90
GS2	Oa1	0 - 12	65	32	2	134.6	2.7	7.8	10.5	0.74
	Oa2	12 - 24	60	32	8	132.4	0.7	4.8	5.5	0.87
	Ah1	24 - 36	57	36	7	133.3	0.5	3.5	4.0	0.89
	2ABhw	36 - 51	28	63	8	87.0	0.3	nd	nd	nd
	2BAwh1	51 - 63	33	56	11	74.8	0.3	nd	nd	nd
	3BAwh2	63 - 71	63	27	10	46.5	0.4	5.0	5.4	0.93
	3Bw	71 - 98	41	38	21	29.4	0.5	5.1	5.7	0.91
GS4	Oa	0 - 11	61	36	3	113.2	3.0	8.0	11.1	0.72
	Ah1	11 - 23	63	32	5	104.3	0.4	8.6	9.1	0.95
	Ah2	23 - 32	62	31	7	92.6	0.2	6.9	7.1	0.97
	Ah3	32 - 44	63	28	9	78.1	0.2	5.6	5.8	0.97
	Ah4	44 - 55	60	29	12	60.1	0.2	5.7	5.9	0.97
	Bw	55 - 59	57	28	15	45.7	0.7	5.2	5.8	0.88
GS5	Ah1	0 - 12	59	33	8	85.2	3.4	6.7	10.1	0.66
	Ah2	12 - 32	58	32	9	72.8	0.6	5.8	6.5	0.91
	Ah3	32 - 52	52	28	20	52.2	0.3	5.2	5.5	0.95
	Ah4	52 - 73	55	27	18	47.6	0.2	4.3	4.5	0.96
	BAwh	73 - 82	39	31	29	33.5	0.2	3.1	3.3	0.94
	Bw	82 - 95	37	34	29	28.3	0.4	4.0	4.4	0.91
P1	Ah1	0 - 13	65	28	7	110.6	1.2	6.1	7.3	0.83
	Ah2	13 - 28	63	29	8	85.6	0.4	6.6	7.0	0.95
	ABhw	28 - 40	66	23	11	55.2	0.3	6.0	6.3	0.96
	BAwh	40 - 48	63	25	12	53.3	0.2	5.9	6.1	0.96
	Bw1	48 - 60	63	24	13	35.2	0.2	3.9	4.1	0.95
	Bw2	60 - 80	63	28	9	41.4	0.3	5.0	5.3	0.95
	Bw3	80 - 100	64	26	10	35.0	0.2	3.9	4.1	0.94
	Bw4	100 - 118	62	26	12	30.4	0.2	3.7	4.0	0.94
	Bw5	118 - 146	62	27	12	31.3	0.3	4.1	4.4	0.92
	2Bgw1	146 - 190	54	26	20	23.9	0.3	4.7	5.1	0.93
	2Bgw2	190 - 224	54	28	18	24.5	0.3	4.3	4.6	0.93
	2Bgw3	224 - 274	53	26	21	22.9	0.2	5.1	5.3	0.96
	2Bgw4	274 - 287	55	25	21	18.8	0.2	3.6	3.8	0.94
	3Bg	287 - 310+	52	26	22	18.3	0.3	7.1	7.4	0.96
P2	Ah1	0 - 12	67	30	4	122.7	1.3	9.8	11.1	0.88
	Ah2	12 - 23	66	28	6	107.5	0.5	8.1	8.6	0.94
	Ah3	23 - 34	63	28	9	89.3	0.2	7.5	7.7	0.97
	ABhw	34 - 41	65	24	11	75.9	0.2	5.8	6.1	0.97
	BAwh	41 - 47	51	30	19	55.3	0.2	5.9	6.1	0.97
	Bw	47 - 55	57	27	16	35.7	0.2	5.3	5.5	0.97
S1	Ah1	0 - 6	71	23	7	70.5	4.4	6.6	11.1	0.60
	Ah2	6 - 21	64	28	7	68.5	1.0	5.2	6.3	0.83
	Ah3	21 - 30	61	29	10	73.3	0.3	5.8	6.1	0.94
	2Ahb	30 - 50	62	22	16	71.2	0.4	6.6	7.0	0.95
	2ABhwb	50 - 60	64	21	16	57.4	0.4	5.2	5.6	0.93
	2Bwb	60 - 93	56	24	20	42.3	0.2	4.2	4.5	0.95

Table 2: continued.

