Fate of Organic Carbon in Soil Fractions Following Land Use Conversion in the Humid Tropics

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Sonja Marit Paul

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Referent: Prof. Dr. Edzo Veldkamp

Koreferent: Prof. Dr. Heiner Flessa

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Zusammenfassung

Die organische Substanz im Boden stellt einen wesentlichen Anteil des terrestrischen Kohlenstoffreservoires dar. Ihre Zersetzung trägt zu bedeutenden Flüssen des globalen Kohlenstoffkreislaufs bei. Um Effekte von Landnutzungs- oder Klimaänderungen in den Tropen verstehen, bewerten und vorhersagen zu können, ist quantitatives Wissen über die Abbauprozesse von organischer Substanz im Boden notwendig. In dieser Arbeit wurde untersucht, wie Bodeneigenschaften verschiedener tropischer Böden die Kohlenstoffgehalte sowie die Stabilität von Kohlenstoff im Gesamtboden und in physikalisch und chemisch definierten Bodenfraktionen beeinflussen. Zudem wurde die Änderung der Kohlenstoffspeicherung im Boden nach einem Landnutzungswechsel (Naturwald zu Weide und Weide zu Sekundärwald) in diesen Fraktionen bestimmt. Schließlich wurde untersucht, in wieweit physikalisch und chemisch definierte Bodenfraktionen hinsichtlich Stabilisierungsmechanismen bedeutsame Speicher widerspiegeln.

Für diesen Zweck wurden unterschiedliche Bodentypen im Nordwesten von Ecuador ausgewählt, die sich bezüglich der Speicherung und Stabilisierung von Kohlenstoff im Boden deutlich unterscheiden: zum einen Böden, die sich aus marinen Sedimenten tertiären Alters entwickelten, zum anderen Vulkanascheböden, die sich auf jungen vulkanischen Ablagerungen entwickelten. Je Bodentyp wurden vier Standorte so gewählt, dass eine breite Spanne von Ton- und Schluffgehalten abgedeckt wurde (62-83% in den Sedimentböden und 35-79% in den Vulkanascheböden). Jeder Standort umfasste einen Naturwald, eine Weide und einen Sekundärwald.

Die Böden wurden in wasserstabile Aggregate verschiedener Größenklassen fraktioniert (8000-2000, 2000-250, 250-53, <53 µm). Dabei wurden zwei verschiedene Probenvorbehandlungen (luftgetrocknet vs feldfeucht) verglichen. An die Aggregatfraktionierung schloss sich eine Dichtefraktionierung an. Es wurden eine freie leichte Fraktion (free light fraction <1.6 g cm^{-3}), zwei weitere leichte Fraktionen, welche in Aggregaten verschiedener Stabilität eingeschlossen waren, sowie eine schwere Fraktion (heavy fraction, >1.6 g cm^{-3}) isoliert. Die leichte, eingeschlossene organische Substanz wurde in einem ersten Schritt nach Aggregatzerstörung durch Schütteln der Aggregate mit Glaskugeln (occluded I light fraction, < 1.6 g cm^{-3}) gewonnen. Im darauf folgenden Schritt wurden die stabilsten Aggregate, welche den ersten Zerstörungsschritt überlebten, manuell zerstört und die zweite Fraktion gewonnen (occluded II light fraction, < 1.6 g cm^{-3}). Die schwere Fraktion wurde im Folgenden jeweils mit drei verschiedenen Chemikalien behandelt (HCl, NaOCl und $Na_4P_2O_7$). Aus der Kombination physikalischer und chemischer Fraktionierungsmethoden mit stabilen Isotopen von Proben, welche von Standorten mit einem C_3-C_4 Vegetationswechsel stammten, konnte Ursprung und Stabilität des Bodenkohlenstoffs in diesen Bodenfraktionen unter Weide und Sekundärwald verfolgt werden.

Die organischen Kohlenstoffgehalte waren in den Vulkanascheböden (47 - 130 g kg^{-1}) höher als in den Sedimentböden (19 - 50 g kg^{-1}). In beiden Böden stiegen sie mit zunehmendem Ton- und Schluffgehalt an. Im Vergleich zu Bodentyp und Textur spielte der Einfluss der Bodennutzung auf die Kohlenstoffgehalte eine

untergeordnete Rolle. Die Abholzung des Waldes und die anschließende Nutzung als Weide reduzierten dennoch in beiden Bodentypen die Kohlenstoffgehalte um 20%. Umgekehrt führte die Wiederaufforstung von Weiden zu einem Anstieg des Kohlenstoffs im Boden, jedoch wurde das Niveau der Naturwälder innerhalb des beobachteten Zeitraums von maximal 23 Jahren nicht in allen Sekundarwäldern erreicht. Die durchschnittliche Verweildauer von waldbürtigem Kohlenstoff in Weiden war deutlich länger als die durchschnittliche Verweildauer von weidebürtigem Kohlenstoff in den Sekundärwäldern. Besonders kurz war sie in den Vulkanascheböden, wo in keinem der vier untersuchten Sekundärwälder noch weidebürtiger Kohlenstoff nachgewiesen werden konnte.

In beiden Bodentypen war der Hauptanteil des Kohlenstoffs in den Makroaggregaten (>250 µm) gespeichert und weniger als 20% (feuchte Vorbehandlung) oder 3% (trockene Vorbehandlung) des Gesamtkohlenstoffs war in der Fraktion <53 µm gespeichert. Sowohl die Aggregierung als auch die absolute Menge des in einzelnen Aggregatklassen gespeicherten Kohlenstoffs nahm mit steigendem Ton- und Schluffgehalt der Böden zu. Ein Einfluss der Landnutzung auf die Aggregierung konnte nicht beobachtet werden. In den Sedimentböden führten die beiden Vorbehandlungen zu unterschiedlicher Kohlenstoffverteilung zwischen den Aggregatgrößenklassen, aber nicht in den Vulkanascheböden. Auch spielte organisches Material nur in den Sedimentböden bei der Stabilisierung von Aggregaten eine entscheidende Rolle.

Ähnlich wie die Kohlenstoffspeicherung im Gesamtboden waren die absoluten Kohlenstoffgehalte in der leichten Fraktion im Vulkanascheboden (15 g kg^{-1}) dreimal höher als im Sedimentboden (5 g kg^{-1}). In beiden Bodentypen beeinflusste die Landnutzung den relativen Anteil der leichten Fraktion im Gesamtboden, mit höheren Anteilen in Natur- und Sekundärwäldern als in Weiden. Die in der 'occluded I light fraction' gespeicherte Menge an Kohlenstoff nahm mit steigenden Ton- und Schluffgehalten sowie mit der Aggregierung zu. Dies deutet auf eine schützende Wirkung der Aggregierung auf den Kohlenstoff im Boden hin. In den Weiden beider Bodentypen hatte organisches Material, welches mit der 'occluded II light fraction' assoziiert war, den höchsten Anteil an neuem, weidebürtigem Kohlenstoff. Der weidebürtige Anteil nahm in den anderen Fraktionen in folgender Reihenfolge ab: 'free light fraction' > 'heavy fraction' > 'occluded I light fraction'. Der schnelle Umsatz der 'occluded II ligth fraction', die aus sehr stabilen Mikroaggregaten isoliert wurde, legt den Schluss nahe, dass diese Fraktion eine wichtige Rolle bei der initialen Bildung von Mikroaggregate spielt.

Von allen chemischen Behandlungen reduzierte NaOCl den Kohlenstoffgehalt im Residuum am stärksten, um 95% in den Sedimentböden und um 82% in den Vulkanascheböden gefolgt von HCl (55% in beiden Bodentypen) und $Na_4P_2O_7$ (26% in Sedimentböden und 46% in Vulkanascheböden). Höhere Kohlenstoffspeicherung in den Vulkanascheböden als in den Sedimentböden wurde in der NaOCl-resistenten sowie in der $Na_4P_2O_7$-löslichen Bodenfraktion gemessen. Dies zeigt, dass die Interaktion mit Mineralen (Komplexierung mit Hydroxylspezies und Adsorption an Mineraloberflächen) in Vulkanascheböden als Stabilisierungsmechanismus stärker ausgeprägt ist als in Sedimentböden. In beiden Bodentypen korrelierte die Kohlenstoffkonzentration in den residualen Fraktionen stark mit den

Anfangskonzentrationen der mineralassoziierten Bodenfraktion. Der Anteil von weidebürtigem Kohlenstoff wurde in den residualen Fraktionen der NaOCl sowie in den Extrakten der mit $Na_4P_2O_7$ behandelten Bodenfraktionen auf die Hälfte reduziert. Die Behandlung mit HCl führte dagegen nicht zu einer präferentiellen Abnahme des weidebürtigen Kohlenstoffs. Alle chemisch separierten Fraktionen waren von der gegenwärtigen Landnutzung beeinflusst. Die chemischen Fraktionierungsmethoden sind deshalb nicht geeignet, einen passiven Pool in diesen kohlenstoffreichen tropischen Oberböden zu isolieren.

Das angewandte Fraktionierungsschema isolierte Fraktionen verschiedener Kohlenstoffspeicherung und Stabilität. Änderungen in der Kohlenstoffspeicherung, die durch Landnutzungswechsel hervorgerufen wurden, waren relativ gering gegenüber den Unterschieden, die durch Textur und mineralogische Zusammensetzung bedingt sind. Der weitaus größte Anteil des Gesamtkohlenstoffs, aber auch des weidebürtigen Kohlenstoffs, war mit der Mineralphase assoziiert. Dies zeigt die dominierende Bedeutung der Mineraloberflächen für die Speicherung und Stabilisierung organischer Substanz in diesen biologisch hoch aktiven Böden. Die leichten Fraktionen der organischen Substanz reagieren am sensitivsten auf Landnutzungsänderung. Die Ergebnisse geben keine Hinweise darauf, dass neu eingetragener Kohlenstoff in den untersuchten Oberböden längerfristig stabilisiert wird. Er bildet viel mehr einen sehr leicht verfügbaren C-Vorrat der insbesondere in den Vulkanascheböden innerhalb weniger Jahre vollständig mineralisiert werden kann. Die Unterschiede in der Stabilität der isolierten C-Fraktionen waren relativ gering, was auf einen raschen Umsatz des Bodenkohlenstoffs hindeutet. In diesen tropischen Oberböden isolierte keine der untersuchten Methoden einen Pool, in dem Kohlenstoff längerfristig stabilisiert wird.

Summary

The soil organic matter pool represents a major part of the terrestrial carbon reservoir. Decomposition of soil organic matter contributes to important fluxes of the global carbon cycle. In order to understand, assess, and predict the impact of land use or climatic changes in the tropics, quantitative knowledge of stabilization and decomposition processes of soil organic matter is necessary. This thesis elucidated how soil properties and parent material influence soil organic carbon (soil C) contents and stability in bulk soil, physically, and chemically defined soil fractions. Furthermore, factors were identified which control changes in soil C storage induced by land use changes (natural forest to pasture and pasture to secondary forest). Finally, it was evaluated whether isolated soil fractions represent meaningful soil C pools with respect to stabilization.

For this purpose, soil types which differ in key factors influencing storage and stabilization of soil C were chosen in Northwest Ecuador. Four sites with soils developed from marine Tertiary sediments and with variable silt + clay content (62-83%), and four sites developed on volcanic ashes (silt + clay content 35-79%) were sampled. Each site consisted of a natural forest, a pasture, and a secondary forest plot.

Soil was fractionated into water-stable aggregate size classes (8000-2000, 2000-250, 250-53, <53 µm). Thereby, two kinds of sample pre-treatments (air-dried vs field-moist soil) were compared. Aggregate fractionation was followed by density fractionation. A free light fraction (<1.6 g cm^{-3}), two further light fractions occluded within aggregates of different stability, and a heavy fraction (>1.6 g cm^{-3}) were separated. Light occluded organic matter was isolated in a first step after aggregate disruption by shaking aggregates with glass pearls (occluded I fraction, <1.6 g cm^{-3}). In a subsequent step by manually destructing of the most stable microaggregates that survived the first step, the occluded II light fraction (< 1.6 g cm^{-3}) was gained. The heavy fraction was further treated with three different chemicals (HCl, NaOCl, and $Na_4P_2O_7$). I traced the origin and stability of soil carbon in these soil fractions under pasture and secondary forest by combining physical and chemical fractionation procedures with ^{13}C isotope analyses on soil samples from sites that had undergone C_3-C_4 vegetation changes.

Soil C contents were higher in volcanic ash soils (47 to 130 g kg^{-1}) than in sedimentary soils (19 to 50 g kg^{-1}). In both soil types soil C increased with the amount of silt + clay. The influence of land use on soil C storage was less important compared to soil type and texture. However, pasture establishment after deforestation reduced soil C storage of about 20% in both soil types. Conversely, afforestation of pastures lead to an increase in soil C contents, but within the observed time frame of a few decades the former soil C levels of natural forests were not reached in all secondary forests. Mean residence times of pasture-derived carbon in secondary forests were considerably shorter than mean residence times of forest-derived carbon in pastures, especially in volcanic ash soils, where no pasture-derived carbon could be detected in any of the four studied secondary forests.

In both soil types, most of the carbon was stored in macroaggregates (>250 µm) and less than 20% (moist pretreatment) or 3% (air-dried pretreatment) of total soil C was stored in the fraction <53 µm. Aggregation and the absolute amount of carbon stored in aggregate size classes increased with increasing silt + clay content. Aggregation was only marginally influenced by land use. In smectitic clay soils, the two pre-treatments resulted in distinct differences of soil C among the aggregate size classes, but not in volcanic ash soils. Soil organic matter plays only in sedimentary soils a major role in the formation and stabilization of aggregates.

Similar to soil C storage in bulk soil, absolute amounts of carbon stored in light fractions of volcanic ash soils (15 g kg^{-1}) were three times higher than in sedimentary soils (5 g kg^{-1}). In both soil types, land use influenced the relative contribution of the light fractions to total soil C being larger under natural forest (20% ± 1%) and secondary forests (17% ± 1%) than under pastures (13% ± 1%). The amount of soil C stored in occluded I light fraction increased with increasing silt + clay and aggregation implying a stabilizing effect of aggregation on soil C. In pastures of both soil types, soil C associated with occluded II light fraction had the highest contribution of new, pasture-derived carbon, which was followed by free light fraction > heavy fraction > occluded I light fraction. Fast turnover of the occluded II light fraction, separated from highly stable microaggregates, strongly suggested that this fraction is important in the initial process of microaggregate formation.

Of all chemical treatments, NaOCl was the most efficient in reducing carbon content in the residuum by 94% in sedimentary soils and 82% in volcanic ash soils, followed by treatment with HCl (55% in both soil types) and $Na_4P_2O_7$ (26% in sedimentary soils and 46% in volcanic ash soils). Higher carbon storage in volcanic ash soils than in sedimentary soils was measured in the NaOCl resistant and also in the $Na_4P_2O_7$ soluble soil C fraction. This revealed that soil C stabilization through interaction with minerals (complexation with hydroxymetal species and adsorption to mineral surfaces) was more pronounced in volcanic ash soils than in sedimentary soils. In both soil types, soil C concentration in all residual fractions strongly correlated with initial concentrations of mineral-associated soil C and was higher in natural forest soils than in pasture soils. The proportion of pasture-derived carbon in residual fraction of NaOCl and in the extracts of $Na_4P_2O_7$ was halved following the chemical treatment. Treatment with HCl was ineffective in preferentially removing pasture-derived soil C. All residual fractions were influenced by current land use, therefore, chemical fractionation methods failed to isolate a passive soil C pool in these organic rich tropical topsoils.

Soil C in the isolated fractions is probably stabilized by more than one of the specific stabilization mechanisms. It is challenging to classify the gained soil C fractions according to individual stabilization mechanisms and conceptual pools in models. Nevertheless, the combined results of soil C distribution and stability of physically and chemically defined soil fractions still provide valuable information about the dominating stabilization mechanism. Aggregation seemed to stabilize soil C to a similar extent in both soil types, even though organic material played a different role in the stabilization of aggregates in volcanic ash and sedimentary soils.

Interaction with minerals was a more important stabilization mechanism in volcanic ash soils than in sedimentary soils.

The applied fractionation scheme isolated fractions of different soil C storage and stability. In most soil C fractions, changes in carbon storage induced through land use changes were relatively small compared to the impact of soil properties. The major part of total soil C and also of pasture-derived carbon was associated with minerals. This demonstrates the importance of mineral surfaces for the storage and stability of organic carbon in these biological highly active soils. Light fractions represent the most sensitive fraction to land use changes. There is no evidence that recently incorporated pasture-derived carbon is stabilized in long-term in the investigated soils. This carbon forms an easily available carbon pool, which can be mineralized in a few years, especially in the volcanic ash soil. The differences in stability of isolated C-fractions were relatively small indicating a fast turnover of soil C. None of the investigated soil fractionation methods successfully isolated a stable soil C pool that is stabilized in long-term in these organic rich tropical topsoils.

1 Introduction

1.1 The Global Carbon Cycle and Climate Change

Recently, the publication of the fourth Assessment Report of the Intergovernmental Panel on Climate Change (Solomon et al., 2007) and reactions in the public demonstrate that global climate change is a major environmental and economical issue. Anthropogenic emissions of greenhouse gasses are very likely to have increased the global surface temperature by 0.74° C from 1906 to 2005 (Trenberth et al., 2007). Already measurable consequences are retreating glaciers, reduced sea ice extension in the Arctic Ocean, rising of global average sea level (0.17 m in total in the 20th century), changes in precipitation and wind patterns, ocean salinity, and aspects of extreme weather including droughts, heavy precipitation, and intensity of tropical cyclones (Bindoff et al., 2007; Lemke et al., 2007; Trenberth et al., 2007).

CO_2 is known as the most important greenhouse gas emitted by humans. Evidence arose from measurements of the composition of air bubbles entrapped in Antarctic ice-cores: Over the past 700,000 years, atmospheric CO_2 concentrations fluctuated between 180 ppmv in Glacials and 280 ppmv in Interglacials (Petit et al., 1999; Siegentahler et al., 2005). A steady rise in CO_2 concentration has been measured from 1850 onwards. Since 1959 direct and continuous atmospheric measurements of CO_2 are showing that the current level of CO_2 concentration of 380 ppmv is unprecedented (Keeling and Whorf, 2000). There are several lines of evidence demonstrating that the recent CO_2 increase is anthropogenically caused mainly due to fossil fuel burning: i) atmospheric O_2 is decreasing at almost the same rate as CO_2 fossil fuel emission increases, as combustion consumes O_2, ii) the CO_2 of the atmosphere has been labelled by the characteristic isotopic signature of fossil fuel (depleted in ^{13}C and lack of ^{14}C) and iii) elevated interhemispheric CO_2 concentration gradient with higher atmospheric CO_2 concentrations in the Northern Hemisphere, where most of fossil fuel burning occurs (Sommerville et al., 2007; Denman et al., 2007). Besides fossil carbon emissions, which average 7.2 Pg C per year in 2000-2005, land use changes contribute with 1.6 Pg C per year over the 1900s to anthropogenic CO_2 emissions (Denman et al., 2007).