Soil	Horizon [a]	Depth (cm)	Clay (%)	Silt	Sand	CEC_b [b] (cmolc kg^{-1})	SEB [c] (cmolc kg^{-1})	Al [d] (cmolc kg^{-1})	CEC_{eff} [e] (cmolc kg^{-1})	Al/CEC_{eff}
FP2	Oa1	0 - 8	61	36	3	131.0	4.5	14.8	19.8	0.75
	Oa2	8 - 24	61	36	3	120.7	2.3	12.6	15.0	0.84
	Ah1	24 - 36	68	27	5	101.8	1.0	10.1	11.2	0.90
	Ah2	36 - 46	70	26	4	68.3	0.3	8.2	8.5	0.97
	Ah3	46 - 63	70	26	5	85.8	0.2	8.6	8.9	0.97
	BAwh	63 - 79	62	28	10	84.2	0.2	7.8	8.1	0.97
	Bw1	79 - 96	60	28	12	48.1	0.2	6.9	7.2	0.97
	Bw2	96- 106	35	21	44	34.6	0.2	5.6	5.8	0.97
F1	Oa	0 - 6	61	29	10	130.6	5.7	7.0	12.8	0.55
	Ah1	6 - 13	60	33	7	127.1	1.0	10.5	11.6	0.91
	2Ah2	13 - 23	64	23	13	133.2	0.7	10.8	11.5	0.94
	2Ah3	23 - 38	60	30	10	106.7	0.3	6.7	7.1	0.95
	2Ah4	38 - 53	65	24	11	100.9	0.3	6.5	6.8	0.96
	2CAwh	53 - 64	59	26	15	74.8	0.2	5.2	5.4	0.96
	2CBw1	64 - 89	44	35	21	42.9	0.5	3.9	4.4	0.89
	2CBw2	89 - 124	37	37	26	30.2	0.4	5.0	5.3	0.93
F2	Ah1	0 - 6	45	48	7	109.3	1.0	8.2	9.3	0.88
	Ah2	6 - 11	48	43	9	98.8	0.5	8.7	9.2	0.94
	2Ah3	11 - 35	51	38	11	115.5	0.2	8.6	8.8	0.97
	2Ah4	35 - 55	44	36	20	118.0	0.1	4.9	5.0	0.97
F5	Oa	0 - 7	61	36	3	115.4	1.9	12.9	15.0	0.86
	Ah1	7 - 17	66	29	5	116.2	0.8	8.2	9.0	0.91
	Ah2	17 - 32	68	26	6	85.8	0.6	9.8	10.4	0.94
F6	Ah1	0 - 10	48	43	10	82.8	0.6	6.9	7.6	0.91
	Ah2	10 - 26	63	29	8	110.6	0.4	6.9	7.3	0.94
	2Ahb1	26 - 33	55	23	22	112.2	0.7	6.6	7.3	0.91
	3Ahb2	33 - 45	55	25	21	100.9	0.4	5.2	5.7	0.93
	3CAwhb	45 - 60	51	26	23	119.0	0.3	4.9	5.2	0.94
	3CBwb	60 - 76	nd	nd	nd	86.3	0.2	5.8	6.1	0.96
F10	Ah	0 - 4	59	33	8	77.9	2.7	7.8	10.7	0.73
	Bw	4 - 40	64	27	10	57.7	0.3	6.0	6.3	0.96
	2Ahb	40 - 54	64	26	9	50.3	1.1	6.2	7.2	0.85
	2Bwb	54 - 72	62	25	13	42.3	0.3	4.9	5.2	0.94
PP1	Ah1	0 - 10	69	25	5	100.7	1.3	11.4	12.7	0.90
	Ah2	10 - 27	69	23	8	101.3	0.5	6.2	6.7	0.92
PP2	Oa	0 - 10	60	39	2	155.2	0.9	13.4	14.3	0.94
	Ah1	10 - 19	61	35	4	121.7	0.4	8.9	9.3	0.96
	Ah2	19 - 33	59	34	7	112.4	0.3	7.7	7.9	0.96
	Ah3	33 - 46	60	31	10	84.8	0.2	8.2	8.4	0.98
	BAwh	46 - 56	61	30	8	47.9	0.2	7.0	7.2	0.97
	Bw1	56 - 69	60	29	11	39.0	0.2	5.7	5.9	0.97
	Bw2	69 - 82	56	30	15	30.4	0.2	4.6	4.8	0.96
	Bw3	82 - 96	56	30	14	26.1	0.2	4.6	4.8	0.96
	Bw4	96 - 120	56	32	13	25.6	0.2	5.1	5.3	0.96
	Cw	120 - 127	52	35	13	28.7	0.2	6.0	6.2	0.97

Soils: G = grassland without shrubs, GS = grassland with shrubs, P = pastureland, S = shrubland, FP = patch of Araucaria forest, F = Araucaria forest, PP = Pinus plantation

a horizon designations according to FAO (2006)
b cation exchange capacity at pH 7 (CEC_b)
c sum of exhcangeable bases (SEB) by 1M ammonium acetate pH7
d KCl extractable Al
e sum of SEB and KCl extractable Al and H

Table 4: δ^{13}C values (‰) of plant species and organic surface layers (Oi and Oe) from grassland, *Araucaria* forest, shrubland and Pine plantation.

Life forms/species	δ^{13}C (‰)	
a) C_4 grasses	Stem	Root
Andropogon lateralis Nees	-12.3	nd
Sorghastrum nutans cf. (L.) Nash	-12.9	nd
grass-mixture (pastureland)	-13.8	-12.2
grass-mixture (at profile G1)	-12.5	-11.7
grass-mixture (at profile G3)	-13.5	-12.4
Mean for C_4 grasses (stems)	-13.0 ± 0.7 ‰	
b) C_3 shrubs	Leaf	Wood
Baccharis crispa Spreng.	-29.4	-29.3
Baccharis uncinella DC.	-28.9	-29.1
Baccharis nummularia Heering ex Malme	-28.2	-28.0
Baccharis cylindrica DC.	-29.1	-29.3
Solanum sp.	-30.1	nd
Calea phyllolepis Bak.	-28.8	nd
Mean for C_3 shrubs (leaf and wood):	-29.0 ± 0.6 ‰	
c) C_3 deciduous trees	Leaf	Wood
Nectandra megapotamica (Spreng.) Mez	-32.0	-31.9
Leandra sublanata Cogn.	-30.1	-29.4
Ilex paraguariensis A. St.-Hil.	-34.4	-32.1
Tibouchina sellowiana (Cham.) Cogn.	-28.2	nd
Myrcia retorta (Camb.)	-32.3	-31.2
Myrcia obtecta (Berg) Kiaerskou	-31.9	nd
Drimys brasiliensis Miers	-32.3	-31.9
Myrsine sp.	-31.1	nd
Myrsine lorentziana (Mez) Arechav.	-31.7	nd
Nectranda grandiflora Nees	-32.5	nd
Siphoneugena reitzii Legrand	-33.3	-32.3
Myrceugenia myrcioides (Camb.) Berg	-32.9	nd
Daphnopsis fasciculata (Meissn.) Nevl.	-30.2	-31.5
Piptocarpha notata (Less.) Bak.	-33.7	nd
Mean for C_3 deciduous trees (leaf and wood):	-31.8 ± 1.4 ‰	
d) Mean for C_3 *Araucaria angustifolia (* Bert.) O. Kuntze:	-24.8 ± 1.2 ‰	
needle: -26.5, bark: -24.1, sapwood: -24.9	(needle, wood)	
heartwood: -24.2, root: -23.7		
e) Mean for C_3 Bamboo (genus Merostachys)	-30.2	
leaf: -30.7, wood: -29.6		
f) Mean for C_3 tree fern *Dicksonia sellowiana* (Presl.) Hook.	-29.5	
leaf: -30.0, wood: -29.0, root: -28.8	(leaf, wood)	
Mean for C_3 plants of the *Araucaria* forest (c-f):	-30.6 ± 2.7 ‰	
(leaf and wood)		
g) C_3 conifer *Pinus taeda* and *elliottii*		
wood and bark	-25.6	
needle	-28.8	
Organic surface layers (Oi and Oe)		
Mean for grasslands with shrubs	-20.0	
GS4: -23.0, GS5: -17.0		
Shrubland (S1)	-28.8	
Mean for Araucaria forest and patches	-28.8 ± 0.9 ‰	
F1: -29.1, F5: -29.3, F6: -27.2, FP1: -29.5, FP2: -28.7		
Mean for Pinus plantation PP1: -28.7, PP2: -28.4	-28.6	

Table 5: Proportions of C_4 derived SOC, ^{14}C contents (pMC) and chemical-physical soil properties.

		Depth	Munsell color		Clay	Silt	Sand	BD	pH		OC	C/N	C stock	C_4 derived SOC (%)		^{14}C content	MI[e]
Pedons / WRB	Horizon[a]	(cm)	(moist)	(dry)	(%)			$(g\ cm^{-3})$	(H_2O)	(KCl)	$(g\ kg^{-1})$	ratio	$(kg\ m^{-2})$	MBE[b]	ME[c]	(pMC)[d]	
Grassland	Ah1	0 - 9	7.5 YR 2/0	7.5 YR 2/0	69	27	4	0.48	4.6	3.7	186.6	19	8.0	97		105.3	1.72
G1	Ah2	9 - 20	7.5 YR 2/0	7.5 YR 2/0	68	26	5	0.53	4.5	4.0	130.5	22	7.6	90			1.67
without shrubs	Ah3	20 - 31	7.5 YR 2/0	7.5 YR 2/0	67	27	6	0.61	4.6	4.0	92.5	26	6.2	90			1.64
Umbrisol	Ah4	31 - 40	7.5 YR 2/0	10 YR 3/0	66	27	7	0.70	4.6	4.0	62.3	29	3.9	93			1.66
	Ah5	40 - 50	7.5 YR 2/0	10 YR 3/0	67	25	8	0.77	4.8	4.0	43.5	37	3.4	90		58.1	1.62
	BAwh	50 - 62	7.5 YR 3/2	10 YR 4/2	65	26	9	0.83	4.5	4.0	31.2	28	3.1	90			1.76
	Bw	62 - 75	10 YR 4/4	10 YR 5/4	61	29	10	0.91	4.7	4.1	18.6	20	2.1	88		45.6	nd
G3	Ah1	0 - 10	5 YR 2/2	10 YR 2/1	62	34	4	0.49	4.7	4.0	199.8	20	9.2	83			1.75
without shrubs	Ah2	10 - 18	5 YR 2/2	10 YR 3/1	63	31	6	0.54	4.8	4.1	152.9	22	7.0	76			1.75
Andosol	Ah3	18 - 31	5 YR 2/2	10 YR 3/1	63	28	8	0.48	4.8	4.1	111.8	30	7.0	82			1.89
GS4	Oi + Oe	2 - 0							4.8	4.1	451.3	47					
with shrubs	Oa	0 - 11	10 YR 2/1	7.5 YR 2/0	61	36	3	0.41	4.7	3.7	244.7	20	11.0	63		103.9	1.70
Andosol	Ah1	11 - 23	10 YR 2/1	7.5 YR 2/0	63	32	5	0.40	4.7	3.9	169.0	26	8.1	88		88.1	1.59
	Ah2	23 - 32	7.5 YR 2.3/0	10 YR 2/1	62	31	7	0.45	4.6	4.0	126.7	42	5.1	93			1.63
	Ah3 #	32 - 44	7.5 YR 2.8/0	10 YR 2.5/1	63	28	9	0.57	4.7	4.2	85.3	43	5.7	89			1.66
	Ah4 #	44 - 55	5 Y 2.5/1	10 YR 3.5/1	60	29	12	0.73	4.6	4.2	52.2	41	3.9	87		49.7	nd
	Bw	55 - 59	2.5 Y 4/3	10 YR 5/2	57	28	15	0.82	4.7	4.3	30.5	28	1.0	84			nd
GS5	Oi + Oe	2 - 0							4.7	4.1	450.3	46					
with shrubs	Ah1	0 - 12	2.5 Y 2/0	10 YR 2.5/1	59	33	8	0.49	4.4	3.8	170.2	25	10.0	75			1.68
Umbrisol	Ah2	12 - 32	2.5 Y 2/0	10 YR 3/1	58	32	9	0.56	4.6	4.0	113.4	38	12.5	72			1.75
	Ah3	32 - 52	10 YR 2/2	10 YR 3.5/1	52	28	20	0.73	4.6	4.1	53.3	47	7.6	81			1.69
	Ah4	52 - 73	10 YR 2/2	10 YR 3.5/1	55	27	18	0.78	4.6	4.2	40.3	45	6.4	82			1.81
	BAwh	73 - 82	10 YR 3/2	10 YR 6/3	39	31	29	0.87	4.7	4.3	18.8	33	0.6	75			nd
	Bw #	82 - 95	10 YR 4/4	10 YR 7/2	37	34	29	0.87	4.5	4.1	11.2	33	1.1	74			nd
Patches of	Oi + Oe	4 - 0							5.1	4.3	500.0	39					
Araucaria	Oa	0 - 10	10 YR 2/2	10 YR 3/1	nd	nd	nd	0.46	3.9	3.4	223.9	21	10.1	18	21		1.97
forest	Ah1	10 - 23	7.5 YR 2/0	10 YR 2/1	nd	nd	nd	0.46	4.5	3.9	140.7	27	8.3	58	62		1.67
FP1	Ah2	23 - 32	7.5 YR 2/0	10 YR 2/1	nd	nd	nd	0.56	4.7	4.0	115.9	32	5.7	63	67		1.76
Umbrisol	AChw	32 - 42	5 YR 2/1	10 YR 2/1	nd	nd	nd	nd	4.8	4.1	89.8	29	nd	74			1.77
	CAwh	42 - 51	10 YR 3/4	10 YR 3/2	nd	nd	nd	nd	4.7	4.3	37.1	36	nd	75			1.80
FP2	Oi + Oe	3 - 0							4.7	4.1	512.3	39					
Andosol	Oa1	0 - 8	5 YR 2/2	7.5 YR 2.5/1	61	36	3	0.37	3.5	3.1	307.7	18	9.2	17	19	114.3	1.95
	Oa2	8 - 24	10 YR 2/1	7.5 YR 2.5/1	61	36	3	0.32	4.2	3.8	206.0	21	10.3	48	52	95.4	1.74
	Ah1	24 - 36	7.5 YR 2/0	7.5 YR 2.5/1	68	27	5	0.49	4.3	3.9	143.9	32	8.5	74	79		1.65
	Ah2	36 - 46	7.5 YR 2.5/0	10 YR 2.5/1	70	26	4	0.56	4.4	4.0	91.5	38	5.1	83	89	67.9	1.67
	Ah3	46 - 63	10 YR 2.5/1	10 YR 3/1	70	26	5	0.56	4.3	4.0	82.1	40	8.1	85	95		1.69
	BAwh	63 - 79	10 YR 3/1+2/1	10 YR 3.5/1+4/1	62	28	10	0.64	4.7	4.1	52.4	33	5.0	74	89		1.77
	Bw1	79 - 96	10 YR 4.5/4	10 YR 5/2.5	60	28	12	0.91	4.7	4.1	21.7	28	3.1	69	83	36.9	nd
	Bw2	96 - 106	10 YR 5/6	10 YR 6/3.5	35	21	44	1.16	4.9	4.1	11.2	23	0.9	58	78		nd