The main characteristic of atmospheric CO_2 is its rapid exchange with both the ocean and the terrestrial biosphere. Although carbonate sediments of the Earth crust constitute the size of 48,000,000 Pg C and dwarfs the ocean (38,000 Pg C), the exchange rates due to weathering on land or sedimentation/dissolution balance within the ocean are relatively small (both around 0.2 Pg C year^{-1}) compared to the ocean and biosphere fluxes (Denman et al., 2007). Gas exchange of the ocean's surface with the atmosphere amounts to 90 Pg C. The reservoir of the terrestrial biosphere (2300 Pg C) is three times larger than of the atmosphere (600 Pg C). Here the main part of carbon is stored in soil organic matter in the uppermost meter (1500 Pg C). An additional 840 Pg C is estimated to be stored between one and two meter depth (Jobbagy and Jackson, 2000). Less than one third of the terrestrial carbon is stored in vegetation. The largest annual carbon gross flux occurs between the terrestrial biosphere and the atmosphere, which amounts to around 120 Pg C. About half of total organic carbon produced by photosynthesis, the gross primary production, is respired by plants. At steady state conditions, the net primary production is balanced by heterotrophic respiration with a smaller contribution of direct combustion through fires. At present day conditions with elevated atmospheric CO_2, however, the terrestrial biosphere as a whole is a net sink of carbon (2.6 Pg C yr^{-1}, Denman et al., 2007). This sink is surprising since the known net carbon losses from forest clearing and other land use changes must be balanced by the CO_2 fertilization effect on plants. Most of the plant tissue enters the detritus pool, which amount to a pool size of 300 Pg C. While some detritus is decomposed and returned quickly to the atmosphere, a part is converted to modified soil organic matter (1050 Pg C) and decomposed slower with turnover times of 10 to 1000 years (Houghton et al., 2001).

1.2 Impacts of Land Use Conversion in the Tropics on Carbon Cycle

Tropical forests play a major role in the global carbon cycle as 45% of carbon stored in total vegetation is located in tropical forests, which amount to 212 Pg C (Watson et al., 2000). A similar amount is stored in tropical forest soils, which represent 11% of the global total soil carbon (soil C) stored in the uppermost meter (Watson et al., 2000). Each year, about 12 % of the atmospheric CO_2 reservoir is cycled in tropical forests through photosynthesis, respiration, and microbial decay (Mahli et al., 1999). Even small changes of these large exchange fluxes between atmosphere and tropical forests can have profound consequences on the global carbon cycle (Denman et al., 2007). Moreover, the connection of high temperatures with high precipitation in the humid tropics results in high productivity and consequently short response and turnover times of tropical forests. Accordingly, response to anthropogenic perturbations may also be rapid (Mahli et al., 1999). Presently it is under discussion if tropical forests represent a source or a sink of carbon as a major uncertainty in the carbon budget relates to possible net change in the carbon stocks in tropical forests. Recent inversion models estimate an overall net tropical land flux from -0.8 Pg C to +2.6 Pg C per year in the 1990s (Clark, 2004).

Although currently deforestation in tropical countries appears to be slowing slightly, about 20% of anthropogenic CO_2 emissions are presently attributed to deforestation in the tropics (Denman et al., 2007). Although these CO_2 emissions are largely caused by the instantaneous loss of above ground biomass, the following net mineralization of soil organic matter also contributes significantly (Detweiler, 1986). As soil mineralization is relatively slow, carbon release from soils continues after land use conversion and it will take decades for the readjustment to be completed. Conversion of tropical forests or pastures to cropland typically decreases soil C stocks by 40 to 60% (van Noordwijk et al., 1997; Guo and Gifford, 2002). In contrast, conversion of forests to pastures can result in both gains and losses of soil C, depending on soil properties, climate, and pasture management (Detweiler, 1986; Lugo and Brown, 1993; Neill et al., 1997).

Forest regrowth and afforestation offers significant, but often temporary, mitigation potential. It was proposed that carbon stocks could be increased by 60 to 87 Pg C over the period 1995 to 2050, mostly in the tropics due to slowing deforestation rates, promoting natural forest regrowth and afforestation (Watson et al., 2000). Both increases and decreases in soil carbon stocks due to afforestation of former pastures have been observed (de Koning et al., 2003; Silver et al., 2004). In view of CO_2 emissions trading carbon sequestration potential is important, but knowledge about factors influencing carbon sequestration is until now limited. Therefore, the understanding of the underlying mechanisms of stabilization and decomposition processes of soil C in tropical soils and their interaction with land use change is essential.

1.3 Mechanisms of Soil C Stabilization

Stabilization is defined as protection of soil C from mineralization and thus leads to prolonged turnover times in soils (von Lützow et al., 2006). Several mechanisms contribute to the stabilization of carbon in soils, which can be broadly divided into three groups: i) selective preservation of recalcitrant compounds, ii) spatial inaccessibility, and iii) interactions between organic and inorganic substances (Sollins et al., 1996; von Lützow et al., 2006).

Selective preservation of recalcitrant compounds refers to molecular level characteristics of organic substances. Plant litter, microbial and faunal products are composed of a complex mixture of compounds (e.g. polysaccharides, lignin, protein, lipids, chitin, and waxes) which differ in their biodegradability due to their structural composition. As microbes selectively degrade the less recalcitrant compounds (e.g. containing hydrolysable bondings; e.g. polysaccharides and proteins) the more recalcitrant compounds (e.g. containing aliphatic structures e.g. waxes, cutin, and suberin) become selectively enriched. Selective preservation of recalcitrant compounds occurs in all soil types.

Spatial inaccessibility comprises the location of organic substances within the soil matrix. The access by microbes and enzymes and the O_2 gas exchange is reduced by spatial inaccessibility. Occlusion of organic substances by aggregation, intercalation within phyllosilicates, hydrophobicity, and encapsulation in organic macromolecules are important processes to reduce accessibility. Occlusion by aggregation occurs at the clay microstructure level by flocculation of clay minerals through abiotic processes e.g. networks of Fe- and Al oxides or hydroxides. Biogenic aggregation enhances the formation of micro- and macroaggregates. Microaggregates (<250 µm) are stabilized by fine particulate organic material as stabilizing agents, or by microbial slime as glue. Compounds involved include lignin degradation products, microbial proteins, and polysaccharides. Coarse particulate organic material as stabilizing agents and enmeshment by roots and fungal hyphae, casts, and feces caused macroaggregation (>250 µm). Lignin and O-alkyl rich macromolecules, chitin, suberin, and in particular plant lipids are examples for compounds involved. Besides biogenic aggregation, abiotic formation of larger aggregates occurs in clayey soils due to the high shrink-swell capacity of smetitic or other 2:1 clay minerals. As clay content and aggregation are correlated, it is difficult to distinguish between stabilization due to aggregation and effects due to sorption to clay surfaces. In all soils with well-developed structure, aggregation is an important stabilization process, whereby macroaggregation is especially important in biological active surface soils.

Interactions between organic and inorganic substances refer to intermolecular interactions that alter the rate of degradation. Various mechanisms contribute to the stabilization: e.g. ligand exchange, polyvalent cation bridges, and weak interactions (hydrophobic interactions, van der Waals forces, H-bonding). Ligand exchange is an anion exchange process of simple coordinated OH groups on mineral surfaces (Fe-, Al-, and Mn-oxides, the edges sites of phyllosilicates, allophane, and imogolite) with aliphatic or phenolic OH-groups of organic matter. Ligand exchange is restricted to acidic soils rich in minerals with protonated hydroxyl groups. Polyvalent cation bridges are electrostatic cation bridges of e.g. Fe^{3+}, Al^{3+}, and Ca^{2+}, which neutralize the negatively charged surface of expandable layer silicates and the negatively charged functional groups of organic matter (e.g. carboxyl and carbonyl). Sorption and complexation are examples for stabilization through interaction. The stabilizing effect is assumed to result from the fact that small molecules, sorbed to mineral surfaces, cannot be utilized by microorganisms (Chenu and Stotzky, 2002). The most significant surface area to which organic matter can adsorb provide clay-sized minerals. The specific surface area of minerals controls the amount of sorbed organic matter (Saggar et al., 1996). Different bonding mechanisms are involved in sorption processes. Sorption is more important in fine-textured soils. Complexation of organic matter with metal ions (Fe^{3+}, Al^{3+}, Ca^{2+}) is considered to stabilize soil organic matter (Baldock and Skjemstad, 2000). The presence of amorphous Al and Fe leads to accumulation of large amounts of soil C (Oades, 1988; Baldock and Skjemstad, 2000). Complexation is especially important in Podzols and volcanic ash soils (Shoji et al., 1993).

These carbon stabilization mechanisms of are not fundamentally different for temperate or tropical soil types, despite their often large differences in soil C stocks and turnover times. The contribution of a specific stabilization mechanism depends on soil properties in tropical as well as in temperate climate soils.

1.4 Fractionation Techniques of Soil C

In order to understand, assess, and predict effects of land use changes on the storage and stability of soil C, quantitative knowledge of stabilization and decomposition processes of soil C fractions and resulting pool sizes is important. Soil C is a complex and heterogeneous mixture of plant- and microbial-derived compounds mainly associated with the mineral phase. This association of soil C with mineral particles is thought to play a key role in decomposition and stabilization processes of soil C (Christensen, 2001; von Lützow et al., 2007). Differences in mean residence time of soil C from months to centuries lead to the conceptual model where soil C is described in multiple pools with different stability. Current models of soil organic matter dynamics all include pools with different turnover rates and pool sizes with first-order decomposition kinetics (Falloon and Smith, 2000). These pools are named as active, slow or intermediate and passive or inert, depending on author (Smith et al., 1997). Methods to directly measure the conceptual pools would be a major step to verify and to validate existing carbon models. However, most studies reported that the conceptual pools were only loosely or even not at all associated with pools isolated in the laboratory (Magid et al., 1996; Helfrich et al., 2007). Consequently, it would be useful to integrate soil C pools defined according to specific stabilization methods which thus represent functional pools in soil carbon models (Sollins et al., 1996; Six et al., 2002; von Lützow et al., 2006). Various biological, physical, and chemical fractionation methods have been developed to obtain soil C fractions with different turnover times, stabilization mechanisms, and functionality. The following chapter reviews these fractionation methods.

1.4.1 Physical Fractionation Methods

Particle size fractionation is an attempt to separate soil organic matter pools associated with mineral particles of different sizes. Quartz particles are dominant in the sand size fraction and interact only weakly with soil organic matter. In contrast, clay size particles are sorbed to soil organic matter by strong ligand-exchange and polyvalent cation bridges. As in temperate soils, mean residence time generally increase from the sand to the clay fraction in tropical soils (Bonde et al., 1992; Feigl et al., 1995).

Aggregate fractionation is used to isolate aggregates of different sizes. Results of aggregate fractionation depend on the methodology, including water content in the field, sample pre-treatment and the sieving procedure (Gollany et al., 1991; Christensen, 1996; Beare and Bruce, 1993; Ashman et al., 2003). The most widely used approach is rapid immersion of air-dried samples in water – a process called slaking – with subsequent wet-sieving of the soil (Kemper and Rosenau, 1986). In most soils, aggregates do not disintegrate into in their primary particles upon slaking, but rather into smaller aggregates. This lead to the hypothesis that stable microaggregates (<250 µm) are bound together to larger units (macroaggregates) by labile organic material (Tisdall and Oades, 1982). This concept, called “soil aggregate hierarchy”, was supported by subsequent studies showing that macroaggregates had a higher carbon content, contained less-decomposed organic material, and had faster soil C turnover compared to microaggregates (Six et al., 2002). Aggregate hierarchy, which has been shown to exits in temperate climate soils so far, should be strongest in soils where organic material is the main binding agent between soil particles (Oades and Waters, 1991).

Density fractionation is applied to separate light organic matter (light fraction) not bound to minerals and the mineral-associated organic matter (heavy fraction) through flotation and sedimentation in heavy liquids. Soil aggregation results in different stability and composition of the free light fraction located between aggregates and occluded light fraction trapped within aggregates (Six et al., 2002). Free light fraction consists mainly of recognizable plant debris, while occluded light fraction has undergone stronger decomposition and consists of more recalcitrant soil C (Golchin et al., 1994 a, b). Correspondingly, soil C in free light fractions, if not affected by charcoal, showed generally higher turnover times than occluded light fractions (von Lützow et al., 2007).

High gradient magnetic separation isolates soil organic matter associated with Fe oxides and Fe-rich clay minerals (Shang and Tiessen, 1997). This approach has been applied mainly to highly weathered tropical soils, where iron oxides are important for carbon stabilization (Shang and Tiessen, 1997).

1.4.2 Chemical Fractionation Methods

Chemical fractionation techniques are based on extraction of soil organic matter in solutions, on hydrolysability with water, acids or bases, on oxidative degradation of organic matter, or on the destruction of mineral phases. Some of these methods are thought to be suitable for the isolation of a stable or passive pool.

Hot water extraction is used to isolate the easily mineralisable soil organic matter pool (Körschens and Schulz, 1999). However, only a small proportion of the assumed total labile pool is extracted (Balesdent, 1996). Standard fractionation of humin, humic acid, and fulvic acid were ineffective to isolate soil organic matter pools with different turnover times (Balesdent, 1996; Balesdent and Mariotti, 1996).

$Na_4P_2O_7$ treatment extracts organic carbon complexed by polyvalent cations as well as carbon attached to mineral surfaces (Shoji et al., 1993; Kaiser and Zech, 1996). Correlation of soil C with pyrophosphate-soluble Al in volcanic ash soils are often explained with stabilization of soil C through Al-humus complexes and non-crystalline hydroxides and related to long-term stabilization of soil C (Torn et al., 1997).

The most widely used method to isolate a stable pool is acid hydrolysis (Six et al., 2002; Paul et al., 2006), which preferentially removes young, potentially biodegradable compounds (e.g. proteins and polysaccharides) and leaves behind recalcitrant biomacromolecules (e.g. long-chain alkyls, waxes, aromatics; Paul et al., 2006). While in temperate soils the non-hydrolysable fraction was found to be generally about 1200 years older (Paul et al., 2006), in tropical Oxisols and Andisols acid hydrolysis was less effective to isolate a stable pool (Trumbore, 1993; Trumbore and Zheng, 1996).

Other methods use oxidative treatments with $KMnO_4$, NaOCl, H_2O_2, or $Na_2S_2O_8$ to imitate natural oxidative processes in soils (Shang and Tiessen, 1997; Eusterhus et al., 2005; Plante et al., 2004; Mikutta et al., 2005). While H_2O_2 and $Na_2S_2O_8$ at 80° C alter the mineral structure, NaOCl leaves mineral surfaces unaffected (Mikutta et al., 2005; Siregard et al., 2005). An increase in mean 14C ages of about 75 to 1800 years after NaOCl treatment was found in a range of acidic subsoil samples from temperate and tropical forests (Kleber et al., 2005). Alternatively, high energy ultraviolet photo oxidation was proposed by Skjemstad et al. (1993) to separate the passive from the active organic matter pool. However, this method does not differentiate between stabilization due to recalcitrance or due to occlusion in microaggregates. In addition, only a limited data set for soils was generated with this method so far.

1.4.3 Biological Fractionation Methods

Biological fractionation methods include ***incubation*** of soil and measurement of the evolved CO_2, which reflects the respired soil C. This approach provides information about the catabolic potential of soil microbial populations, decomposition of specific organic compounds and soil C availability, size and activity of biomass and pool size, and fluxes of organic matter (Paul et al., 2006). Incubation was found useful in interpreting soil C dynamics influenced by management effects (Paul et al., 2003). However, to determine different soil C pools, soils have to be incubated for a long time (>800 days). Accordingly, this method is very time consuming.

1.4.4 Evaluation of Fractionation Methods

A general problem of the above described methods is that they often do not represent homogenous soil C pools but contain organic compounds of various genesis and turnover times. Separation of specific organic compounds by wet chemical analyses and subsequent determination of their isotope ratio are achieved by coupling of gas chromatography and isotope ratio mass spectroscopy (GC-IRMS). Applications in soil science include amino sugars, phenols, and phospholipid fatty acids (Goni et al., 1998; Amelung et al., 2001; Burke et al., 2003; Glaser and Gross, 2005). Although these methods allow a detailed analysis of carbon transformation and turnover of individual compounds and may allow differentiation of functional fractions within heterogeneous fractions, their use to identify meaningful soil C pools to simulate soil C dynamic remains challenging.

A combination of methods, such as density fractionation prior to chemical fraction methods or other new promising methods such as oxidation with NaOCl yielded more homogenous soil C fractions (von Lützow et al., 2007). However, until now data on pool sizes and mean residence times in different soil types is limited, so a validation of a more mechanistic model based on functional pools is still not possible (von Lützow et al., 2007).

1.5 The Use of ^{13}C as a Soil C tracer in Deforestation Studies in the Tropics

In case of the primary production of terrestrial plants, fractionation of stable carbon isotope occurs during the photosynthesis and the heavier isotope ^{13}C is discriminated against ^{12}C. As a consequence, plants are isotopically depleted in the heavier carbon isotope compared to the atmospheric reservoir. The degree with which plants discriminate carbon isotopes primarily depends on the photosynthetic pathway (C_3, C_4 and CAM pathway; O'Leary, 1981). Plants using a C_3 pathway (Calvin-cycle) have δ^{13}C values from -32‰ to -22‰ VPDB with a mean of -27‰, while plants (mainly tropical grasses) using a C_4 pathway (Hatch-Slack-cycle) are characterized by δ^{13}C values of about -13‰ (Lloyd and Farquhar, 1994). The stable carbon isotope composition of soil C developed under C_3 and C_4 plants reflects the δ^{13}C signature of its vegetation (Balesdent and Mariotti, 1996). Over the past decade, stable isotopes has increasingly been used to trace origin and turnover of soil organic matter after land-use changes associated with C_3-C_4 vegetation in deforestation studies in the tropics (e.g. Veldkamp, 1994; Detwiller, 1996; Rhoades et al., 2000; Schwendenmann and Pendall, 2006). A review on soil C turnover times calculated from C_3-C_4 vegetation changes showed that the mean residence time of soil C was considerably shorter for tropical soils (36 years) than for temperate soils (63 years; Six et al., 2002). However, soil C turnover may vary considerably depending on soil type and related chemical and physical interactions of soil C with mineral soil particles (Torn et al., 1997; Telles et al., 2004).