Table 5 (continued).

Pedons (WRB)	Horizon^a	Depth (cm)	Munsell color		Clay (%)	Silt	Sand	BD (g cm^{-3})	pH		OC (g kg^{-1})	C/N ratio	C stock (kg m^{-2})	C_4 derived SOC (%)		^{14}C content (pMC)^d	MI^e
			(moist)	(dry)					(H_2O)	(KCl)				MBE^b	ME^c		
Araucaria	Oi + Oe	7 - 0							5.3	4.6	457.3	28					
forest	Oa	0 - 6	10 YR 2/2	7.5 YR 2/0	61	29	10	0.31	4.8	3.5	224.3	15	4.1	6	8		1.89
F1	Ah1 #	6 - 12	5 YR 3/2	5 YR 3/1.5	60	33	7	0.40	4.5	3.6	161.8	16	3.8	19	21	98.4	1.87
Andosol	2Ah2 #	12 - 23	10 YR 2/2	2.5 YR 2/0	64	23	13	0.41	4.5	3.9	149.4	16	6.6	29	33	93.8	1.80
	2Ah3	23 - 38	5 YR 3/2	10 YR 3/2	60	30	10	0.42	4.5	4.0	103.0	19	6.2	31	36	84.5	1.90
	2Ah4 #	38 - 53	5 YR 3/3	5 YR 4/1	65	24	11	0.52	4.4	4.0	86.4	20	6.5	34	40	80.9	1.88
	2CAwh	53 - 64	5 YR 4/3	7.5YR 4/2	59	26	15	nd	4.6	4.1	68.7	17	nd	38			nd
	2CBw1	64 - 89	2.5 YR 4/3	5 YR 6/2	44	35	21	nd	4.7	4.1	21.3	23	nd	31			nd
	2CBw2	89 - 124	10 R 3.5/3	10 R 5/1	37	37	26	nd	4.4	4.0	13.9	29	nd	28		72.7	nd
F5	Oi + Oe	5 - 0							5.2	4.5	516.0	35					
Andosol	Oa	0 - 7	10 YR 2/2	7.5 YR 2.5/0	61	36	3	0.25	4.2	3.5	277.2	23	4.9	21	23		1.95
	Ah1	7 - 17	7.5 YR 2/0	7.5 YR 2.5/0	66	29	5	0.41	4.4	3.8	181.2	28	8.1	59	63	92.7	1.76
	Ah2	17 - 32	7.5 YR 2/0	7.5 YR 2.5/0	68	26	6	0.48	4.6	4.1	128.4	38	8.5	73	78	77.9	1.76
F6	Oi + Oe	4 - 0							5.4	4.7	504.4	40.0					
Andosol	Ah1 #	0 - 10	7.5 YR 3.5/2	10 YR 4/3	48	43	10	0.70	4.1	3.8	80.6	21	5.5	17	19	99.9	2.33
	Ah2	10 - 26	10 YR 3.5/4	10 YR 5/4	63	29	8	0.64	4.3	4.1	57.7	20	5.7	21	24	82.8	2.34
	2Ahb1 #	26 - 33	10 YR 3.5/3	10 YR 4/3	55	23	22	0.58	4.6	4.2	62.7	19	2.5	24	28		1.87
	3Ahb2	33 - 45	10 YR 3.5/2.5	10 YR 4/3	55	25	21	0.62	4.8	4.3	66.7	27	4.6	27	33	67.5	2.06
	3CAwhb	45 - 60	10 YR 4/2	10 YR 5/2	51	26	23	nd	4.7	4.2	49.2	23	nd	26			2.18
F10	Ah	0 - 4	10 YR 3/1.5	10 YR 3/4	59	33	8	0.41	4.2	3.3	157.4	13	2.6	-4	-2	111.8	2.42
Andosol	Bw	4 - 40	10 YR 3/4	10 YR 4-4.5/4	64	27	10	0.68	4.6	4.0	42.1	19	10.2	13	16	84.7	2.47
	2Ahb	40 - 54	10 YR 3/1	10 YR 3/2-2.5	64	26	9	0.64	4.8	4.0	40.8	26	3.6	35	42	57.0	2.03
	2Bwb	54 - 72	10 YR 4/4	10 YR 5/5	62	25	13	0.71	4.7	4.2	24.9	23	2.9	31	46	47.3	2.57
Shrubland	Oi + Oe	3 - 0							5.8	5.3	474.0	41					
S1	Ah1 #	0 - 6	7.5 YR 3/2	5 YR 4/1	71	23	7	0.52	4.4	3.9	108.0	18	3.1	16	18		2.22
Andosol	Ah2 #	6 - 21	10 YR 3/2	10 YR 4.5/3	64	28	7	0.68	4.4	3.9	90.1	21	9.2	12	15		2.22
	Ah3 #	21 - 30	10 YR 3/3.5	10 YR 4/3	61	29	10	0.55	4.5	4.1	76.6	24	3.8	14	19		2.30
	2Ahb #	30 - 50	10 YR 3/1	10 YR 4/1.5	62	22	16	0.55	4.4	4.2	66.3	27	7.3	25	31		2.04
	2ABhwb	50 - 60	10 YR 4.5/4	10 YR 5.5/4	64	21	16	0.73	4.5	4.1	48.8	24	2.8	25	39		2.15
	2Bwb	60 - 93	10 YR 5/6	10 YR 6.5/6	56	24	20	0.83	4.5	4.2	24.4	25	3.0	28	44		2.50
Pinus	Oi + Oe	7 - 0							4.2	3.3	465.0	60					
plantation	Ah1	0 - 10	10 YR 2/1	10 YR 2.5/1	69	25	5	0.62	4.3	3.7	143.8	19	8.8	82			1.72
PP1, Umbrisol	Ah2	10 - 27	5 YR 2/1	10 YR 2.5/1	69	23	8	0.62	5.5	4.0	116.2	22	12.2	89			1.76
PP2	Oi + Oe	10 - 0							4.0	3.0	441.7	57					
Andosol	Oa	0 - 10	10 YR 2/1	7.5 YR 2/0	60	39	2	0.36	4.3	3.5	238.2	19	8.4	99			1.52
	Ah1	10 - 19	10 YR 2/1	10 YR 2/1	61	35	4	0.53	4.4	4.0	170.7	20	8.5	103			1.67
	Ah2	19 - 33	10 YR 2/1.5	10 YR 2/1	59	34	7	0.59	4.3	4.0	105.1	24	8.3	101			1.65
	Ah3	33 - 46	10 YR 2/1.5	10 YR 2/1	60	31	10	0.69	4.4	4.0	69.1	36	6.3	97			1.70
	BAwh	46 - 56	10 YR 3/1+ 5/3	10 YR 4/2+ 6/3	61	30	8	0.95	4.4	4.0	28.9	32	2.6	90			1.68
	Bw1	56 - 69	10 YR 5/4	10 YR 6/3	60	29	11	0.97	4.5	4.0	16.4	22	2.1	83			nd
	Bw2	69 - 82	2.5 Y 5/4	10 YR 7/3	56	30	15	1.17	4.5	3.9	9.1	19	1.3	85			nd
	Bw3	82 - 96	2.5 Y 5/4	10 YR 8/2	56	30	14	1.19	4.3	3.8	6.3	14	1.0	81			nd

a) horizon designation according to FAO (2006), # charcoal

b) soil organic carbon (%) derived from C_4 plants as calculated by mass balance (equation 3)

c) soil organic carbon (%) derived from C_4 plants as calculated by mixing equation with grassland reference soil (equation 4)

d) percent modern carbon (100 pMC = 1950 AD)

e) melanic index according to Van Reeuwijk (2002)

Table 6: Proportions of functional groups according to ^{13}C NMR spectra, contents of lignin-derived phenols (CuO oxidation) and δ ^{13}C values of plant samples.

	Chemical shift regions / p.p.m.[1]				alkyl C /	CuO oxidation products[2] / mg VSC g^{-1} OC								$\delta^{13}C$
plants	alkyl C	O/N-alkyl C	aromatic C	carboxyl C	O/N-alkyl C	V	S	C	V+S+C	C/V	S/V	$(ac/al)_v$	$(ac/al)_s$	/‰
Araucaria angustifolia - needle	23.1	59.0	15.2	2.8	0.39	15.7	5.4	3.3	24.3	0.21	0.34	0.16	3.44	-26.5
Araucaria angustifolia - wood	nd	nd	nd	nd	nd	45.0	1.1	1.0	47.1	0.02	0.02	0.12	0.00	-24.6
Araucaria angustifolia - root	nd	nd	nd	nd	nd	11.8	1.0	0.7	13.6	0.06	0.09	0.24	0.00	-23.7
grass-mix	11.8	79.8	8.8	1.3	0.15	14.6	17.0	37.4	69.0	2.74	1.19	0.22	0.29	-13.8
grass-mix	8.4	76.4	12.2	3.0	0.11	nd	nd	nd	nd	nd	nd	nd	nd	-12.5
Andropogon lateralis (grass)	8.6	75.6	12.5	4.0	0.11	15.1	20.3	30.8	66.2	2.04	1.34	0.14	0.38	-12.3
Myrcia retorta - leave (tree)	16.3	62.2	16.2	5.5	0.26	6.4	25.1	5.0	36.5	0.78	3.92	0.28	0.14	-32.3
Baccharis uncinella - leave (shrub)	29.8	49.9	13.7	6.8	0.60	4.1	6.8	5.9	16.8	1.45	1.69	0.44	0.17	-28.9

1 alkyl C (0 - 45), O/N-alkyl C (45 - 110), aromatic C (110 - 160), carboxyl C (160 - 220)

2 V = vanillyl units, S = syringyl units, C = cinnamyl units, (ac/al)v = acid to aldehyde ratio of vanillyl units, (ac/al)s = acid to aldehyde ratio of syringyl units

Table 7: Proportions of functional groups according to ^{13}C NMR spectra, contents of lignin-derived phenols (CuO oxidation), soil organic carbon (OC) contents, C/N ratios, δ ^{13}C values and soil lightness values of heavy organo-mineral fractions.