Moreover, several deforestation studies have tried to separate soil C fraction with different mean residence times. Using particle size fractionation it was found that the mean residence time generally increased from sand size fraction to the clay fraction in tropical soils (Desjardins et al., 1994; Feigl et al., 1995; Koutika et al., 1997; Solomon et al., 2002). Separation of light fractions was done by Cadisch et al. (1996), Guggenberger and Zech (1999), Schwendenmann and Pendall (2006), and Denef et al. (2007). They all found indications that the light fraction turned over faster than the whole soil organic matter and can serve as an early indicator of land use changes. However, information on the influence of soil type and soil properties such as clay content on the amount and stability of free and occluded light fraction is very limited and restricted to temperate and subtropical soils (Golchin et al., 1994b; Kölbel and Kögel-Knabner, 2004).

Although it is well documented that different soil types go along with different soil C stocks and a range of mean residence times of forest-derived carbon, it is presently unknown how the soil type affects the stability of recently incorporated soil C. Land use sequences from natural forests to pasture and pasture to secondary forests provide information about stability of recently incorporated pasture-derived carbon in secondary forests. In combination with fractionation of soil C into different soil C pools new insight into the involved stabilization mechanisms can be gained.

1.6 Objectives and Outline of the Thesis

This study focuses on different tropical soils. The objectives of this study were:

i) to determine how soil properties and parent material influence soil C contents in bulk soil, physically, and chemically defined soil fractions;

ii) to quantify the influence of soil properties and parent material on soil C changes in these fractions induced by different land-use changes (natural forest to pasture and pasture to secondary forest);

iii) to evaluate the stability of old forest-derived carbon under pasture and of recently incorporated pasture-derived carbon under secondary forests in these fractions with stable carbon isotopes and to identify how the stability of these fractions is influenced by soil properties and parent material;

iv) to elucidate whether physically and chemically defined soil fractions represent meaningful soil C pools with respect to stabilization mechanisms.

Organic matter was investigated in the following different operationally defined soil fractions:

a) Physically defined soil fractions:

i) ***Aggregate size fractions***

(8000-2000; 2000-250, 250-53, <53µm)

ii) ***Density fractions***

(a free light fraction and two occluded light fractions with <1.6 g cm^{-3}, and a heavy fraction >1.6 g cm^{-3})

b) Chemically defined soil fractions:

i) Mineral-associated soil C resistant to acid hydrolysis
(treatment with HCl)

ii) Mineral-associated soil C resistant to oxidative degradation with NaOCl
(treatment with NaOCl)

iii) Mineral-associated soil C resistant to extraction with $Na_4P_2O_7$
(treatment with $Na_4P_2O_7$)

For this purpose four sites with soils developed from marine Tertiary sediments varying in silt + clay content (62 to 83%) and four sites developed on volcanic ashes also varying in silt + clay content (35 to 79%) and in pyrophosphate soluble Al (3-11 g kg^{-1}) were chosen from a subset of 40 sites used by de Koning et al. (2003) and López-Ulloa et al. (2005) in Northwest Ecuador. In these studies, the potential to increase soil C stocks after forest regrowth on abandoned pastures was analysed (Koning et al., 2003) along with the effect of soil properties on long-term stabilization of soil C (López-Ulloa et al., 2005).

All sites selected by de Koning et al. (2003) consisted of a secondary forest plot and a pasture plot. For this thesis, at each site an additional 'natural' forest plot as a C_3 reference plot was selected. In order to separate different soil C pools according to their stabilization mechanisms, the following fractionation scheme was applied: Fractionation of water-stable aggregates was followed by density fractionation of these aggregates. Density fractionation separated light fractions (<1.6 g cm^{-3}) according to their location in the soil matrix. The free light fraction is located outside aggregates and the occluded light fraction is found inside aggregates. In addition, density fractionation separated according to the degree with which soil C is associated with minerals. Soil C in the heavy fraction (>1.6 g cm^{-3}) is intimately associated with minerals and therefore also called mineral-associated soil C. Mineral-associated soil C was further fractionated into soil C fractions resistant to treatment with HCl, NaOCl, and $Na_4P_2O_7$.

Combining physical and chemical fractionation procedures with ^{13}C isotope analyses on soil samples from sites that had undergone C_3-C_4 vegetation changes I traced the origin of soil carbon in these soil fractions under pasture and secondary forest. Moreover, mean residence times of old forest-derived carbon under pasture and recently incorporated pasture-derived carbon under secondary forests were calculated for bulk soil. From this fractionation scheme I expected a better insight in quantitative changes of soil C fractions followed land-use changes and a better understanding of soil C stabilization mechanisms in different tropical topsoils.

This thesis is structured as follows: **Chapter 2** provides a short overview of the study area in Northwest Ecuador and of the applied fractionation scheme. Changes in total soil organic matter and in physically separated fractions induced by land-use changes are described in Chapter 3 to 5. **Chapter 3** focuses on methodical aspects of aggregate fractionation. The effect of soil pretreatment prior to the sieving procedure (air-dried vs field-moist soil adjusted to 75% of maximum field capacity) on the outcome of the distribution of dry matter, soil C, and the proportion of pasture-derived soil C in different aggregate size classes. **Chapter 4** analyzes the main controls of soil C storage in bulk soil. Mean residence times of forest-derived soil C in pastures and of pasture-derived soil C in secondary forests were calculated of bulk soil. In addition, this chapter focuses on the importance of aggregation for the stabilization of soil C in natural forests, pastures, and secondary forests. **Chapter 5** deals with the effect of soil type on soil C storage in density fractions (free light fraction, two occluded light fractions, and the heavy fraction) and the quantification of soil C changes in these fractions induced by different land use changes (natural forest to pasture and pasture to secondary forest). In addition, general soil properties that influence the amount and stability of light and occluded fractions were determined. **Chapter 6** assesses how these two soil types affect size and origin of soil C resistant to treatment with HCl, NaOCl, and $Na_4P_2O_7$. In addition, it was determined if soil C storage in these fractions depended on land use (natural forest, pasture, secondary forest). Finally, the suitability of these methods to isolate a passive soil C pool from theses tropical soils was evaluated. **Chapter 7** synthesises the results of these studies and provides an overview of soil C storage in the different fractions to total soil C and the stability of these fractions under pasture. In addition, the different soil C fractions were evaluated for being a sensitive indicator of land use changes. Furthermore, the suitability of the applied fractionation procedures to separate soil C according to its stabilization mechanisms is discussed. Finally, on the basis of the results of this thesis I provide recommendations for future research.

2 Material & Methods

2.1 Study Area

The investigated sites are located in tropical Northwest Ecuador, within the geographical coordinates 79°05′W, 1°04′N and 78°37′W, 0°01′N. The study area's boundaries are the Pacific Ocean in the West, Colombia in the North, and the Western Cordillera of the Andes in the East. Figure 2-1 shows the eight sampled sites in Northwest Ecuador. Four sites are located in the coastal region, in the Province of Esmaraldas. This area is characterized by low mountains with elevations mostly between 400 and 600 m. Elevation of the four sites varies between 30 and 200 m above sea level. The other four sites are located in the north-western part of the Province Pichincha at the foot slope of the Western Cordillera. Elevation of these four sites varies between 300 and 1700 m above sea level.

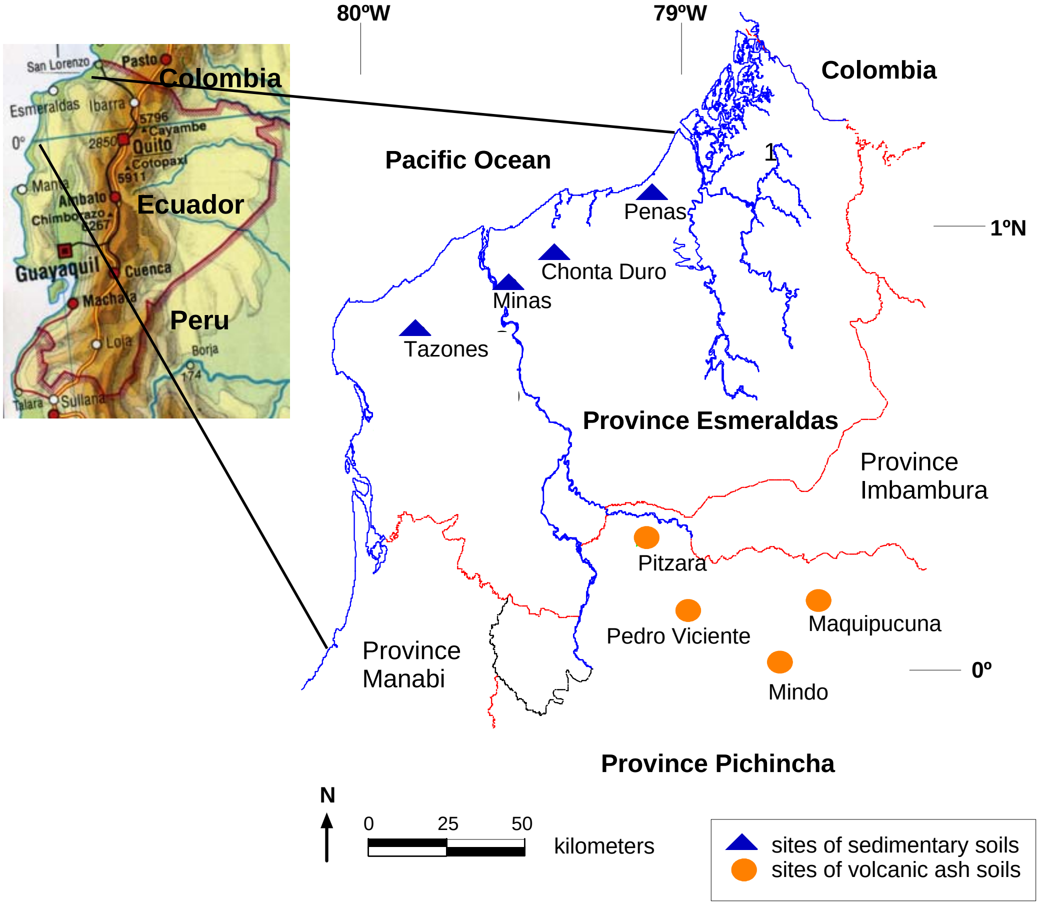

Figure 2-1: Map of Northwest Ecuador with sampling sites (maps modified after Westermann, 1992 and de Koning et al., 2003).

2.1.1 Geology and Soil Formation

The present-day coastal range of north-western Ecuador is formed by marine deposits of limestones and shales, and subordinate by igneous rocks particularly submarine pillow lavas alternating with marine sediments in the Oligocene and Miocene (Neill, 1999). Soils developed from this parent material were classified as Haplustepts and Paleustalfs (Soil Survey Staff, 1998). The soils are slightly acidic to neutral and generally have a clayey or loamy clay texture and a cation exchange capacity of about 40 $\mathrm{cmol_c\ kg^{-1}}$. Smectite is the dominating clay mineralogy. Throughout this thesis, soils developed from marine Tertiary sediments will be called 'sedimentary soils'.

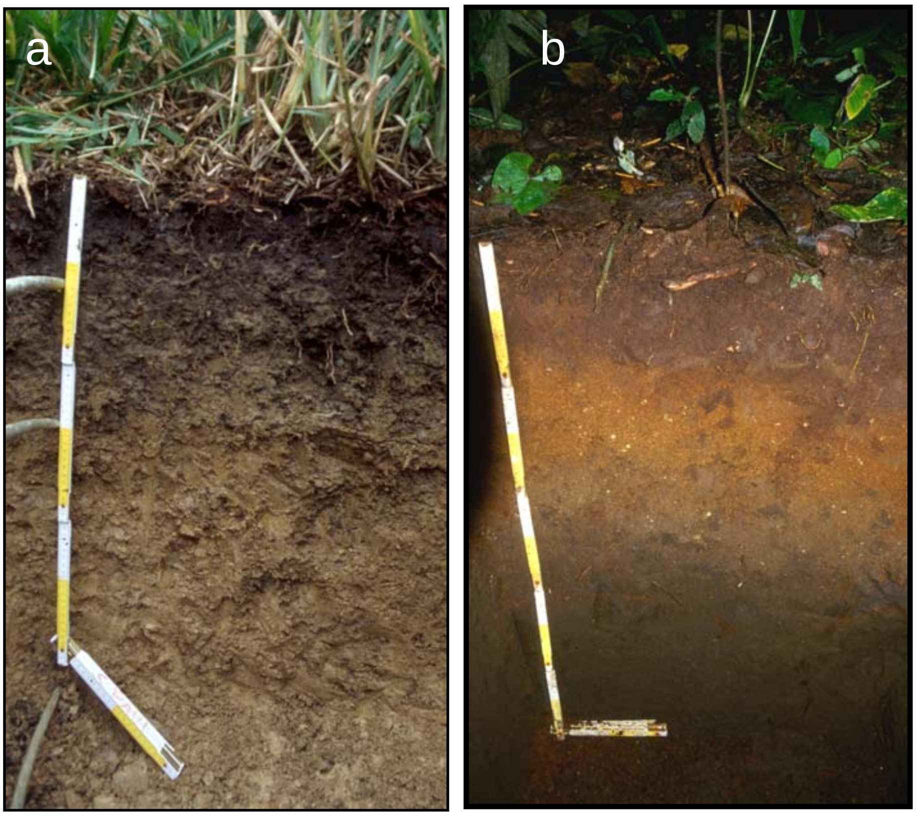

Figure 2-2: Example of a) a sedimentary soil profile (Minas) and b) a volcanic ash soil profile (Maquipucuna).

The base of the Western Cordillera is mostly Cretaceous volcanic and pyroclastic rocks. Intensive volcanic activity during the mid to late Tertiary and also throughout the Quaternary period on top of the uplifted basal rocks built up the Andes to their recent heights. Lava flows and lahars, deposits of volcanic ashes and pumice played a major role in building the land surface of the four sites at the foot slopes of the Western Cordillera of the Andes and some lower lying valleys (Neill, 1999). Soils developed from parent material of volcanic origin are relatively young: for example, at the site Maquipucuna, soils developed from andesitic volcanic ash, which was deposited 2500 years ago (Papale and Rossi, 1993). Soils developed from this parent material were classified as Hapludands (Soil Survey Staff, 1998). The clay mineralogy is characterized by the presence of allophane. The soils are generally slightly acidic, have a sandy or loamy texture, a low bulk density, and a low cation exchange capacity of less than 10 $\text{cmol}_c\ \text{kg}^{-1}$. Throughout the thesis, soils developed from volcanic ashes will be called ‘volcanic ash soils’. Typical examples of a volcanic ash soil profile and a sedimentary soil profile are given in Figure 2-2. Detailed chemical analyses of all soil profiles are given in the Appendix, more information about the soil of upper 0.1 m is provided in Chapter 4, Table 4-2.

2.1.2 Climate

Due to the position near the equator, the daily mean temperature is rather constant throughout the year. The mean annual temperature is modulated by the altitude. It is about 25° C at sea level in coastal Ecuador and following the adiabatic lapse rate it decreases with elevation and mean annual temperatures of 18° C are found at the highest investigated sites in the submontane area of the Western Cordillera. In the coastal region of Ecuador, annual rainfall patterns are under the influence of the two principal ocean currents in the Pacific: The cold Humboldt Current, which flows northward along the coast of Chile and Peru until southern Ecuador, and the warm equatorial current that flows southward from the Gulf of Panama and meets the Humboldt Current near the equator along the north-central coast of Ecuador. While the Humboldt Current brings arid conditions to the adjacent coast in the South, the warm equatorial current that bathes the northwest coast of Ecuador brings moist air and rainfall. Accordingly, sites in the southern part of the coastal region receive a mean annual precipitation of only about 1500 mm, while the most northern site Penas gets about 2500 mm. The duration of the dry season is about three months. Higher mean annual precipitation is found at the north-western part of the Province Pichincha at the foot slope of the Western Cordillera, which amounts to 5000 mm at the site Pedro Viciente.

2.1.3 Vegetation and Land Use

According to climate and topography, several vegetation types are found in the study area. Semi-deciduous forest covered the drier sites at the coastal region in western Ecuador receiving between 1300 and 2000 mm precipitation (Kvist et al., 2004). This vegetation type is intermediate in the moisture gradient between deciduous forest, which occurs mostly in south-western Ecuador, and lowland rain forest in the northwest. *Centrolobium ochroxylum*, *Erythrina poeppigiana*, *Gallesia integrifolia*, *Castilla elastica*, and *Pseudobombax millei* are typical canopy tree species which shed their leaves during the dry season. Other canopy trees retain them, such as *Brosimum alicastrum*, *Poulsenia armata*, and species of Ficus. The canopy palm *Attalea colenda* and the understory palm *Phytelephas aequatorialis* are ubiquitous in the semi-deciduous forest (Jørgensen and León-Yánez, 1999). Lowland rain forest covers the northern Pacific coastal lowlands below about 700 m elevation, including most of Esmeraldas and adjacent parts of Pichincha provinces. Climatically, lowland rain forest is characterized by annual rainfall in excess of 3000 mm and lack of a distinct dry season. The lowland rain forest is tall, dense, and evergreen, with a canopy height of usually 30 m or taller, and characterized by a high species diversity.

Figure 2-3: Example of the three land use types a) pasture, b) natural forest, and c) secondary forst of a sedimentary soil site (Tazones).

Common canopy tree species in this region include *Brosimum utile*, *Humiriastrum procerum*, *Dacryodes cupularis*, *Nectandra guadaripo*, *Virola dixonii*, and *Otoba novogranatensis*. The subcanopy is dominated by two species of very abundant palms, *Iriartea deltoidea* and *Wettinia quinaria*, and by several species of Matisia. The dense understory is composed of Rubiaceaea and small palms, mostly Geonoma species. Epihytic Araceae, Cylanthaceaea, and ferns are covering the lower trunks of the trees (Davis et al., 1997). The lower montane rain forest occurs on the western slopes between 700 and 2500 m elevation. Dense loads of vascular epiphytes and bryophytes on tree branches and trunks in this vegetation type as well as constantly high humidity and fog-associated precipitation are characteristics of this cloud forest. *Ruagea glabra*, *Ruagea pubescens*, *Dussia lehmannii*, *Meriania tomentosa*, *Cinchona pubescens*, *Roupala obovata*, and *Nectandra acutifolia* are common tree species of the western slope (Jørgensen and León-Yánez, 1999). Due to heterogeneous conditions with respect to climate and topography as well as the natural fragmentations, the flora of western Ecuador is highly diverse and endemic. It is estimated that about 20% of the 6300 species of lowland western Ecuador are endemic, but recently many species are at high risk to extinct (Dodson and Gentry, 1991).