		Depth	OC	C/N	Functional group/chemical shift (ppm)[1]				alkyl C /	δ ^{13}C			CuO oxidation products[4] (mg VSC g^{-1} OC)							
Soils	Horizon	(cm)	(g kg^{-1})	ratio	alkyl C	O/N-alkyl C	aromatic C	carboxyl C	O/N-alkyl C	(‰)	L value[2]	MI[3]	V	S	C	V+S+C	(ac/al)$_V$	(ac/al)$_S$	C/V	S/V
Grassland	Ah1	0 - 9	186.6	18.5	23.0	46.7	16.2	14.1	0.49	-14.3	36.9	1.72	0.5	0.6	0.5	1.6	1.53	1.12	0.9	1.0
without shrubs	Ah2	9 - 20	130.5	22.3	20.9	39.8	22.4	16.9	0.52	-15.1	38.1	1.67								
(G1)	Ah3	20 - 31	92.5	26.1	18.5	34.7	26.9	19.8	0.53	-15.1	40.1	1.64	0.7	0.5	0.2	1.4	0.77	1.46	0.3	0.7
Umbrisol	Ah4	31 - 40	62.3	29.1	16.0	34.3	31.1	18.6	0.47	-14.8	42.5	1.66								
	Ah5	40 - 50	43.5	36.5	16.2	30.7	33.2	19.8	0.53	-15.1	47.7	1.62	1.1	0.7	0.4	2.2	1.73	9.45	0.4	0.7
Grassland	Oi+Oe	2 - 0	451.3	47.0	11.1	65.6	17.2	6.4	0.17	-23.0			8.3	8.6	6.1	23.0	0.22	0.27	0.7	1.0
with shrubs	Oa	0 - 11	244.7	20.4	28.2	41.7	15.8	14.5	0.68	-18.7	40.7	1.70	0.4	0.2	0.3	1.0	2.64	1.49	0.9	0.6
(GS4)	Ah1	11 - 23	169.0	26.0	22.1	39.9	21.4	16.6	0.55	-15.4	36.4	1.59								
Andosol	Ah2	23 - 32	126.7	42.3	19.3	39.9	25.8	15.0	0.48	-14.7	38.8	1.63								
	Ah3	32 - 44	85.3	43.0	12.8	36.6	32.5	18.7	0.35	-15.3	39.9	1.66	0.4	0.5	0.2	1.1	0.90	0.63	0.5	1.3
	Ah4	44 - 55	52.2	40.7	17.3	36.5	31.0	14.8	0.47	-15.6	46.5	1.64								
Patch of	Oi+Oe	3 - 0	512.3	39.0	18.5	60.3	16.2	5.0	0.31	-28.7			3.9	6.4	1.8	12.1	0.41	0.15	0.5	1.7
Araucaria	Oa	0 - 8	307.7	17.8	32.9	39.3	14.2	13.6	0.84	-25.0	40.9	1.95	0.4	0.3	0.2	0.9	0.99	1.08	0.7	0.8
forest	Oa2	8 - 24	206.0	21.1	22.0	42.1	21.3	14.7	0.52	-20.8	35.8	1.74	0.5	0.3	0.3	1.1	3.22	1.64	0.6	0.6
(FP2)	Ah1	24 - 36	143.9	32.4	25.1	41.5	24.1	9.4	0.61	-17.3	37.7	1.65	0.6	0.3	0.2	1.1	2.69	1.48	0.5	0.6
Andosol	Ah2	36 - 46	91.5	37.7	20.5	39.6	28.3	11.6	0.52	-16.0	38.1	1.67								
	Ah3	46 - 63	82.1	40.1	16.7	33.9	33.5	15.9	0.49	-15.8	38.7	1.69	0.7	0.3	0.2	1.2	2.73	0.00	0.4	0.5
Araucaria forest	Oi+Oe	5 - 0	516.0	35.0	21.6	54.4	17.7	6.3	0.40	-29.3										
(F5)	Oa	0 - 7	277.2	22.8	36.8	38.5	12.3	12.7	0.96	-24.4	40.4	1.95	0.3	0.4	0.3	1.0	0.85	0.29	1.3	1.7
Andosol	Ah1	7 - 17	181.2	27.5	23.9	36.8	20.4	18.9	0.65	-19.2	40.4	1.76	0.7	0.5	0.3	1.6	1.44	1.62	0.5	0.8
	Ah2	17 - 32	128.4	37.5	17.7	41.5	25.2	15.6	0.43	-17.4	40.7	1.76	1.5	1.1	0.7	3.2	1.30	0.97	0.5	0.8

Table 7: continued.

		Depth	OC	C/N	Functional group/chemical shift (ppm)[1]				alkyl C /	δ^{13}C			CuO oxidation products[4] (mg VSC g^{-1} OC)							
Soils	Horizon	(cm)	(g kg$^{-1)}$	ratio	alkyl C	O/N-alkyl C	aromatic C	carboxyl C	O/N-alkyl C	(‰)	L value[2]	MI[3]	V	S	C	V+S+C	(ac/al)$_v$	(ac/al)$_s$	C/V	S/V
Araucaria forest	Oi+Oe	7 - 0	457.3	28.0	17.8	60.4	16.5	5.3	0.29	-29.1			7.7	10.1	3.7	21.5	0.85	0.27	0.5	1.3
(F1)	Oa	0 - 6	224.3	14.5	29.7	32.1	17.7	20.5	0.92	-26.4	45.0	1.89	0.3	0.3	0.2	0.7	7.33	2.61	0.8	1.0
Andosol	Ah1	6 - 13	161.8	16.5	25.7	37.1	22.2	14.9	0.69	-24.7	42.5	1.87	0.6	0.5	0.3	1.4	1.41	1.28	0.5	0.8
	2Ah2	13 - 23	149.4	16.3	18.9	36.4	28.3	16.4	0.52	-23.3	43.2	1.80	0.3	0.3	0.2	0.8	2.18	0.60	0.6	0.9
	2Ah3	23 - 38	103.0	19.3	19.4	25.1	26.8	28.7	0.78	-23.1	47.8	1.90	0.8	0.4	0.3	1.5	3.20	1.55	0.5	0.5
	2Ah4	38 - 53	86.4	20.2	23.1	37.0	28.6	11.3	0.62	-22.7	47.8	1.88	0.9	0.6	0.2	1.7	0.50	1.76	0.3	0.6
Araucaria forest	Oi+Oe	4 - 0	504.4	40.0	18.0	58.8	17.1	6.1	0.31	-27.2			16.9	13.1	3.1	33.0	0.26	0.70	0.2	0.8
(F6)	Ah1	0 - 10	80.6	21.1	28.8	40.5	19.5	11.2	0.71	-24.9	53.2	2.33	2.5	1.1	2.1	5.8	2.68	1.42	0.9	0.5
Andosol	Ah2	10 - 26	57.7	20.3	28.8	39.0	20.6	11.6	0.74	-24.4	54.1	2.34	1.3	0.5	0.8	2.6	2.37	1.45	0.6	0.4
Araucaria forest (F10)	Ah	0 - 4	157.4	13.5	34.0	42.3	15.7	8.1	0.80	-27.7	51.2	2.42	0.3	0.5	0.3	1.0	1.09	0.21	1.0	1.7
Shrubland	Oi+Oe	3 - 0	474.0	41.0	18.2	59.3	16.6	6.0	0.31	-28.8			7.5	10.0	3.6	21.1	0.40	0.22	0.5	1.3
(S1)	Ah1	0 - 6	108.0	18.3	28.4	36.3	19.1	16.5	0.78	-25.1	45.9	2.22	1.5	2.6	0.6	4.7	1.33	1.56	0.5	1.9
Andosol	Ah2	6 - 21	90.1	21.1	27.9	38.2	20.2	13.8	0.73	-25.6	48.5	2.22								
	Ah3	21 - 30	76.6	23.6	24.5	30.2	23.2	22.4	0.81	-25.3	48.5	2.30								

1 functional group/chemical shift (ppm): alkyl C (0 - 45), O/N-alkyl C (45 - 110), aromatic C (110 - 160), carboxyl C (160 - 220)

2 soil lightness value

3 melanic index (values are determined from bulk soils)

4 V = vanillyl units, S = syringyl units, C = cinnamyl units, (ac/al)$_v$ = acid to aldehyde ratio of vanillyl units, (ac/al)$_s$ = acid to aldehyde ratio of syringyl units

Table 10: δ ^{13}C values (‰) of bulk materials and lignin-derived phenols and VSC contents (mg VSC g^{-1} OC) from plants, organic surface layers and heavy organo-mineral fractions.