While at the end of the 19th century most of western Ecuador was still covered by intact forest (75%), most deforestation occurred between 1960 and 1980 due to road construction and demographic explosion, primarily along rivers and roads (Sierra and Stallings, 1998). By the 1990s, 90% of the original forests had been cleared for timber extraction and conversion to agricultural land (Sierra and Stallings, 1998). Additionally, selective logging may have affected a large percentage of the remaining forest (Sierra and Stallings, 1998). The current estimated forest cover including primary and secondary forests is about 50% (de Koning et al., 2003). Grassland for cattle grazing is the dominant agriculture land use with low stocking densities (on average one animal per hectare). Most pastures had been established after cutting and burning the natural or intervened forests. Common grass species are *Paspalum dilatatum*, *Panicum maximum*, and *Cynodon plectostachyus*. It is common practise that pastures are not fertilized. Other agriculture land uses include the following crops: oil palm, banana, cacao, coffee, maize, rice, and cassava. When pastures are abandoned, rapid regrowth of secondary forests occurs. Typical tree species of secondary forests found in the coastal region include *Cordia alliodora*, *Inga sp*, *Castilla elástica*, *Erytrina poeppigiana*, *Eugenia sp.* and on volcanic ash soils *Chinchona pubescens*, *Acacia sp.*, *Matisia sp.*, *Cyathea sp.*, *Miconia sp.*, *Vernonia baccharoides*, and *Ocotea sp.* The area of forest plantations is limited, estimated to about 10000 ha and common tree species are *Jacaranda superba*, *Hyeronima chocoensis*, *Carapa guianensis*. Recently *Eucalyptus sp.* is used for afforestation. Figures 2-3 and 2-4 illustrate the different land use types of a sedimentary soils site and of a volcanic ash soils site.

Figure 2-4: Land use types of volcanic ash soil sites: a) pasture (Maquipucuna), b) natural forest (Pedro Viciente) and c) secondary forest (Pedro Viciente).

For this thesis I used a selection of sites in Nortwest Ecuador already used by a de Koning et al. (2003) and Lopez et al. (2005). These sites were selected using the following criteria: i) each site has paired pasture and secondary forest, under very similar biophysical conditions (soil type, landscape position, climate); and ii) sites were chosen so that pastures (C_4 plants) were established on sites that were natural forest before (C_3 plants). Secondary forest sites were chosen so that they were established on former pastures to be able to use the $\delta^{13}C$ signal as a tracer. Within the existing data set of 40 sites, de Koning et al. (2003) differentiated two main soil groups with different parent material i) volcanic ashes and ii) sediments. These two soil groups differed in their carbon stabilization mechanisms of soil C. Soils developed from volcanic ash soils showed higher total soil C stocks than sedimentary soils. Soil C concentration in volcanic ash soils was related to the amount of non-crystalline minerals (amount of Aluminium extracted with $Na_4P_2O_7$ (Al_p)). For sedimentary soils, soil C was correlated with the amount of clay (de Koning et al., 2003). In addition, Lopez et al. (2005) speculated from the correlation of Alp with forest-derived carbon that the long-term stabilization of soil C in volcanic ash soils was associated with the formation of metal-humus complexes and allophanes. In sedimentary soils, soil C was stabilized primarily through sorption to clay. Furthermore, they found first indications that recently incorporated soil C was not stabilized in volcanic ash soils, but rather in sedimentary soils.

In order to elucidate the different factors influencing soil C storage and stabilization in these two soil groups, four sites on volcanic ashes and four sites on sedimentary soils were selected. Within these two different soil groups, variations in soil properties connected to soil C storage and stabilization were chosen: clay content for sedimentary soils (29 to 64%) and Al_p content (3 to 11 g kg^{-1}), which correlated with silt + clay content (35 to 79%) for volcanic ash soils. In addition, a natural forest was important as a C_3 reference plot at each site. At each plot, a transect was installed consisting of four sampling points and one soil profile. At each point, vegetation samples, litter layer (if existing), root and soil samples of the uppermost 0.1 m were taken. I only sampled the uppermost 0.1 m since effects of land use changes on soil aggregation and soil C stocks of different origin and stability are most pronounced in the top soil (Desjardins et al., 1994; Bashkin and Binkley, 1998). Detailed soil analyses and a more detailed description of sites are provided in Chapter 4; the results of the soil profiles are given in the Appendix.

2.2 Applied Fractionation Scheme

A sequential fractionation scheme was applied to all soil samples (Figure 2-5). The principle of the fractionation scheme is explained below. The first **physical fractionation procedure** was **aggregate fractionation**. Bulk soil < 8000 µm was submersed in water for 5 minutes on top of a 2000 µm sieve and the sieve was manually moved 3 cm up and down 50 times. Aggregates of 8000-2000 µm were collected and sieving was repeated with sieves of 250 µm and 53 µm (modified after Elliott, 1986). I used moist soil, which was adjusted to 70% of its maximum water holding capacity. Moist soil samples for aggregate fractionation were used because volcanic ash soils containing allophane display irreversible flocculation and changes in aggregate distribution upon drying (Churchman and Tate, 1987; Wells and Theng, 1988). After aggregate fractionation, two aggregate size classes of macoraggregates (2000-8000 µm and 2000-250 µm), one microaggregate size class (53-250 µm), and the smallest fraction (<53 µm), which contains the smallest microaggregates, silt and clay particles were obtained. To determine the effect of air-drying prior to the sieving procedure, a set of sample was air-dried prior sieving.

The following **density fractionation** was applied to the combined macoraggregate and the microaggregate class. Sodium polytungstate solution (SPT) with a density of 1.6 g cm^{-3} was used for the separation of light and heavy fractions. Particulate light organic matter not occluded in aggregates was isolated by putting air-dried aggregates in a centrifuge tube together with SPT and gently shaken by hand. After 30 min of sedimentation, the solution was centrifuged for one hour at 5100 g. The supernatant, including floating particles, was filtered and washed with distilled water under vacuum. This fraction is called ***free light fraction***. For the separation of the particulate organic matter, which was occluded in aggregates, aggregates were destroyed by adding again SPT and 18 glass pearls to the residue and shaking the test tube for 16 h at a frequency of 120 movements per minute (Balesdent et al., 1991; John et al., 2005, modified). Then the soil solution was centrifuged and the supernatant with the floating material was filtered and washed to gain the occluded light fraction (further on called '***occluded I light fraction***'). The residue was washed four times with distilled water, sieved (53 µm) until all aggregates >53 µm were broken and both fractions (>53 µm and <53 µm) were dried at 40° C. The fraction <53 µm and >1.6 g cm^{-3} will be called ***heavy fraction*** and soil C in this fraction is associated with the mineral phase. The fraction >53 µm was again treated with a SPT solution of 1.6 g cm^3 as described above and a third light fraction (further on called '***occluded II light fraction***') was attained.

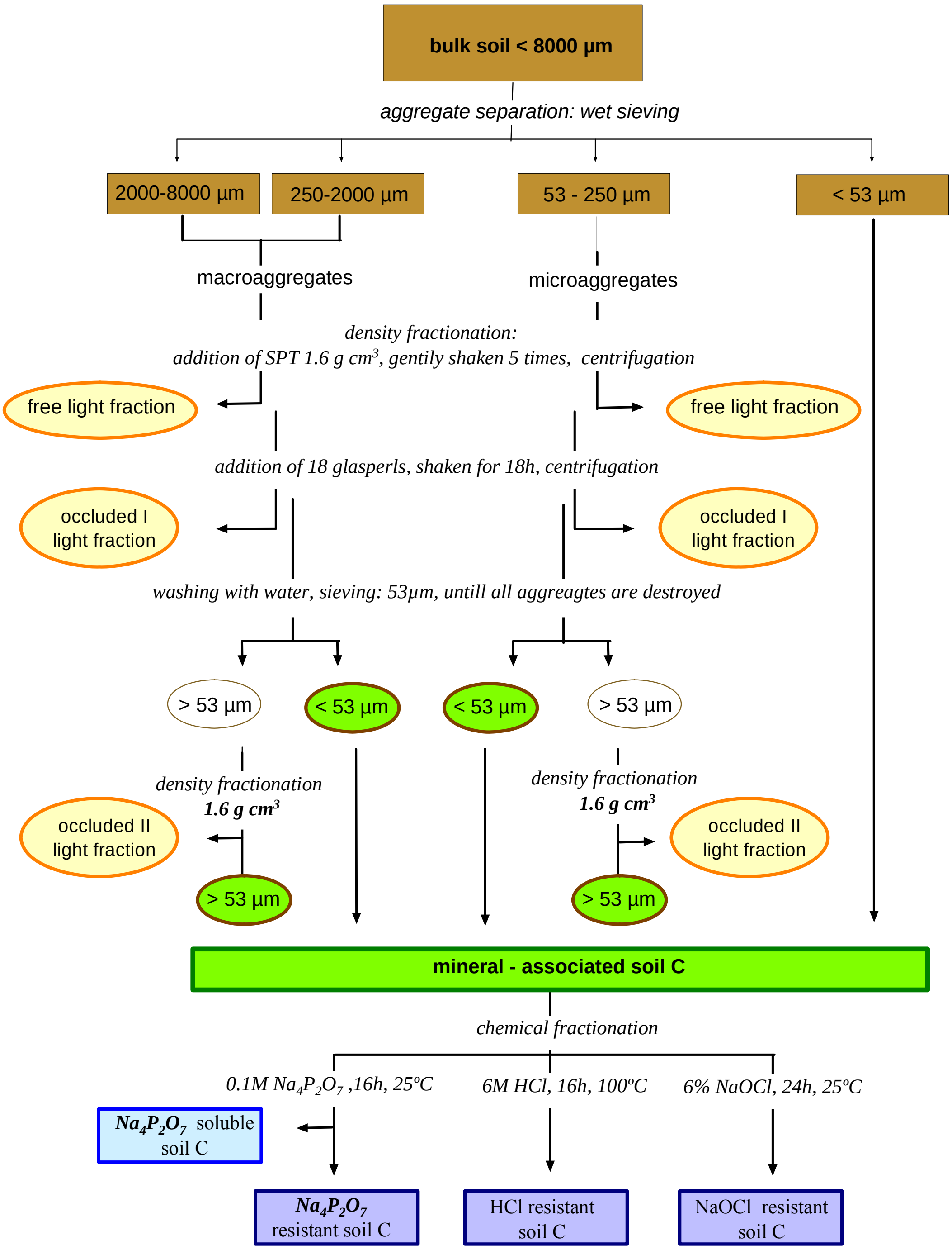

Figure 2-5: Applied fractionation scheme. Bulk soil of <8000 µm was separated into four aggregate size classes (brown squares), followed by density fractionation of macro- and microaggregates resulting in free light, occluded I light fraction, and occluded II light fraction (all red ovals), heavy fraction <53 µm and >53µm (green ovals). Mineral-associated soil C (<53 µm aggregate size fraction + <53 µm heavy fraction from macro-and microaggregates; green squares) was further chemically fractionated resulting in fractions resistant to chemical treatments (blue squares) and soluble by pyrophosphate (light blue squares).

For the **chemical fractionation procedures,** all fractions <53 µm were proportionally recombined (called 'mineral-associated soil C') and served as starting material. **Acid hydrolysis** was carried out according to Plante et al. (2006): 0.5 g mineral-associated soil was treated with 25 mL of 6M HCl for 16 h. The residuum was washed with distilled water until free of acid and finally freeze-dried. The **sodium hypochlorite procedure** was modified after Siregard et al. (2005). One g of mineral-associated soil was placed in 50 mL bottles and treated four times with 20 mL of 6% NaOCl (pH 8) for a total of 24 h. **Extraction with pyrophosphate** was done after Buurman et al. (1996). Briefly, 0.5 g of mineral-associated soil was shaken for 18 h in 50 mL (sedimentary soils) or 100 mL (volcanic ash soils) 0.1M $Na_4P_2O_7$. Samples were centrifuged, the residuum was washed with distilled water and dried at 40° C.

All separated fractions were analysed for total C and N with an automated C and N analyzer (Elementaranalysator CNS, Vario EL, Elementar, Hanau, Germany) and the $^{13}C/^{12}C$ isotope ratio was measured using an isotope ratio mass spectrometer (IRMS, Finnigan MAT, DELTA^{plus}, Bremen, Germany).

3 Methodical Aspects of Aggregate Size Fractionation*

3.1 Abstract

Soil aggregation is an important mechanism for the stabilization of soil organic carbon (soil C). The distribution of soil C among aggregate classes depends on sample pretreatment and on the applied method of aggregate fractionation. Here, we examine the effect of soil pretreatment (air-dried vs field-moist soil) on the yield, and C content of aggregate size fractions (8000-2000, 2000-250, 250-53, <53 µm). Aggregate size fractions were separated by wet-sieving tropical soils of different parent material and mineralogy (volcanic ashes - dominated by short-range-order aluminosilicates and Marine Tertiary sediments - dominated by smectitic clays) which were used as pastures for 13 to 50 years after deforestation. In addition, the proportion of pasture- and forest-derived organic carbon in aggregate fractions was determined using the $^{13}C/^{12}C$ isotope ratio. In volcanic ash soils, there was no clear effect of soil pretreatment on the distribution of aggregates into aggregate size classes. Furthermore, the soil C concentration and proportion of pasture-derived carbon of aggregates within each size class did not differ across treatments. However, in smectitic clay soils, the two pretreatments resulted in distinct differences in the distribution of dry matter yield and also of soil C among the aggregate fractions. Wet-sieving of dry soil led to a separation of macroaggregates rich in pasture-derived carbon, whereas wet-sieving of moist soil isolated microaggregates with high contents of pasture-derived organic matter. This implies that soil organic matter plays a major role both in the formation and stabilization of macroaggregates and in the early stage of microaggregate formation in sedimentary soils, but not in volcanic ash soils.

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3.2 Introduction

Soil aggregation can decrease accessibility of enzymes to substrate and thus contributes to the physical protection of soil C (Sollins et al., 1996). Several methods have been developed to fractionate soil into different aggregate size classes. Their results depend on water content in the field, sample pretreatment and the sieving procedure (Gollany et al., 1991; Christensen, 1996; Beare and Bruce, 1993; Six et al., 2000b; Ashman et al., 2003). The most widely used approach to separate aggregate size classes is rapid immersion of air-dried samples in water with subsequent wet-sieving of the soil (Kemper and Rosenau, 1986). When air-dried aggregates are rapidly immersed in water, water enters the pores of the aggregates and air gets entrapped inside the aggregate. Increasing pressure may destroy the aggregate and air bubbles emerge, a process called slaking (Kemper and Rosenau, 1986). In addition, the combination of wet-sieving of air-dried and rewetted soil is used to separate stable and unstable aggregates (Six et al., 2000b; Denef et al., 2002). Several methods have been suggested to rewet soil before aggregate size fractionation: rewetting by tension, vapour, under vacuum, or capillary wetting to field capacity plus 5% (Kemper and Rosenau, 1986; Beare and Bruce, 1993; Puget et al., 1995; Le Bissonnais, 1996; Six et al., 1998). Differences between these rewetting methods are comparatively small to the large differences found between rewetted and air-dried slaked treatments (Beare and Bruce, 1993). In temperate climate soils, wet-sieving of air-dried and slaked soil is considered to be the most appropriate procedure to separate aggregate size classes which differ in soil C storage and stability (Puget et al., 1995; Six et al., 2000a).

In 1982, Tisdall and Oades formulated the hypothesis that stable microaggregates (<250 µm) are bound together to larger units (macroaggregates, > 250 µm) by labile organic material. This concept, which they called “soil aggregate hierarchy”, was supported by subsequent studies which showed that macroaggregates had higher carbon contents, contained less decomposed organic material, and had faster soil C turnover compared to microaggregates in temperate climate soils with 2:1 clays (Jastrow et al., 1996; Six et al., 2002; John et al., 2005). This concept of aggregate hierarchy, that relies on organic matter as main binding agent, may not be suitable for heavily weathered tropical soils with 1:1 clays nor for volcanic ash soils, as in these iron and aluminium oxides rich soils formation of aggregates by mineral–mineral bindings is more important (Oades and Waters, 1991; Hoyos and Comerford, 2005; Schwendenmann and Pendall, 2006). In addition, sample pretreatments like air-drying can induce an irreversible flocculation in volcanic ash soils (Churchman and Tate, 1987; Wells and Theng, 1988). However, studies determining the effect of drying on aggregate size distribution in volcanic ash soils are rare (Churchman and Tate, 1987) and its influence on the partitioning of organic carbon among aggregate classes is not clear.

The objective of our study was to determine the effect of sample pretreatment (dry vs. field moist soil adjusted to 75% of field capacity) on: i) the distribution of aggregate size fractions in different tropical pasture soils (volcanic ash soils dominated by short-range-order aluminosilicates and Marine Tertiary sedimentary soils with smectitic clays); ii) the distribution of total soil C among aggregate classes; and iii) the proportion of recently incorporated organic carbon from pasture vegetation in aggregate size fractions.

3.3 Material & Methods

3.3.1 Sites and Soils

We selected four sites in Northwest Ecuador with different texture and parent material: two soils were developed on Marine Tertiary sediments (Chonta Duro, Haplustept and Tazones, Paleustalf) and two sites had soils developed from volcanic ashes (Maquipucuna and Pedro Viciente, both Hapludands, Soil Survey Staff, 1998). As the determination of clay content for allophane-containing soils reveals ambiguous results due to incomplete dispersion, we did not determine the clay content in volcanic ash soils (Nanzyo et al., 1993). X-ray diffraction of clay fraction of sedimentary soils revealed that sedimentary soils were dominated by smectite with marginal contribution of illite, chlorite, and kaolinite. None of the investigated sites contained inorganic carbon. At each site, we selected a pasture plot, dominated by C4 grasses and natural forest plot as C3 reference. Pasture plots had been established after cutting and burning natural forest. Natural forest plots with similar overall environmental characteristics of pasture plots were selected as close as possible. Duration of pasture period was 35 yr for both sedimentary soils, 50 yr for Maquipucuna, and 13 yr for Pedro Viciente. The duration of pasture period influences the amount of pasture-derived carbon in soils. This has to be taken into account when comparing absolute amounts of pasture-derived carbon in different soils or comparing calculated turnover rates of soil carbon (Feigl et al., 1995). Here we evaluated the effect of pretreatment on C distribution among aggregate fractions for the same soils and we compared only relative differences of pasture-derived carbon between different soils. This data evaluation is not biased by the duration of pasture period. Four soil samples (depth: 0-0.1 m, 0.09 m^2) and root samples were taken at each site. Selective dissolution of all soil samples was done using acid ammonium-oxalate extraction of aluminium (Al_o), iron (Fe_o) and silica (Si_o); dithionite-citrate extraction of iron (Fe_d) and pyrophosphate extraction of aluminum (Al_p; Buurmann et al., 1996). Fe, Al, and Si concentrations in these extracts were measured by inductively coupled plasma emission spectroscopy (Flame-ICP, Spectro Analytical Instruments, Kleve, Germany). General soil properties of the plots are summarized in Table 3-1.

Table 3-1: Location and general site characteristics (clay and sand content, soil organic carbon (soil C), total nitrogen (N_t), Aluminium extracted by pyrophosphate (Al_p) and acid-oxalate (Al_o), Iron extracted by acid-oxalate (Fe_o), dithionite (Fe_d), and pH of the pastures soils.