	C_3 conifer	C_4 grass	organic surface layers		heavy organo-mineral fractions								
	A. angustifolia	*Andropogon*	in Araucaria forest		G1		FP2		F6			F10	S1
δ ^{13}C values (‰)	needle	*lateralis*	F6	F1	Ah1	Ah3	Oa	Ah1	Ah1	Ah2	2Ah2	Ah1	Ah1
bulk sample	-26.5	-12.3	-27.4	-29.0	-14.3	-15.1	-25.0	-17.3	-24.9	-24.4	-23.6	-27.7	-25.1
lignin-derived phenols													
vanillin	-31.3	-16.3	-32.2	-33.0	-14.8	-12.5	-26.0	-24.7	-27.0	-28.6	-27.8	-32.4	-30.6
acetovanillone	-31.5	-13.1	-32.5	–	–	–	–	–	-30.1	–	–	–	-29.7
syringaldehyde	-34.2	-20.3	-39.5	-35.5	-16.8	-19.8	-27.4	-27.2	–	-27.7	-26.9	-32.1	-31.3
vanillic acid	-31.2	-17.5	-36.2	-35.5	-11.8	-11.4	-26.4	-23.1	-31.8	-25.5	-24.7	-33.4	-34.0
acetosyringone	-31.9	-23.2	-30.1	-37.6	-20.3	-19.7	-25.1	-26.4	-30.6	-26.2	-27.0	-35.7	-31.8
syringic acid	-24.9	-20.8	-30.6	-35.0	-22.2	-13.8	-26.2	-26.0	-28.3	-26.0	-26.3	-33.7	-33.6
p-coumaric acid	-28.0	-14.3	-29.6	-29.2	-15.8	-15.3	-23.8	-20.4	-27.5	-24.1	-23.0	-28.5	-27.4
ferulic acid	-27.1	-13.8	–	-30.5	-13.6	-12.9	-25.6	-22.3	-28.0	-26.0	-24.5	-29.2	-28.2
means*													
V units	-31.3	-16.0	-32.9	-34.2	-13.0	-12.0	-26.2	-23.6	-30.4	-26.5	-25.7	-32.9	-30.4
S units	-28.5	-21.1	-34.8	-35.6	-20.0	-17.9	-26.2	-26.5	-30.0	-26.6	-26.4	-32.9	-32.5
C units	-27.7	-14.1	-29.6	-30.3	-14.3	-13.9	-24.8	-21.6	-27.9	-25.3	-23.9	-29.0	-27.8
VSC	-30.2	-16.7	-33.6	-35.1	-16.0	-14.8	-25.8	-24.1	-29.3	-26.1	-25.9	-31.7	-31.2
lignin contents (mg VSC g^{-1} OC)													
V units	15.7	15.1	16.9	7.7	0.5	0.7	0.4	0.6	2.5	1.3	1	0.3	1.5
S units	5.4	20.3	13.1	10.1	0.6	0.5	0.3	0.3	1.1	0.5	0.2	0.5	2.6
C units	3.3	30.8	3.1	3.7	0.5	0.2	0.2	0.2	2.1	0.8	0.2	0.3	0.6
VSC	24.3	66.2	33.0	21.5	1.6	1.4	0.9	1.1	5.8	2.6	1.5	1.0	4.7
C/V	0.2	2.0	0.2	0.5	0.9	0.3	0.7	0.5	0.9	0.6	0.2	1.0	0.5
S/V	0.3	1.3	0.8	1.3	1.0	0.7	0.8	0.6	0.5	0.4	0.2	1.7	1.9
$(ac/al)_V$	0.16	0.14	0.26	0.85	1.53	0.77	0.99	2.69	2.68	2.37	1.19	1.09	1.33
$(ac/al)_S$	3.44	0.38	0.70	0.27	1.12	1.46	1.08	1.48	1.42	1.45	2.43	0.21	1.56

* weighted by the contents of lignin-derived phenols

V = vanillyl units, S = syringyl units, C = cinnamyl units

(ac/al)v = acid to aldehyde ratio of vanillyl units, (ac/al)s = acid to aldehyde ratio of syringyl units

G: grassland; FP: patch of Araucaria forest; F: Araucaria forest; S: shrubland

Table 12: Light fractions: proportions of functional groups according to ^{13}C CPMAS NMR spectrsocopy.

	functional group/chemical shift (ppm) according to ^{13}C CPMAS NMR spectroscopy								
soil - horizon	carbonyl C 245-185 ppm	carboxyl C 185-160 ppm	carbonyl + carboxyl C	aromatic C 160-110 ppm	O-alkyl C 110-60 ppm	N-alkyl C, methoxyl C 60-45 ppm	O-/N-alky C 110 - 45 ppm	alkyl C 45-0 ppm	alkyl C / O-/N-alkyl C
F10 - Ah1	2.1	8.7	10.7	19.3	39.7	9.5	49.2	20.8	0.42
F10 - 2Ah2	7.2	10.6	17.7	27.0	33.5	8.0	41.4	13.8	0.33
F10 - Bw1	1.4	8.0	9.4	21.3	37.2	10.4	47.5	21.8	0.46
FP2 - Ah1	2.8	8.2	11.0	19.8	36.0	9.0	45.1	24.2	0.54
G1 - Ah1	0.2	4.5	4.7	16.5	54.7	9.6	64.3	14.6	0.23
G1 - Ah3	2.2	5.9	8.1	21.3	49.9	8.7	58.6	12.0	0.21
GS4 - Ah1	1.9	7.8	9.6	22.0	40.6	8.0	48.6	19.8	0.41

F: Araucaria forest, FP: patch of Araucaria forest, G: not managed grassland without shrubs, GS: not managed grassland with shrubs