	Sites			
	Sedimentary soils		Volcanic ash soils	
	Chonta Duro	Tazones	Pedro Viciente	Maquipucuna
Latitude N (°)	00°55.26	00°43.24	00°05.65	00°07.21
Longitude W(°)	79°25.30	79°50.09	79°01.51	78°37.55
Clay (g kg^{-1})	324 (54)	607 (59)	nd	nd
Sand(g kg^{-1})	377 (29)	27 (1)	383 (30)	597 (32)
Soil C (g kg^{-1})	33.0 (3.8)	20.2 (1.7)	73.7 (8.0)	63.3 (11.2)
N_t (g kg^{-1})	3.4 (0.4)	2.1 (0.2)	6.1 (0.6)	5.0 (1.0)
Al_p (g kg^{-1})	1.1 (0.9)	0.3 (0.1)	6.3 (0.8)	4.4 (0.5)
Al_o (g kg^{-1})	1.3 (0.3)	0.8 (0.0)	16.4 (3.0)	7.3 (0.9)
Si_o (g kg^{-1})	0.3 (0.1)	0.3 (0.1)	5.0 (1.5)	0.3 (0.1)
Fe_o (g kg^{-1})	4.7 (0.6)	2.5 (0.4)	6.5 (0.3)	5.4 (1.0)
Fe_d (g kg^{-1})	6.5 (0.9)	5.4 (0.3)	7.0 (0.4)	6.1 (0.9)
pH†	5.7	6.2	5.6	5.4

† based on the soil profile (n=1), all other values were expressed as mean and SD (n=4)

3.3.2 Aggregate Fractionation

Prior to wet-sieving, field moist samples were carefully broken into aggregates <8000 µm by hand. Initial gravimetric moisture content was 68% ± 15% for sedimentary soils and 75% ± 9% for volcanic ash soils (mean ± standard deviation). One sub-sample was air-dried and one sub-sample was adjusted to 75% of the maximum field capacity by air-drying or adding distilled water. Maximum field capacity was determined by saturation of soils with distilled water and a subsequent draining of water until no further loss of water was measured (Schachtschabel et al., 1998). Fractionation of water-stable aggregates was done following Elliot (1986) in four size classes (8000-2000; 2000-250; 250-53, <53 µm). In brief, a soil sample (equivalent to 100 g air dried soil was used for both treatments) was submersed in distilled water for 5 minutes on top of a 2000 µm sieve and the sieve was manually moved 3 cm up and down for 50 times. Aggregates of 8000-2000 µm were collected and sieving was repeated with sieves of 250 µm and 53 µm. Sand content (particles >53 µm) was determined in sub-samples of all aggregate classes >53 µm by dispersion with sodium pyrophosphate and wet sieving at 53 µm. Organic carbon content of aggregates is expressed as soil C in sand-free aggregates (Elliott et al., 1991). The relative contribution of soil C stored in an aggregate size class to the total soil C content of the bulk soil (= F (%)) was calculated as follows:

$$F = C_{agg} / C_{bulk} \times 100, \qquad (3\text{-}1)$$

where C_{agg} is the absolute amount of carbon stored in an aggregate size fraction of 1 kg bulk soil (g kg^{-1}) and C_{bulk} represents the amount of carbon stored in 1 kg bulk soil (g kg^{-1}). Mean Weight Diameter (MWD) of water-stable aggregates was calculated as:

$$MWD = \sum_{i=1}^{n} \bar{x}_i \times w_i \,, \tag{3-2}$$

where $\bar{x}_i$ is the mean diameter of each size fraction, and w_i is the proportional weight of the corresponding size fraction (Kemper & Rosenau, 1986).

3.3.3 Amount and Proportion of Pasture-derived Carbon

Carbon content was measured with a total C and N analyzer (Heraeus Elementar Vario EL, Hanau, Germany), the $^{13}C/^{12}C$ isotope ratio was measured using an isotope ratio mass spectrometer (IRMS, Finnigan MAT, $DELTA^{plus}$, Bremen, Germany). The $^{13}C/^{12}C$ isotope ratios are expressed as $\delta^{13}C$ values:

$$\delta^{13}C\ (‰) = [(R_{sam} / R_{std}) - 1] \times 10^3, \tag{3-3}$$

with R_{sam} = $^{13}C/^{12}C$ isotope ratio of the sample and R_{std} = $^{13}C/^{12}C$ isotope ratio of the reference standard V-PDB (Vienna PeeDee Belemnite). The proportion of soil C derived from pasture vegetation (= soil C_4-C) was calculated from the ^{13}C abundance of samples from pasture and reference sites according to Balesdent and Mariotti (1996):

$$f = (\delta_{sam} - \delta_{ref}) / (\delta_{pasture} - \delta_{forest}), \tag{3-4}$$

where f is the proportion of soil C_4-C, δ_{sam} is the measured $\delta^{13}C$ (‰) value of the pasture topsoil sample, δ_{ref} is the $\delta^{13}C$ value of the corresponding sample from forest soil, and $\delta_{pasture}$ and δ_{forest} are the $\delta^{13}C$ values of roots from pastures and forests. The $\delta^{13}C$ value of the roots from all pastures and forests differed by 15.5‰ ± 1.4‰. We used the $\delta^{13}C$ values of roots for this calculation because all A horizons under pasture were intensively rooted and we assume that the pasture-derived soil C in these horizons originated mainly from grass roots. The contribution of pasture-derived soil C to total organic carbon in aggregate size fractions soil was used to evaluate the partitioning of young pasture-derived soil C among different aggregate size classes.

3.3.4 Statistics

The significance of differences among aggregate size fractions was assessed by ANOVA and post hoc Fisher LSD at $p \leq 0.05$. Differences between treatments were tested with a paired t-test at a significance level of 0.05 with STATISTICA 6.1 software package (StatSoft Inc., Tulsa, Oklahoma, USA).

3.4 Results

3.4.1 Sample Pretreatment and Aggregate Size Distribution

In sedimentary soils, pretreatment affected the distribution of dry matter yield of different aggregate size classes. Air-drying and slaking of soil prior to the sieving procedure reduced the proportion of large macroaggregates (8000-2000 µm) by about 50%, whereas the proportion of small macroaggregates (2000-250 µm) and microaggregates (250-53 µm) increased (Table 3-2). The proportion of the fraction <53 µm that consisted of smallest microaggregates and fine non-aggregated mineral particles was smaller for the moist pre-treatment (4%) than for the air-dried pretreatment (13 to 16%). Large macroaggregates were the dominant aggregate size fraction (60 to 74%) of the moist pretreatment, whereas small macroaggregates were the most important fraction of the air-dried pretreatment. The mean weight diameter of soil aggregates (MWD) was about 40% smaller for air-dried pretreatment than for moist pretreatment (Figure 3-1).

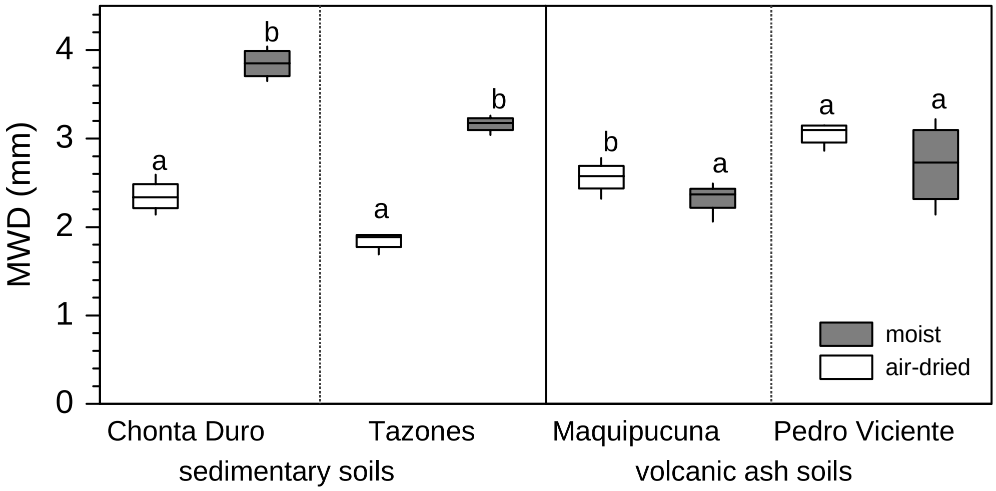

Figure 3-1: Box-plots of the mean weight diameter of aggregates (MWD) of tropical pasture sites using either air-dried soil or moist soil prior to aggregate fractionation by wet-sieving (median, upper and lower quartile and extreme values, n=4). Values within one site followed by different letter are different ($p<0.05$).

For volcanic ash soils the order of dry matter yield of aggregate size fraction was not changed by different pretreatments. Large macroaggregates were the most important aggregate fraction (41 to 53% of total yield). Drying and slaking resulted in a decrease of the smallest fraction (<53 µm) from about 10% to 2% at both volcanic ash sites (Table 3-2). There was no effect of sample pretreatment on MWD of aggregates at the site Pedro Viciente, while air-drying resulted in a slight increase (10%) of MWD at Maquipucuna (Figure 3-1).

3.4.2 Sample Pretreatment and Soil C in Aggregate Fractions

In the moist pretreatment of sedimentary soils, 54% to 70% of total soil C was stored in the large macroaggregates followed by the fractions <53 µm (11 to 24%), small macroaggregates (9 to 10%) and the microaggregates (3 to 6%; Table 2). In contrast, the outcome of air-drying and slaking was that most total soil C was found in small macroaggregates (40 to 50%), followed by large macroaggregates (29 to 38%), microaggregates (9 to 14%) and the <53 µm fraction which only contributed 3 % to total soil C. Soil C concentration of sand-free aggregates was also influenced by pretreatment: air-drying and slaking caused C concentrations to increase with aggregate size and C concentration were highest (34 to 35 g kg^{-1}) in large macroaggregates. In contrast, wet-sieving of moist soil resulted in highest C concentration in the 53-250 µm fractions.

The partitioning of pasture-derived soil carbon among aggregate fractions was also influenced by soil pretreatment. Highest proportion of pasture-derived carbon of total soil C was found in macroaggregates and decreased with decreasing aggregate size in the air-dried pretreatment. In contrast, the microaggregate class of moist pretreatment showed highest contribution of pasture-derived soil C to total soil C (Figure 3-2). Most of the total pasture-derived carbon was stored in the large macroaggregate class (73 to 57% of total C_4-C) using moist soil, while in the air-dried and slaked pretreatment, highest proportion of the total pasture-derived carbon was found in small (47 to 48% of total C_4-C) and large (38 to 41% of total C_4-C) macroaggregate classes (Table 3-3).

In volcanic ash soils, pretreatment caused only slight differences in the carbon concentrations of different aggregate classes and the partitioning of soil C among aggregate sizes. If differences occurred, they were not consistent comparing the two sites. Air-drying resulted in a higher contribution of small macroaggregates to total soil C storage at Maquipucuna and in a lower contribution of the <53 µm fraction at Pedro Viciente (Table 3-2). Lowest carbon concentrations were found in the fraction <53 µm of the air-dried pretreatment, while the moist pretreatment resulted in no differences between carbon concentrations of aggregate classes at this site (Table 3-2). At Maquipucuna soil C concentration increased with decreasing aggregate size till microaggregate class in the air-dried pretreatment, while a higher C concentration was found in the small macroaggregate class of the moist pretreatment.

Pasture-derived carbon storage was higher in the small microaggregate class and lower in the fraction <53 µm of the air-dried pretreatment compared to the moist pretreatment (Table 3-3). The relative proportions of pasture-derived carbon to total soil C within each fraction were equally distributed between all aggregates classes and independent of pretreatment (Figure 3-2).

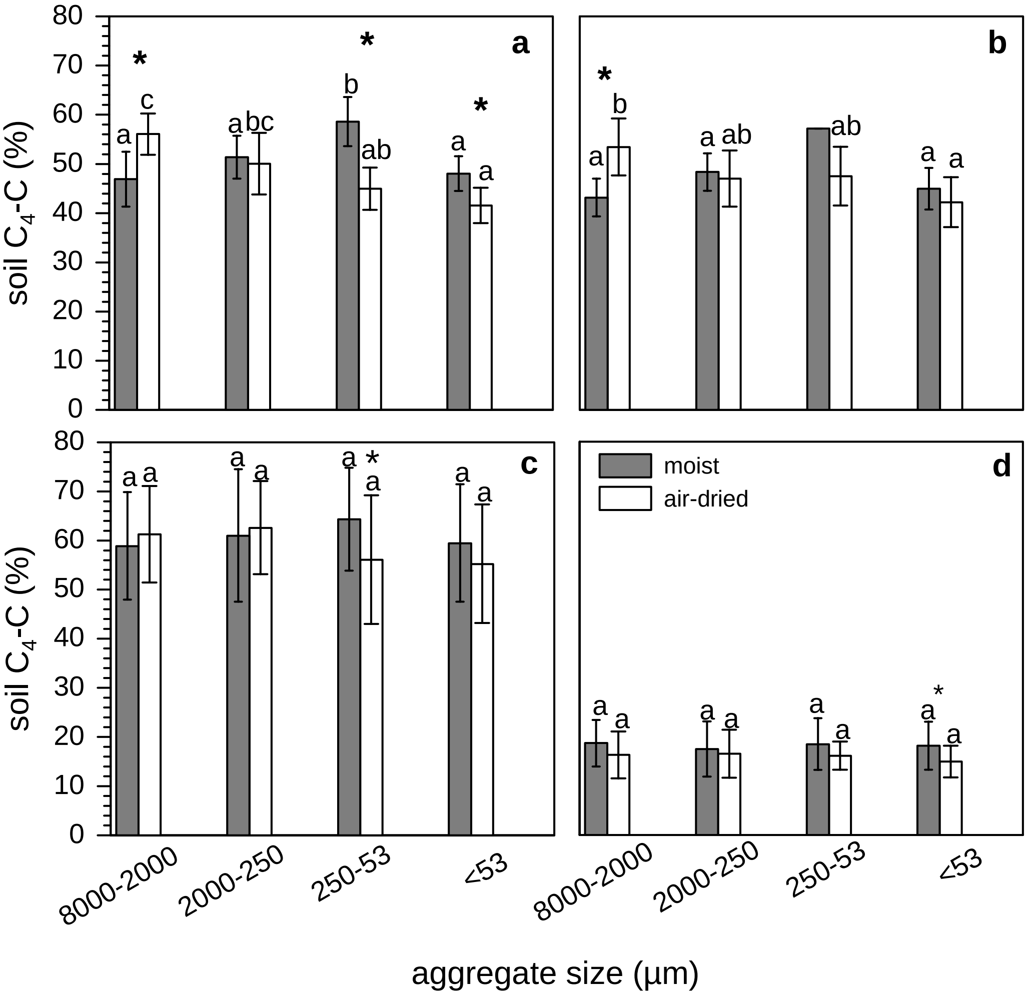

Figure 3-2: Percentage (means n=4, standard deviation) of pasture derived soil organic carbon (soil C_4-C) in aggregate classes produced by wet-sieving of sedimentary soils (a: Tazones, b: Chonta Duro) and volcanic ash soils (c: Maquipucuna, d: Pedro Viciente) using moist soil (without prior drying) and air-dried soil prior to wet-sieving; bars within one aggregate size class followed by * are significantly different between treatments; bars within one treatment followed by a different lowercase letter are significantly different ($p<0.05$). In one case (Chonta Duro, 250-53µm) it was not possible to test significance due to insufficient sample replicates.

Table 3-2: Dry matter yield of aggregate size fraction, relative contribution of soil C stored in aggregate size fraction to total soil C storage of the bulk soil, and soil C concentration in aggregates size fractions of tropical pastures sites using either air-dried soil (air-dried) or moist soil (moist) prior to aggregate fractionation by wet-sieving (means n=4, standard deviation).

		Yield		Soil C			
Sites	Aggregate size	Air-dried	Moist	Air-dried	Moist	Air-dried	Moist
	µm	— % of total dry matter —		— % of total soil C —		— g kg^{-1} sand-free aggregates —	
Sedimentary soils							
Chonta Duro	8000-2000	35 (4)^{b,A†}	74 (4)^{c,B}	38 (7)^{b,A}	70 (8)^{c,B}	34 (7)$^{b, A}$	32 (6)^{ab,A}
	2000-250	51 (4)^{c,B}	10 (2)^{b,A}	50 (7)^{c,B}	10 (2)^{b,A}	30 (4)$^{b, A}$	36 (4)^{b,B}
	250-53	9 (3)^{a,B}	2 (1)^{a,A}	9 (5)^{a,A}	3 (1)^{a,A}	31 (4)^{b}	43 (nd)
	<53	4 (1)^{a,A}	13 (3)^{b,B}	3 (1)^{a,A}	11 (3)^{b,B}	22 (2)^{a,A}	28 (3)^{a,B}
Tazones	8000-2000	26 (3)^{b,A}	60 (2)^{c,B}	29 (2)^{c,A}	54 (6)^{c,B}	35 (6)^{c,A}	30 (5)^{a,A}
	2000-250	42 (2)^{c,B}	11 (3)^{a,A}	40 (2)^{d,B}	9 (3)^{a,A}	35 (1)^{c,B}	29 (5)^{a,A}
	250-53	27 (1)^{b,B}	12 (1)^{a,A}	14 (3)^{b,B}	6 (2)^{a,A}	25 (5)^{b,A}	54 (8)^{b,B}
	<53	4 (1)^{a,A}	16 (1)^{b,B}	3 (0)^{a,A}	24 (3)^{b,B}	18 (1)^{a,A}	29 (1)^{a,B}
Volcanic ash soils							
Pedro Viciente	8000-2000	53 (4)^{d,A}	48 (9)^{c,A}	60 (7)^{d,A}	48 (9)^{c,A}	122 (17)^{b,A}	120 (11)^{a,A}
	2000-250	34 (3)^{c,B}	24 (3)^{b,A}	39 (2)^{c,B}	23 (3)^{b,A}	128 (13)^{b,A}	119 (24)^{a,A}
	250-53	11 (1)^{b,A}	15 (6)^{ab,A}	9 (1)^{b,A}	8 (2)^{a,A}	130 (12)^{b,B}	104 (9)^{a,A}
	<53	2 (0)^{a,A}	12 (6)^{a,B}	3 (1)^{a,A}	17 (10)^{ab,A}	88 (8)$^{a, A}$	105 (14)^{a,A}
Maquipucuna	8000-2000	41 (4)^{c,A}	35 (6)^{c,A}	38 (7)^{b,A}	31 (10)^{b,A}	130 (15)^{b,A}	138 (15)^{ab,A}
	2000-250	43 (2)^{c,B}	36 (2)^{c,A}	39 (15)^{b,A}	24 (10)^{a,A}	152 (21)^{bc,A}	161 (48)^{b,A}
	250-53	13 (3)^{b,A}	19 (5)^{b,A}	11 (1)^{a,A}	16 (4)^{a,A}	177 (33)^{c,B}	133 (34)^{ab,A}
	<53	2 (1)^{a,A}	10 (3)^{a,B}	3 (1)^{a,A}	23 (10)^{ab,B}	74 (9)$^{a A}$	112 (6)^{a,B}

† Values within one aggregate size class followed by different upper case letter are different, values within one treatment and site followed by a different lowercase letter are different ($p<0.05$), nd= not determined as sub-samples were pooled due to insufficient samples size

Table 3-3: Partitioning of pasture-derived carbon (soil C_4-C) and forest-derived carbon (soil C_3-C) of aggregates size fractions of tropical pastures sites using either air-dried soil (air-dried) or moist soil (moist) prior to aggregate fractionation by wet-sieving (means n=4, standard deviation).

		Soil C_4-C		Soil C_3-C	
Sites	Aggregate size	Air-dried	Moist	Air-dried	Moist
	µm	g kg^{-1} soil			
Sedimentary soils					
Chonta Duro	8000-2000	6.0 (1.3)^{b,A†}	10.2 (3.3)^{b,A}	5.1 (0.3)^{b,A}	13.1 (2.1)^{b,B}
	2000-250	7.1 (1.9)^{b,B}	1.7 (0.5)^{a,A}	7.8 (0.8)^{c,B}	1.8 (0.4)^{a,A}
	250-53	1.2 (0.7)^{a,A}	0.5 (0.1)^{a,A}	1.3 (0.5)^{a,B}	0.4 (0.1)^{a,A}
	<53	0.4 (0.2)^{a,A}	1.6 (0.3)^{a,B}	0.5 (0.2)^{a,A}	1.9 (0.4)^{a,B}
Tazones	8000-2000	3.3 (0.5)^{c,A}	5.2 (1.4)^{c,B}	2.5 (0.1)^{c,A}	5.8 (0.3)^{d,B}
	2000-250	4.0 (0.8)^{d,A}	0.9 (0.2)^{a,B}	4.0 (0.4)^{d,B}	0.9 (0.2)^{b,A}
	250-53	1.3 (0.3)^{b,A}	0.7 (0.2)^{a,A}	1.6 (0.2)^{b,B}	0.5 (0.1)^{a,A}
	<53	0.3 (0.1)^{a,A}	2.3 (0.2)^{b,B}	0.4 (0.1)^{a,A}	2.5 (0.3)^{c,B}
Volcanic ash soils					
Pedro Viciente	8000-2000	6.7 (2.6)^{b,A}	6.9 (3.5)^{b,A}	33.7 (6.2)^{c,A}	28.4 (5.4)^{c,A}
	2000-250	4.3 (1.7)^{b,B}	3.1 (1.5)^{a,A}	21.5 (2.2)^{b,B}	14.0 (2.3)^{b,A}
	250-53	1.0 (0.3)^{a,A}	1.0 (0.4)^{a,A}	5.0 (0.6)^{a,A}	4.6 (1.6)^{a,A}
	<53	0.3 (0.0)^{a,A}	2.1 (1.1)^{a,B}	1.7 (0.4)^{a,A}	10.7 (7.2)^{ab,A}
Maquipucuna	8000-2000	15.8 (3.8)^{b,A}	15.3 (6.2)^{b,A}	9.9 (3.2)^{b,A}	9.9 (1.7)^{c,A}
	2000-250	17.0 (8.3)^{b,B}	10.7 (5.9)$^{ab;A}$	9.2 (1.4)^{b,B}	5.9 (1.8)^{b,A}
	250-53	4.4 (1.1)^{a,A}	5.6 (2.4)^{a,A}	3.4 (1.1)^{a,A}	2.8 (0.3)^{a,A}
	<53	1.0 (0.4)^{a,A}	7.7 (2.0)^{ab,B}	0.9 (0.5)^{a,A}	5.4 (2.6)^{ab,A}

† Values within one aggregate size class followed by different upper case letter are different, values within one treatment and site followed by a different lowercase letter are different ($p<0.05$)

3.5 Discussion

3.5.1 Sample Pretreatment and Aggregate Size Distribution

3.5.1.1 Sedimentary Soils

Published studies that report differences in aggregate-size distribution of air-dried slaked and rewetted non-slaked soil samples from temperate climate soils agree with our observation that air-drying and slaking reduces the amount of macroaggregates and decreases MWD compared to moist pretreatment of sedimentary soils (Puget et al., 1995; Six et al., 2000a; Denef et al., 2002). Generally, in these studies the non-slaked treatments were achieved by rewetting air-dried soil. A comparable decrease in the MWD of 42% to 65% was found by Six et al. (2000a) in temperate grassland soils. The use of moist or rewetted soil probably reduces the stress on aggregates as the pores are already partly filled with water and consequently also less stable macroaggregates survive the procedure thereby increasing the MWD (Kemper and Rosenau, 1986).

The use of field-moist soil samples in our study resulted in a <53 µm fraction that was about 3 to 4 times higher than in the air-dried and slaked treatment. Comparable results have also been documented by others who compared the use of field-moist and air-dried soils from temperate areas (Haynes, 1993; Beare and Bruce, 1993). Rewetting of air-dried soil before aggregate fractionation did not result in an increase in the fraction <53 µm (Beare and Bruce, 1993; Six et al., 2000b). More specific, Beare and Bruce (1993) analysed the effect of rewetting by comparing the distribution of water-stable aggregates of air-dried, capillary wetted and field-moist, capillary wetted soil. Differences in the size distribution of macroaggregates were negligible, while a higher proportion of soil was recovered in the <53 µm fraction of the field-moist than in the rewetted soil treatment. Precipitation of bonding agents and an increase in the solid phase cohesion of aggregated particles was proposed to increase aggregate stability of air-dried soil (Kemper and Rosenau, 1984). These additional intermolecular associations might be formed between organic macromolecules such as polysaccharides and mineral surfaces and might persist after rewetting and reduce dispersion and the release of particles <53 µm from the surface of aggregates (Haynes and Swift, 1990; Haynes, 1993). These processes may also explain the observed higher proportion of fraction <53µm recovered in the air-dried pretreatment compared to the moist pretreatment in the sedimentary soils.

3.5.1.2 Volcanic Ash Soils

In the volcanic ash soils, differences in aggregate size distribution among air-dried and moist pretreatment were minimal, which contrasts with other soil types that have 2:1 and 1:1 clay minerals (Six et al., 2000b; Denef et al., 2002). Moreover, rapid immersion in water of air-dried volcanic ash soils did not lead to a slaking process. Air-drying of soil resulted in a higher yield in macroaggregates compared to the moist soil pretreatment, a result that was also reported for allophanic soils from New Zealand (Churchman and Tate, 1987). Higher MWD of air-dried pretreatment may be a result of irreversible flocculation which occurs upon drying (Wells and Theng, 1988). Thus, it is not possible to define stable and unstable aggregates using this method in volcanic ash soils.

3.5.2 Sample Pretreatment and Soil C in Aggregate Fractions

3.5.2.1 Sedimentary Soils

The correlation of aggregate size with carbon concentration in sand-free aggregates and proportion of recently incorporated soil C in air-dried and slaked soils can be explained by the stabilising effect of fresh organic matter on macroaggregates (e.g. Jastrow et al., 1996; Six et al., 2002). However, our finding that in the moist pretreatment of smectitic clay soils microaggregates have a higher carbon concentration than macroaggregates contrasts with other studies where no differences in soil C concentration of rewetted or misted aggregate sizes were found (Elliot, 1986; Cambardella and Elliott, 1993; Six et al., 2000b). Other studies that reported the highest carbon concentration in the non-slaked (soil was rewetted before sieving) microaggregate class were done in soils with mixed-clay mineralogy (2:1 and 1:1 clays; Six et al., 2000b) or soils with 1:1 clays (Beare et al., 1994). This led Six et al. (2000b) to conclude that the carbon enrichment in non-slaked microaggregate was specific for soils containing 1:1 clays. Our results show that this effect can also be found in smectitic dominated soils by using moist soil.

Our finding that the use of moist soil resulted in microaggregates in which higher carbon concentration correlated with higher contribution of new carbon, while wet-sieving of air-dried soil separated macroaggregates enriched in carbon and higher proportion of new soil C has been also reported for arable soils (Gale et al., 2000). However, differences in the relative increase of recently incorporated carbon in stable macroaggregates were higher (89% to 27%) than in our tropical pastures (19% to 23%; Puget et al., 1995).

The observed results suggest that during slaking of air-dried soil unstable macroaggregates not enriched in carbon disintegrate into smaller particles and are therefore recovered in the microaggregate class. Consequently, the microaggregate class of the air-dried and slaked treatment contain both stable microaggregates and also parts of the broken macroaggregates. In contrast, the moist pretreatment resulted in fewer broken macroaggregates recovered in the microaggregate fraction. Both the soil C content and ^{13}C signal of the microaggregates in the moist pretreatment show that these microaggregates contain a higher proportion of pasture-derived carbon, which is characteristic for newly formed microaggregates. These results support the notion that the initial formation of microaggregates is caused by encapsulation of fresh plant residues (Oades, 1984; Oades and Waters, 1991), and that these newly formed aggregates should have higher carbon concentrations and proportions of recently incorporated carbon. In the air-dried pretreatment the simultaneous of carbon concentration and proportions of recently incorporated carbon with aggregate size supported the concept of aggregate hierarchy.

3.5.2.2 Volcanic Ash Soils

In contrast to sedimentary soils, pretreatment caused no systematic changes in carbon concentration of macro- and microaggregates. In agreement with our results, no aggregate hierarchy was expressed by wet-sieving of air-dried volcanic ash soils (Huygens et al., 2005; Hoyos and Comerford, 2005). In addition, soil pretreatment caused only slight differences in C_4 proportions, which is in contrast to the sedimentary soils. As none of the previously applied aggregate fractionation methods found a relationship between aggregate size and soil C concentration and proportion of pasture-derived carbon, other binding agents such as metal-humus complexes and electrostatic forces dominate the aggregate stability in these soils (Nanzyo et al., 1993; Huygens et al., 2005). In addition, the even distribution of pasture-derived carbon among aggregate size classes may indicate that disaggregation and reformation of aggregates is a relatively rapid process under field conditions.

3.6 Conclusions

Our results demonstrated that in smectitic clay soils both soil sample pretreatments resulted in distinct aggregate fractions with different soil C content and proportion of recently incorporated soil C. Wet-sieving of air-dried soil provided information of the stabilising effect of fresh organic matter on macroaggregates. In contrast, wet-sieving of moist soil separated a microaggregate fraction that was characterized by a high proportion of microaggregates in an early stage of aggregate formation and less broken parts of unstable macroaggregates. In volcanic ash soils none of the pretreatments was able to separate aggregate size fractions with a distinct carbon concentration and proportions of pasture-derived carbon illustrating that aggregates in these soils are not predominantly stabilized by soil organic matter.

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4 Soil C in Bulk Soil and in Aggregate Size Fractions[*]

4.1 Abstract

Quantitative knowledge of stabilization- and decomposition processes is necessary to understand, assess and predict effects of land use changes on storage and stability of soil organic carbon (soil C) in the tropics. Although it is well documented that different soil types have different soil C stocks, it is presently unknown how different soil types affect the stability of recently formed soil C. Here, we analyze the main controls of soil C storage in the top 0.1m of soils developed on Tertiary sediments and soils developed on volcanic ashes. Using a combination of fractionation techniques with ^{13}C isotopes analyses we had the opportunity to trace origin and stability of soil carbon in different aggregate fractions under pasture and secondary forest. Soil C contents were higher in volcanic ash soils (47 to 130 g kg^{-1}) than in sedimentary soils (19 to 50 g kg^{-1}). Mean residence time of forest-derived carbon in pastures increased from 37 to 57 years with increasing silt+clay content in sedimentary soils, but was independent from soil properties in volcanic ash soils. Mean residence times of pasture-derived carbon in secondary forests were considerably shorter, especially in volcanic ash soils, where no pasture-derived carbon could be detected in any of the four studied secondary forests. The implications of these results are that the mean residence time of recently incorporated organic carbon depends on clay mineralogy and is longer in soils dominated by smectite than non-crystalline minerals. Our results show that the presence of soil C stabilization processes, does not necessarily mean that recent incorporated soil C will also be effectively stabilized.

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[*] Stabilization of Recent Soil Carbon in the Humid Tropics following Land Use Changes: Evidence from Aggregate Fractionation and Stable Isotope Analyses. Paul, S., Veldkamp, E., Flessa, H., Lopez-Ulloa, M. Biogeochemistry (DOI: 10.1007/s10533-008-9182-y)

4.2 Introduction

Globally, soils contain about 75% of the terrestrial organic carbon pool (Post et al., 1982). About 1500 Gt of organic carbon are stored in the top meter of soils, of which 32% are located in tropical soils (Jobbagy & Jackson, 2000). Presently, about one fourth of anthropogenic CO_2 emissions are attributed to deforestation in the tropics (Denman et al., 2007). Although these CO_2 emissions are mainly caused by the loss of above ground carbon stocks, mineralization of soil organic matter also contributes significantly (Detweiler, 1986). Conversion of tropical forests and pastures to cropland typically decreases soil organic carbon (soil C) stocks by 40 to 60% (van Noordwijk et al., 1997; Guo & Gifford, 2002) with coarse textured soils being more susceptible to soil C losses than soils with finer textures (Zinn et al., 2005). In contrast, conversion of forests to pastures can result in both gains and losses of soil C, depending on soil properties, climate, and pasture management (Detweiler, 1986; Lugo & Brown, 1993; Powers & Veldkamp, 2005). Forest regrowth on former pastures was found to be associated either with increases or decreases in soil carbon stocks depending on land use history and soil properties (de Koning et al., 2003).

Quantitative knowledge of stabilization and decomposition processes of organic matter in different soils is necessary in order to understand, assess and predict effects of land use changes on the storage and stability of soil C. Several mechanisms can contribute to stabilization of carbon in soils, which can be broadly divided into three groups: recalcitrance, interactions and accessibility (Sollins et al., 1996; von Lützow et al., 2006). Aggregation reduces accessibility of microbial biomass to substrate and thus contributes to the physical protection of soil C (Sollins et al., 1996). In 1982, Tisdall and Oades formulated the hypothesis that stable microaggregates (<250 µm) are bound together to larger units (macroaggregates) by labile organic material. This concept, which they called “soil aggregate hierarchy”, was supported by subsequent studies which showed that macroaggregates had higher carbon contents, contained less decomposed organic material, and had faster soil C turnover compared to microaggregates (Six et al., 2002; John et al., 2005). However, the concept of aggregate hierarchy, that relies on organic matter as main binding agent, may not be suitable for heavily weathered tropical soils with 1:1 clays nor for volcanic ash soils, as in these soils, rich in iron and aluminium oxides, formation of aggregates by mineral–mineral bindings is more important (Oades and Waters, 1991; Hoyos and Comerford, 2005, Schwendenmann and Pendall, 2006).

Changes in $\delta^{13}C$ of soil C following conversion from tropical forests to grassland or cropland have been used widely to determine soil C stability in tropical soils (e.g. Veldkamp, 1994; Desjardins et al., 1994). A review of available data on soil C turnover times calculated from C_3/C_4 vegetation changes showed that the mean soil C turnover time was considerably shorter for tropical soils (36 years) than for temperate soils (63 years; Six et al., 2002). The higher turnover in tropical soils was related to faster decomposition rates due to high temperatures in connection with high precipitation in the tropics. However, the review also revealed a substantial overlap in estimated turnover times (13-108 years for tropical soils versus 14-141 years for temperate soils; Six et al., 2002), indicating no simple relationship between climate and organic matter stabilization. In addition to climatic conditions, soil C turnover may vary considerably depending on soil mineralogy and related chemical and physical interactions of soil C with mineral soil particles (Torn et al., 1997), which may differ in tropical and temperate soils. It was found that soil C associated with smectite had considerably longer mean residence time than soil C associated with kaolinite (Wattelkoek et al.; 2003). Current knowledge is very limited how soil properties influence soil C turnover rates (Desjardins et al., 2004). Even less is know about the differences in stabilization processes of recently incorporated carbon compared to older carbon in different soil types.

In the humid tropics of Northwest Ecuador, both forest clearing for pasture and pasture abandonment followed by forest regrowth have occurred during the past few decades. In this area, de Koning et al. (2003) analyzed the potential to increase soil C stocks after forest regrowth on abandoned pastures. Forest regrowth led to a yearly increase of soil C stocks in the upper 50 cm of about 1.4 Mg C ha^{-1} yr^{83} if the secondary forest had at least 20 years to grow (de Koning et al., 2003). In a correlative study on a selection of these sites, long-term stabilization of soil C in volcanic ash soils was associated with the formation of metal-humus complexes and allophanes, whereas in soils with smectitic clay minerals soil C was stabilized primarily through sorption to clay (López-Ulloa et al., 2005). In the present study, our objectives were: í) to determine how important aggregation is for the stabilization of soil C in the topsoil of different soil types in natural forests, pastures and secondary forests of the humid tropics of Ecuador and ii) to determine the stability of forest-derived soil C in pastures and of pasture-derived soil C in secondary forests in different aggregate fractions.

4.3 Material & Methods

4.3.1 Site description

We selected a subset of eight sites used by de Koning et al., (2003) and López-Ulloa et al., (2005). In addition to the sites which consisted of paired secondary forest (or tree plantation) and pasture we selected an additional natural forest site with similar overall environmental characteristics of pasture and secondary forest plots as close as possible. In most cases, the natural forests plots (nf) were well protected and showed no evidence of human activity. However, in a few cases (Chonta Duro), individual trees had been extracted in the past from the natural forest plot. Pasture plots had been established after cutting and burning natural forest. Pastures (ps) were dominated by C_4 grasses (*Papsalum dilatatum* Poir., *Panicum maximum* Jaqc., *Cynodon plectostachyus* (K. Schum.) Pilger). Secondary forests formed on abandoned pastures due to natural succession without management, whereas the plantations were established on former pastures by planting trees. As there were no differences in soil C contents between secondary forests and plantations (de Koning et al., 2003), these sites were grouped and analyzed together (we call these sites 'secondary forest' (sf)).

Our sites were located in the Northwest of Ecuador (Table 4-1). Four sites had soils developed in volcanic ashes and differed in silt+clay content and were classified as Hapludands. The mineralogy was characterized by the presence of allophane (de Koning et al., 2003). Soils of the other four sites were developed in marine Tertiary sediments and covered a gradient in clay content. These soils were classified as Haplustepts and Paleudalfs (Soil Survey Staff, 1998). X-ray diffraction of clay fraction of sedimentary soils revealed that sedimentary soils were dominated by smectite with only marginal contribution of illite, chlorite, and kaolinite. In the following, soils developed in marine Tertiary sediments we call 'sedimentary soils' and soils developed in volcanic ashes 'volcanic ash soils'.