Table 13: Particle-size separates: δ ^{13}C values (‰), SOC (g kg^{-1}) and C/N ratios.

soil - horizon	particle-size separates	SOC (g kg^{-1})	C/N	δ ^{13}C (‰)
F1 - 2CAwh	bulk soil	68.7	17.1	-22.1
	< 2 µm	74.3	16.4	-21.8
	2 - 20 µm	59.0	19.3	-22.4
	20 - 63 µm	68.9	19.1	-22.6
F1 - 2Ah4	bulk soil	86.4	20.2	-22.7
	< 2 µm	95.8	16.4	-22.3
	2 - 20 µm	79.8	18.9	-22.9
	20 - 63 µm	88.5	18.4	-23.0
F6 - 3Ahb2	bulk soil	66.7	27.1	-23.6
	< 2 µm	82.2	14.9	-23.6
	2 - 20 µm	48.6	16.6	-23.7
	20 - 63 µm	74.8	17.2	-23.8
F10 - 2Ahb	bulk soil	40.8	25.9	-22.4
	< 2 µm	58.5	13.4	-22.4
	2 - 20 µm	27.6	17.2	-22.6
	20 - 63 µm	21.3	15.6	-22.8
F10 - 2Bwb	bulk soil	24.9	23.4	-23.0
	< 2 µm	48.5	10.8	-22.9
	2 - 20 µm	10.5	14.6	-23.6
	20 - 63 µm	4.3	14.6	-23.6
G1 - Ah5	bulk soil	43.5	36.5	-15.1
	< 2 µm	58.8	19.1	-15.3
	2 - 20 µm	34.5	24.5	-15.4
	20 - 63 µm	27.7	26.0	-15.6
FP2 - Bw1	bulk soil	21.7	27.5	-18.0
	< 2 µm	-	-	-18.3
	2 - 20 µm	-	-	-18.8
	20 - 63 µm	-	-	-21.2

F: Araucaria forest, G: not managed grassland without shrubs,
FP: patch of Araucaria forest

Table 14: Particle-size separates: proportions of functional groups according to ^{13}C CPMAS NMR spectrsocopy.

		Functional group/chemical shift (ppm) according to ^{13}C NMR spectroscopy								
soil - horizon	particle-size separates	carbonyl C 245-185	carboxyl C 185-160	carbonyl + carboxyl C	aromatic C 160-110	O-alkyl C 110-60	N-alkyl C, methoxyl C 60-45	O-/N-alkyl C 45 - 110	alkyl C 45-0	(alkyl C) / (O-/N-alkyl C)
G1 - Ah5	< 2 µm	11.4	16.4	27.8	32.6	24.4	4.2	28.7	10.9	0.38
	2 - 20 µm	7.5	17.1	24.6	39.1	20.5	4.3	24.9	11.4	0.46
	20 - 63 µm	5.0	14.9	19.9	29.1	31.0	6.1	37.1	13.9	0.38
	bulk soil	4.5	15.4	19.8	33.2	24.3	6.4	30.7	16.2	0.53
F10 - 2Ahb	< 2 µm	3.1	15.2	18.3	25.1	24.4	8.8	33.1	23.5	0.71
	2 - 20 µm	5.2	19.0	24.3	31.0	18.8	5.8	24.6	20.2	0.82
	20 - 63 µm	8.4	15.5	23.9	27.4	24.6	6.5	31.1	17.7	0.57
	bulk soil	10.2	16.8	27.0	25.4	18.4	6.3	24.7	23.0	0.93
F1 - 2Ah4	< 2 µm	7.5	18.1	25.6	25.9	24.5	6.8	31.3	17.2	0.55
	2 - 20 µm	7.2	21.4	28.6	31.9	20.0	6.2	26.2	13.3	0.51
	20 - 63 µm	8.3	17.5	25.9	28.5	22.5	6.5	29.0	16.6	0.57
	bulk soil	0.0	11.3	11.3	28.6	28.0	8.9	37.0	23.1	0.62
F6 - 3Ahb2	< 2 µm	5.9	16.7	22.6	23.3	24.8	7.6	32.3	21.8	0.68
	2 - 20 µm	6.1	21.4	27.5	28.7	23.3	6.2	29.5	14.4	0.49
	20 - 63 µm	7.7	16.2	23.9	24.8	25.3	7.2	32.5	18.8	0.58
	bulk soil	7.6	16.9	24.5	24.3	22.4	7.2	29.6	21.6	0.73

G: not managed grassland without shrubs, F: Araucaria forest

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LEBENSLAUF

Alexander Dümig
geboren am 20. 08. 1974 in Bamberg
Nationalität: deutsch

Derzeitige Tätigkeit
seit 07/2007
Wissenschaftlicher Mitarbeiter, Lehrstuhl für Bodenkunde, Technische Universität München (SFB-TRR Projekt 38 „Strukturen und Prozesse der initialen Ökosystemgenese“)

Promotion
seit 01/2004
am Lehrstuhl für Bodenkunde, Technische Universität München
Titel der Dissertation: Soils in the southern Brazilian highlands: genesis, soil organic matter composition, and relations to vegetation history

Studium
10/2001 - 11/2003 Masterstudiengang
Sustainable Resource Management, Technische Universität München
Abschluss als M. Sc.
Masterarbeit: GIS-gestützte Modellierung des Eintrages von Stickstoff und Phosphor in den Starnberger See

10/1994 - 09/2000 Forstwirtschaft, Fachhochschule Weihenstephan
Abschluss als Diplom-Ingenieur für Forstwirtschaft (FH)
Diplomarbeit: Auswirkungen von *Eucalyptus grandis* - Plantagen auf ausgewählte physikalische und chemische Bodeneigenschaften in der Provinz Entre Ríos, Argentinien

Zivildienst
11/1992 - 01/1994 Bezirksklinikum Kutzenberg

Schulbildung

09/1990 - 07/1992 Staatliche Fachoberschule in Bamberg (Ausbildungsrichtung Technik)

PUBLIKATIONEN & PRÄSENTATIONEN

Publikationen:

Dümig, A., Schad, P., Kohok, M., Beyerlein, P., Schwimmer, W., Kögel-Knabner, I., 2008. A mosaic of nonallophanic Andosols, Umbrisols and Cambisols on rhyodacite in the southern Brazilian highlands. Geoderma, 145: 158 – 173.

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