At all sites, we combined fractionation of water-stable aggregates with ^{13}C isotope analyses, which gave us the opportunity to trace origin and stability of soil C pools in different aggregate fractions and to calculate mean apparent residence times of soil C under different land use types in the humid tropics of northwest Ecuador. At each plot, we sampled and described one soil profile and we selected four additional sampling points along a 50 m transect. At each sampling point fine root samples were taken using a root corer. We only sampled the upper 0.1m since we expected that effects of land use changes on soil aggregation and soil C stocks of different origin and stability are most pronounced in the top soil (Desjardins et al., 1994; Bashkin and Binkley, 1998). History of land use and site management was obtained by interviewing current and former landowners (Table 4-1).

4.3.2 General Soil and Vegetation Analyses

For all individual sampling points of sedimentary soils particle size distribution was analyzed using sieving and the pipette method with sodiumpyrophosphate as a dispersing agent (Köning & Fortmann, 1996). As the determination of clay content for the volcanic ash soils reveals ambiguous results due to incomplete dispersion (Nanzyo et al., 1993), we did not determine the clay content of these volcanic ash soils. The silt+clay content was determined by difference from sand. Bulk soil density was determined gravimetrically at each sampling point from undisturbed soil cores (300 cm^3) after drying at 105°C. Soil pH_{H_2O} and effective cation exchange capacity (ECEC) were determined using composite samples from the A horizon of the soil profiles. ECEC was determined by leaching soil samples with 100 ml of unbuffered 1M ammonium chloride (NH_4Cl) for 4–5 h. Cations in extracts were quantified by atomic absorption spectroscopy (König & Fortmann, 1996). Total C and N were measured with an automated C and N analyzer (Elementaranalysator CNS, Vario EL, Elementar, Hanau, Germany) after milling the samples.

All soil samples were characterized using selective dissolution techniques. Selective dissolution was done using acid ammonium-oxalate extraction of aluminium (Al_o) and iron (Fe_o); dithionite-citrate extraction of iron (Fe_d) and pyrophosphate extraction of aluminum (Al_p) (Buurmann et al., 1996). Fe and Al concentrations in these extracts were measured by inductively coupled plasma emission spectroscopy (Flame-ICP, Spectro Analytical Instruments, Kleve, Germany). Acid ammonium-oxalate extracts Al in allophane and imogolite; Al and Fe in organic complexes and Fe and Al in non-crystalline hydrous oxides (Wada, 1989). Dithionite-citrate solution extracts Al and Fe in organic complexes; Al from non-crystalline hydrous oxides and Fe from crystalline and non-crystalline hydrous oxides. Finally, pyrophosphate extracts Al and Fe from organic complexes only (Wada, 1989). The ratio of Alp/Alo indicates the proportion of Al humus complexes versus allophane content. Soils dominated by humus complexes are characterized by a ratio near 1, while soils dominated by allophane have ratios < 0.5 (allophanic soils; Nanzyo et al., 1993). The difference between Al_o and Al_p gives a measure of non-crystalline compounds.

Samples of fine roots (down to 0.1m depth) were dried at 60°C, weighed, milled and analyzed for total carbon and nitrogen contents by an automated C and N analyzer (Heraeus Elementar Vario EL, Hanau, Germany).

4.3.3 Fractionation of Water-Stable Aggregates

Fractionation of water-stable aggregates was modified from the method described by Elliott (1986). The main difference with his method was that we used moist soil, which was adjusted to 70% of its maximum water holding capacity. We did not use air-dried soil samples for aggregate fractionation because volcanic ash soils display irreversible flocculation and changes in aggregate distribution upon drying (Wells & Theng, 1988). Other studies that did aggregate fractionations in volcanic ash soils also used moist soil samples (Churchman & Tate, 1986; Parfitt et al., 2002). For a comparison of the effect of aggregate fractionation on dry versus moist soil samples, see chapter 3.

Soil samples were first gently broken by hand and passed through a 8000 μm sieve. This sample (equivalent to 100 g dry soil) was submersed in distilled water for 5 minutes on top of a 2000 μm sieve and the sieve was manually moved 3 cm up and down, 50 times within 2 minutes. Aggregates of 8000-2000 μm were collected and sieving was repeated with sieves of 250 μm and 53 μm. The fraction <53 μm was precipitated using a 1M $CaCl_2$ solution and the supernatant was discarded. All fractions were oven-dried at 40°C. Roots were hand-picked and samples were milled using a ball mill. At one site (pasture of Minas) we found carbonates in the C horizons. Therefore, aggregate fractions of the site Minas were leached with liquid HCl (10%) prior to analyses. Sand content was determined in sub-samples of all aggregate classes >53 μm and organic carbon content of aggregates was expressed as soil C in sand-free aggregates (Elliott et al. 1991). Mean Weight Diameter (MWD) of water-stable aggregates was calculated as: MWD = Σ (Weight % sample on sieve ×

mean inter-sieve size/100), where the upper limit was 8000 µm (Kemper and Rosenau, 1986).

Table 4-1: Location, general site characteristics and land use history.

Site	Latitude N (°)	Longtude W (°)	Elevation (m)	Precipitation (mm yr^{-1})	Temperature (°C)	Age of current pasture[a] (yr)	Age of secondary forest[b] (yr)	Age of former pasture[c] (yr)
Sedimentary soils								
Tazones	00°43.24	079°50.09	95	1800	26	35	14	21
Penas	01°04.37	079°08.09	45	2500	27	30	10	20
Chonta Duro	00°55.26	079°25.30	30	1800	27	35	17	20
Minas	00°51.86	079°34.24	191	1300	27	33	10	20
Volcanic ash soils								
Mindo	00°01.45	078°46.16	1665	3500	18	20	23	5
Maquipucuna	00°07.21	078°37.55	1359	2300	19	50	20	30
PedroViciente	00°05.65	079°01.51	690	4900	22	13	15	8
Pitzara	00°16.22	079°09.74	294	3500	23	20	10	10

[a] pastures were established after clearing of natural forest
[b] secondary forests were established on former pastures
[c] duration of pasture before the site was changed to secondary forest.

4.3.4 Isotope Analyses

The $^{13}C/^{12}C$ isotope ratio was measured using an isotope ratio mass spectrometer (IRMS, Finnigan MAT, DELTA^{plus}, Bremen, Germany) at the Center for Stable Isotopes Research and Analysis, University of Göttingen. The C isotope ratios are expressed as $\delta^{13}C$‰ (V-PDB). Standard deviation of measurements was less than 0.1‰. The proportion of soil C derived from pasture vegetation (= soil C_4-C) was calculated according to Balesdent & Mariotti (1996):

$$f = (\delta_{sam} - \delta_{ref}) / (\delta_{pasture} - \delta_{forest}) \qquad (4\text{-}1)$$

where f is the proportion of pasture-derived C in the sample, δ_{sam} is the measured $\delta^{13}C$ value of the topsoil sample, δ_{ref} is the $\delta^{13}C$ value of the corresponding sample from the natural forest as C_3 reference soil, and $\delta_{pasture}$ and δ_{forest} are the $\delta^{13}C$ values of fine roots collected from the topsoil of the pastures and forests, respectively. The standard deviation S_f of the pasture-derived proportions was calculated from the standard deviations of δ_{ref}; δ_{sam}; $\delta_{pasture}$; and δ_{forest} using a first-order Taylor series approximation.

4.3.5 Calculation of Mean Residence Time of Soil C

The mean apparent residence time of forest-derived soil C was calculated from the decrease of the proportion of soil C derived from forest (= soil C_3-C) in pasture under the assumptions that soil C fractions are homogeneous and that decomposition can be described with a single pool model. Describing soil C decomposition with a single pool model is a rough simplification (Davidson and Janssens, 2006). Studies of chronosequences with different land use ages show that soil C pools of different stability exist (Veldkamp, 1994; Feigl et al., 1995) which is also reflected in most soil C models which assume the existence of several soil C pools with different turnover times. Nevertheless, the single pool approach can be useful to obtain a first impression of soil C stability. The mean residence time (MRT) is an inverse function of the turnover rate k (1 years^{-1}) and defined as:

$$\mathrm{MRT} = 1 / k = -(t - t_0) / \ln(C_t / C_{t0}), \qquad (4\text{-}2)$$

where k = rate constant of first-order decay, t = year of sampling (in our case 2004), t0 = the year of vegetation change (conversion from natural forest to pasture), C_t = soil C_3-C (g kg^{-1}, corrected for the sand content of the sample) in the pasture soil at time of sampling, and C_{t0} = initial soil C_3-C (g kg^{-1}; corrected for the sand content of the sample) at t_0 in the soil of the natural forest. We calculated sand-free soil C concentrations because the sand content of some of our experimental plots (natural forest, pasture, secondary forest) within the same site differed slightly (Table 4-2). The sand-free soil C concentration was calculated:

$$\text{Soil C (g kg}^{-1}\text{ sand free soil)} = \text{Soil C (g kg}^{-1}\text{) } 1000 / (1000 - \text{Sand (g kg}^{-1}\text{)}), \qquad (4\text{-}3)$$

where soil C is the soil organic carbon concentration (g kg^{-1}) and Sand is the sand concentration (g kg^{-1}).

We also calculated mean apparent residence times for C_4-derived soil C found in secondary forest soils. This soil C pool was built up under the former pasture. In this case also equation 4-2 was used with the following variables: C_t = soil C_4-C (g kg^{-1} corrected for the sand content of the sample) in the secondary forest soil at the time of sampling, C_{t0} = soil C_4-C (g kg^{-1} corrected for the sand content of the sample) in the pasture soil before the secondary forest was established, t = duration of the former pasture period (Table 4-1) and the observed accumulation of soil C_4-C in the existing pasture plot:

$$C_{t0} = C_{tps} - C_{tnf}\, e^{(-k \cdot t)}, \qquad (4\text{-}4)$$

where C_{tps} = carbon concentration in the pasture soil at the time of vegetation change (it is assumed that C_{tps} was the same as the measured soil C concentration in the existing pasture soil and that the term $C_{tnf}\, e^{(-k\, t)}$ that is remaining concentration of soil C_3-C in the former pasture at the time of pasture abandonment), C_{tnf} = carbon concentration in the natural forest soil, t is the duration of the former pasture period, k is the decay constant of the soil C_3-C pool in the existing pasture.

4.3.6 Statistical Analyses

At each site and land use, four soil samples (replicates) were taken at equal distances along a 50m transect. As is typically the case with soil C, normal distribution was assumed. Analyses were carried out using ANOVA; multiple comparisons of dry matter yield, soil C, C/N ratio, bulk density among land use types and soil types were conducted using Tukey's posthoc test. Multiple comparison of pasture-derived carbon was analyzed among sites and clay content, and MRT of sedimentary soils was analyzed among sites and land use. Pearson correlation was used to assess the relationships of soil C with MWD, silt+clay content, Al_p, Al_o, Fe_o, Al_o+0.5 Fe_o, Al_o-Al_p and Al_p/Al_o. Multiple regression with stepwise variable selection was used to relate MWD to clay+silt content and to soil C content. All statistical analyses were carried out using the STATISTICA 6.1 software package (StatSoft Inc., Tulsa, Oklahoma, USA).

4.4 Results

4.4.1 Soil Organic Matter Influenced by Soil Type and Land Use

Soil C concentrations in volcanic ash soils were 1.5 to 3 times higher than in sedimentary soils ($P< 0.001$; Table 4-2). In both soil types, soil C content increased with increasing silt+clay content ($P<0.001$; Figure 4-1a). However, the amount of C stored per unit silt+clay was about four times higher in volcanic ash soils than in sedimentary soils ($P<0.001$). In volcanic ash soils, soil C concentrations were positively correlated with the contents of silt+clay ($r = 0.88$; $P < 0.001$), Al_p ($r = 0.83$; $P < 0.001$), Al_o ($r = 0.66$; $P < 0.001$) Fe_o ($r = 0.58$; $P < 0.001$), and with Al_o+0.5 Fe_o ($r = 0.67$; $P < 0.001$), and Al_o-Al_p ($r = 0.50$; $P < 0.001$). Natural forest soils showed higher carbon storage than pasture soils ($P< 0.01$). This effect was more pronounced at sites with high Al_p content (>6 g kg^{-1}; Pedro Viciente and Pitzara). The C/N ratio of volcanic soils was influenced by the type of land use with pastures having a lower C/N (12.6 ±1.2) than primary forests (14.4±1.3; $P<0.01$). In sedimentary soils, carbon content was higher in natural forest soils (36.4±11.0 g kg^{-1}) than in pastures (29.1 ±11.0; $P<0.01$). The mean C/N ratio of the sedimentary soils was 9.9 (±1.0) and independent of land use. Soil C was positively correlated with Al_o ($r = 0.83$; $P < 0.001$) and with Al_o+0.5 Fe_o ($r = 0.50$; $P < 0.001$), and Al_o-Al_p ($r = 0.55$; $P < 0.001$) under all land uses. In the pasture soils, soil C correlated with Al_p ($r = 0.55$; $P < 0.05$) and Fe_o ($r = 0.56$; $P < 0.05$).

Table 4-2: Soil organic carbon (soil C), total nitrogen (N_t), soil bulk density (BD), cation exchange capacity (CEC), pH, clay and sand content, Aluminium extracted by pyrophosphate (Al_p) and acid-oxalate (Al_o), Iron extracted by acid-oxalate (Fe_o) and dithionite (Fe_d) of the different sites . nf =natural forest, ps = pasture, sf = secondary forest.

Site	Land use	Soil C		N_t		BD		CEC[a]	pH[a]	Clay		Sand		Al_p		Al_o		Fe_o		Fe_d	
		(g kg^{-1})				(g cm^{-3})		($cmol_c$ kg^{-1})		(g kg^{-1})											
Sedimentary soils																					
Tazones	nf	30.8	(6.4)	3.3	(0.5)	0.96	(0.14)	35	7.1	287	(45)	269	(64)	0.2	(0.0)	1.3	(0.1)	1.0	(0.1)	2.9	(1.0)
	ps	20.2	(1.7)	2.1	(0.2)	1.30	(0.06)	25	6.2	324	(54)	377	(29)	0.3	(0.1)	0.8	(0.0)	2.5	(0.4)	5.4	(0.3)
	sf	21.7	(7.2)	2.4	(0.6)	1.19	(0.12)	25	6.5	360	(79)	266	(86)	0.2	(0.1)	0.9	(0.1)	1.9	(0.2)	5.5	(1.5)
Penas	nf	28.7	(7.0)	3.0	(0.6)	1.00	(0.12)	27	6.0	369	(30)	190	(51)	0.2	(0.1)	1.1	(0.1)	1.9	(0.1)	6.8	(2.7)
	ps	19.3	(4.2)	2.0	(0.4)	1.44	(0.10)	27	6.4	293	(35)	340	(32)	0.3	(0.2)	0.5	(0.0)	1.7	(0.3)	2.7	(0.2)
	sf	34.4	(3.2)	3.6	(0.3)	0.93	(0.09)	47	5.6	532	(26)	40	(9)	0.5	(0.2)	1.6	(0.1)	3.2	(0.5)	10.9	(1.3)
Chonta Duro	nf	35.1	(10.9)	3.4	(0.7)	0.89	(0.07)	46	6.0	592	(30)	37	(3)	0.3	(0.1)	1.4	(0.1)	3.7	(0.5)	10.5	(1.5)
	ps	33.0	(3.8)	3.4	(0.4)	0.93	(0.07)	nd	5.7	607	(58)	27	(1)	1.1	(0.9)	1.3	(0.3)	4.7	(0.6)	6.5	(0.9)
	sf	30.4	(5.4)	3.3	(0.3)	0.96	(0.05)	45	5.8	603	(17)	35	(2)	0.5	(0.3)	1.1	(0.1)	3.1	(0.5)	7.5	(0.8)
Minas	nf	49.6	(2.9)	4.4	(0.1)	0.69	(0.11)	48	6.9	622	(33)	33	(5)	0.3	(0.1)	1.5	(0.1)	2.8	(0.4)	11.1	(0.9)
	ps	44.0	(3.2)	4.4	(0.2)	0.85	(0.02)	47	7.4	619	(37)	39	(17)	0.6	(0.4)	1.6	(0.1)	3.5	(0.7)	7.7	(2.0)
	pf	48.2	(4.5)	4.3	(0.2)	0.79	(0.03)	61	6.9	639	(22)	17	(6)	0.5	(0.2)	1.6	(0.1)	1.5	(0.3)	5.4	(1.1)
Volcanic ash soils																					
Mindo	nf	62.3	(12.5)	4.5	(0.8)	0.57	(0.12)	7.6	5.1	nd[b]		655	(38)	4.9	(0.9)	5.5	(1.0)	3.6	(0.7)	3.8	(0.8)
	ps	60.5	(16.3)	5.0	(1.7)	0.81	(0.07)	5.9	5.0	nd		624	(61)	3.3	(0.5)	4.4	(0.7)	3.8	(0.6)	4.9	(1.3)
	sf	59.0	(4.7)	4.2	(0.5)	0.63	(0.13)	6.7	5.0	nd		664	(30)	4.3	(0.4)	5.0	(0.4)	4.2	(1.7)	4.7	(2.0)
Maquipucuna	nf	60.9	(12.5)	4.2	(0.5)	0.64	(0.10)	9.7	5.3	nd		597	(32)	4.7	(0.6)	8.2	(0.4)	4.5	(0.6)	5.6	(0.2)
	ps	63.3	(11.2)	5.0	(1.0)	0.62	(0.06)	6.9	5.4	nd		560	(134)	4.4	(0.5)	7.3	(0.9)	5.4	(1.0)	6.1	(0.9)
	sf	46.5	(10.0)	3.7	(0.8)	0.78	(0.10)	7.1	5.3	nd		622	(47)	4.4	(0.3)	8.3	(1.1)	5.1	(0.4)	5.4	(0.7)
PedroViciente	nf	114.7	(5.9)	7.5	(0.3)	0.46	(0.04)	6.0	4.7	nd		323	(26)	7.3	(0.4)	10.1	(1.3)	5.9	(0.9)	6.6	(0.8)
	ps	73.7	(8.0)	6.1	(0.6)	0.61	(0.07)	4.4	5.6	nd		383	(30)	6.3	(0.8)	16.4	(3.0)	6.5	(0.3)	7.0	(0.4)
	sf	86.6	(8.5)	6.2	(1.0)	0.57	(0.02)	3.8	5.1	nd		372	(24)	8.4	(1.1)	17.3	(3.3)	6.5	(0.7)	7.2	(0.7)
Pitzara	nf	129.8	(35.3)	9.2	(1.9)	0.48	(0.06)	9.8	4.7	nd		262	(75)	10.8	(1.5)	19.0	(2.4)	6.8	(0.4)	7.7	(0.4)
	ps	106.2	(11.8)	8.0	(0.0)	0.50	(0.05)	7.1	5.3	nd		219	(38)	8.6	(2.2)	21.7	(1.4)	6.7	(0.3)	7.8	(0.7)
	pf	116.2	(6.3)	8.6	(0.1)	0.45	(0.05)	9.7	5.3	nd		217	(11)	8.4	(0.6)	26.7	(1.6)	6.2	(0.1)	8.3	(0.3)

[a] based on the soil profile (n=1), all other values were expressed as mean and SD (n=4), [b] nd = not determined

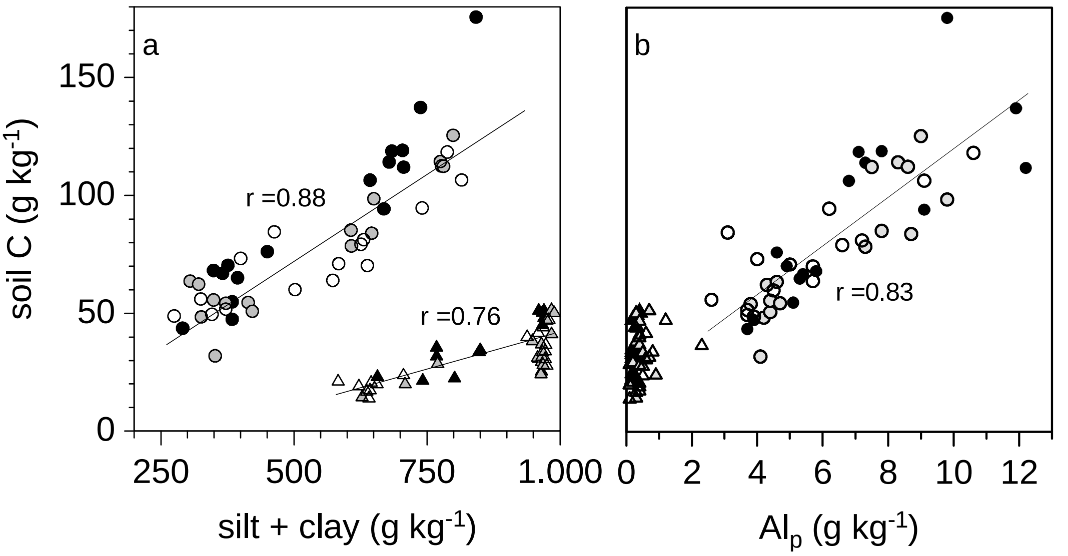

Figure 4-1: Relation of the silt + clay content with soil C (a) in volcanic ash soils (circles) and sedimentary soils (triangles) and Alp content with soil C (b) in volcanic ash soils and sedimentary soils of different land use types (white = pasture, grey = secondary forest, black = natural forest).

4.4.2 Water-Stable Aggregates Influenced by Soil Type and Land Use

Mean Weight Diameter (MWD) of water-stable aggregates was higher in sedimentary (3.6±0.4mm), soils than in volcanic ash soils (2.4±0.4mm; $P < 0.001$; see also Figure 4-2). Silt+clay content was positively correlated with MWD ($r = 0.86$; $P < 0.001$), for the whole dataset but also separately for each soil type (Figure 4-2a). In sedimentary soils, soil C was not correlated with MWD of natural forest ($P<0.05$) but in secondary forest ($r = 0.83$; $P < 0.001$) and in pastures ($r = 0.89$, $P < 0.001$; Figure 4-2b), soil C did correlate with MWD. In volcanic ash soils MWD was correlated with soil C under all land uses ($r = 0.59$; $P < 0.001$). Using multiple regression, soil C could not explain additional variation in MWD in addition to silt+clay content.

In sedimentary soils, macroaggregates of 2000 to 8000 µm were the largest fraction containing between 60% and 79% of total soil mass and between 58% and 74% of total soil carbon. Microaggregates (53-250 µm) contained only between 1% and 12% of soil mass and between 3% and 9% of soil carbon. Yield of macroaggregates increased with soil carbon content independent of land use ($P< 0.05$; see Appendix A, Table A1). Natural forest soils contained more small macroaggregates (2000-250 µm) than the corresponding pasture soils ($P<0.001$). In sedimentary soils mean C concentration (corrected for sand content) was highest in microaggregates (52 g kg^{-1}), followed by small macroaggregates (42 g kg^{-1}), and than by large macroaggregates (36 g kg^{-1}), and the <53 µm fraction (34 g kg^{-1}, all at $P<0.001$ means calculated from Appendix A, Table A1). Mean C/N ratio of aggregates from the sedimentary soils increased in the order: fraction <53 µm (C/N = 9.4) < large macroaggregates (10.0) ≤ small macroaggregates (10.5) ≤ microaggregates (10.9; $P<0.05$ means calculated from Appendix A, Table A1). The

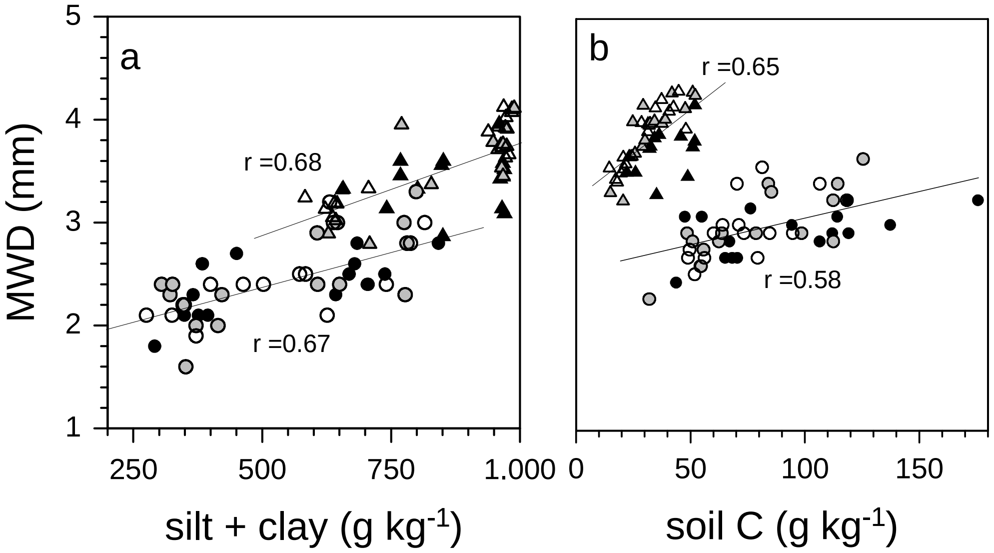

Figure 4-2: Relation of Mean Weight Diameter (MWD) of water stable aggregates with a) silt+clay content in volcanic ash soils (circles) and sedimentary soils (triangles) and b) MWD with soil C in volcanic ash soils and sedimentary soils of the different types of land use (white = pasture, grey = secondary forest, black = natural forest).

general pattern of the distribution of soil C among the aggregate fractions was similar under all land use types.

Land use did not influence aggregate size distribution of volcanic ash soils. In this soil type both macroaggregate fractions (2000-8000 µm and 250-2000 µm) contained most of the soil mass (41% and 34%) and soil C (44% and 30%, see Appendix A, Table A2). The size class <53 µm contained the smallest amount of soil (6%-17%) and contributed only 8% to 25% of soil C. With the exception of the fraction <53 µm which had less soil C and a lower C/N ratio, soil C concentration and C/N ratio were similar in all aggregate size fractions ($P<0.001$; see Appendix A, Table A1).

4.4.3 δ^{13}C Values and Mean Residence Time of Soil C

Mean δ^{13}C values (n = 32) of above ground vegetation / litter layer was – 11.8‰ (±0.6)‰ / -14.8‰ (±4‰) for pastures, -30.1‰ (±1.0‰) / -29.3‰ (±0.8‰) for secondary forests, and -29.9‰ (±1.3‰) / -29.4‰ (±0.8‰) in natural forests. Mean δ^{13}C values (n = 32) of fine roots were -13.4‰ (±1.7‰) in pastures, -28.8‰ (±0.8‰) in secondary forests and -29.1‰ (±0.7‰) in natural forests.

After 30 to 35 years of pasture three of four sedimentary sites contained about 50% pasture-derived soil C (Table 4-3) whereas at the site Minas this was only 38%. The corresponding mean residence times of forest-derived soil C varied between 37 and 57 years (Figure 4-3). Mean residence time of soil C_3-C tended to increase with silt+clay content and was significantly higher at Minas compared to Tazones and Penas ($P<0.05$; Figure 4-3). All secondary forest plots on sedimentary soils had a pasture history of about 20 years (Table 4-1). After 10 to 17 years of secondary forest between 5% and 18% of soil C was pasture-derived (this was equal to 13% to 65% of the former soil C_4-C; Table 4-3). The resulting MRT of C_4-derived carbon in the secondary forests were considerably shorter (between 8 and 25 years) than the corresponding MRT of soil C_3-C in the pastures at all sites except for Penas ($P<0.01$; Figure 4-3).

Table 4-3: $\delta\ ^{13}$C of soil C in soils of natural forest, pasture, and secondary forest and pasture-derived soil C (soil C_4-C) in pasture and secondary forest soils of the different sites.

Site	Natural Forest	Pasture	Secondary Forest	Pasture	Secondary Forest
	δ^{13}C (‰ V-PDB)[a]			soil C_4-C (%)[a]	
Sedimentary soils					
Tazones	-26.9 (0.4)	-19.4 (0.6)	-24.2 (0.4)	50 (5)	18 (5)
Penas	-26.9 (0.2)	-20.0 (0.6)	-24.5 (0.7)	47 (5)	16 (5)
Chonta Duro	-26.5 (0.4)	-18.9 (0.8)	-25.9 (0.4)	48 (6)	5 (4)
Minas	-25.9 (0.3)	-20.3 (0.4)	-23.8 (0.8)	38 (4)	14 (6)
Volcanic ash soils					
Mindo	-27.1 (0.3)	-18.2 (1.2)	-27.7 (0.5)	50 (7)	nd[b]
Maquipucuna	-27.3 (0.6)	-16.5 (1.9)	-27.1 (0.4)	62 (12)	nd
Pedro Viciente	-28.6 (0.5)	-26.0 (0.7)	-28.3 (0.3)	19 (6)	nd
Pitzara	-27.9 (0.2)	-23.5 (0.3)	-27.7 (0.2)	31 (7)	nd

[a] Values are given as mean and SD (n=4)

[b] nd = not determined as it is not possible to calculate pasture-derived carbon due to missing difference in δ^{13}C values between natural and secondary forest soils

In volcanic ash soils MRT of forest-derived soil C ranged from 24 to 56 years (Figure 4-3). At Maquipucuna MRT was higher (56 years) than at Mindo even though both sites are characterized by low Al_p and carbon content. At Pitzara and Pedro Viciente, both with high Al_p and carbon contents, MRT did not differ (36 and 24 years). No pasture-derived soil C could be detected in any of the secondary forests on volcanic ash soils. In Maquipucuna, no C_4 carbon was found in a 20 years old secondary forest even though the period with pasture lasted for 30 years.

In volcanic soils under pasture, pasture-derived soil C was homogenously distributed among aggregates whereas in sedimentary soils different aggregate fractions had different percentages of soil C_4-C (Table 4-4). In sedimentary soils under pasture, the proportion of pasture-derived carbon was highest in microaggregates and decreased further from small to big macroaggregates ($P<0.001$). In secondary forests, we detected no differences in C_4-derived soil C among aggregate fractions (Table 4-4).

4.5 Discussion

4.5.1 Effects of Soil Type and Land Use on Soil C Storage

Texture strongly influenced soil C storage in both soil types: increasing silt+clay contents were associated with higher soil C storage (Figure 4-1), as has been reported by other studies (e.g. Feller & Beare, 1997). Even more important for carbon storage was mineralogy. In agreement with Feller and Beare (1997) we found that volcanic ash soils have higher carbon storage per unit silt+clay compared to the sedimentary soils. Normally this is explained by the high specific surface area of allophane in combination with large amounts of non-crystalline compounds which cause the higher carbon storage per unit silt+clay in volcanic ash soils (Saggar et al., 1996; Six et al., 2002).

Strong correlations of soil C with Al_p were reported for volcanic ash soils (e.g. Percival et al., 2000; de Koning et al., 2003) and in a range of other soil types (Percival et al., 2000) and were explained with stabilization of soil C through Al-humus complexes and non-crystalline hydroxides (Torn et al., 1997; Masiello et al., 2004). This has also been shown in laboratory experiments in which non-crystalline Al-hydroxides, Al-complexes, and allophane were efficient in retarding decomposition of citric acid (Boudot, 1992).

Soil C storage is expected to be higher under wetter and cooler conditions than in warmer and drier soils (Admundson, 2001). However, within the volcanic ash soils we measured higher soil C storage at the warmer and less wet soils. Furthermore, the relatively small differences in temperature are not enough to explain why there is three times more soil C in the volcanic ash soils compared to the sedimentary soils. Thus the results indicate that soil C storage was dominated by soil properties rather than by climatic differences between sites.

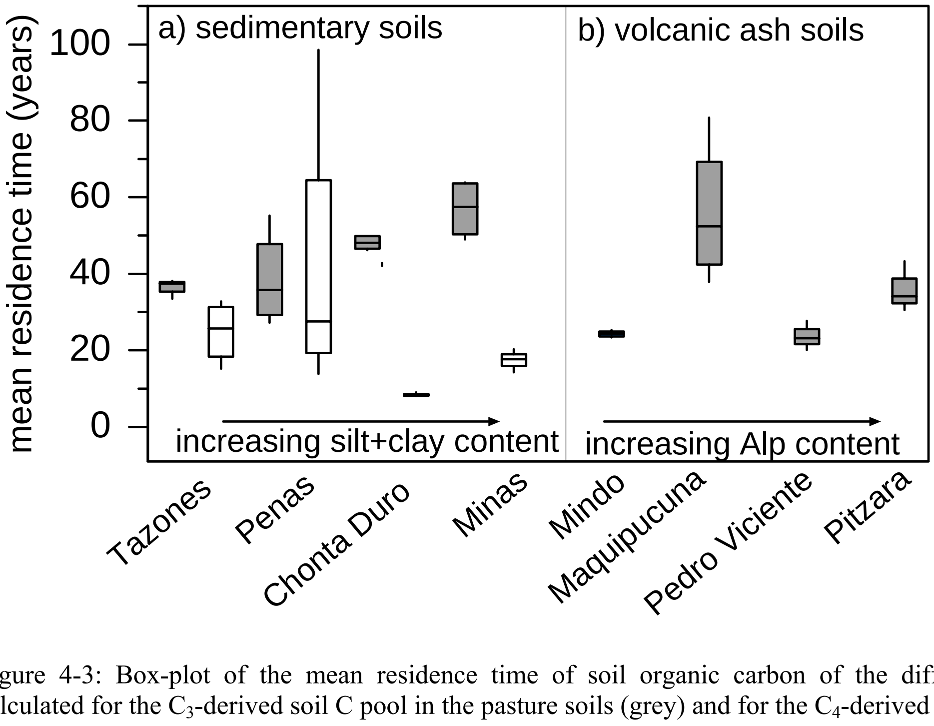

Figure 4-3: Box-plot of the mean residence time of soil organic carbon of the different sites calculated for the C_3-derived soil C pool in the pasture soils (grey) and for the C_4-derived soil C pool in the secondary forests soils (white). (Minas, Chonta: n=3; Penas: C_4-turnover times in secondary forest soils were overestimated due to differences in clay content and consequently carbon content in the secondary forest soil compared to the pasture soil). C_4-derived mean residence time could not be calculated for volcanic ash soils as no C_4-derived soil C could be detected at all secondary forests on volcanic ash soils).

Changes on soil C storage induced by land use change were influenced by soil properties within volcanic ash soils: at sites with high Al_p and Al_o content (Pitzara and Pedro Viciente) natural forest soils contained more carbon per unit silt+clay than corresponding pasture soils. This may indicate that soils with high Al_p and Al_o were more sensitive to changes in land use than soils containing less Al_p and Al_o.

4.5.2 Influence of Aggregation on Soil C Storage in Different Soil Types and Land Use Types

Normally texture strongly influences aggregation: higher clay content leads to increased aggregate stability (Edwards & Bremner, 1967). In other studies, a positive correlation has also been found between MWD and both clay and soil C content (Franzluebbers & Arshad, 1996) or between MWD and soil C only (Koutika et al., 1997) suggesting that both texture and soil C may influence aggregation. Our results suggest that texture played the dominant role in formation and stabilization of aggregates.

For the sedimentary soils we found an “inverse” aggregate hierarchy (decreasing soil C concentration and proportion of pasture-derived carbon with increasing aggregate sizes) which may be a result of the sample treatment before aggregate fractionation. Wet-sieving of air-dry soil led to increasing soil C concentration with increasing aggregate sizes (Puget et al., 1995). During slaking of air-dried soil, unstable macroaggregates (with low soil C content) disintegrated into smaller particles and were recovered in the microaggregate class. In contrast, the moist pretreatment that was applied in this study, resulted in fewer broken macroaggregates recovered in the microaggregate fraction and resulted in decreasing soil C content with increasing aggregate size (chapter 3).

In our volcanic ash soils, aggregate distribution was not affected by land use. Huygens et al. (2005) found no differences in the aggregate distribution of natural forest, grassland, and a pine plantation. The absence of an aggregate hierarchy suggests that in volcanic ash soils aggregates are not predominantly stabilized by particulate organic matter. Formation and stabilization of aggregates is more likely to occur by electrostatic attractions among amorphous Al components and clay minerals in addition to metal-humus complexes acting as binding agents through ligand exchange between functional groups of soil C and Al (Nanzyo et al., 1993; Huygens et al., 2005). Comparable results have been reported in Chile, where no aggregate hierarchy was found in a volcanic ash soil.

4.5.3 Mean Residence Time of Pasture- and Forest-derived Carbon

Our results suggest a trend of longer mean residence time (MRT) of forest-derived carbon associated with higher silt+clay content for sedimentary soils. A study in Brazil also reported a more rapid increase of pasture-derived carbon in a coarse textured soil than in a clay soil (Desjardins et al., 2004). However, other field studies do not support this observation (Desjardins et al., 1994; Feigl et al., 1995; Koutika et al., 1997; Desjardins et al., 2004; Powers & Veldkamp, 2005; Schwendenman & Pendall, 2006). Texture effects are often masked by other effects like clay mineralogy, land use history, or management (Saggar et al., 1996; de Koning et al., 2003; Powers & Veldkamp, 2005). In the volcanic soils, we found no evidence that the amount of non-crystalline compounds contribute to stabilization of recently incorporated soil C. In contrast, the mean ^{14}C age of total soil C was related to non-crystalline compounds in soils of volcanic parent material (Torn et al., 1997) and to the chelation of Al and Fe by organic ligands in temperate Inceptisols, Mollisols and Alfisols (Masiello et al., 2004).

Published data on MRT derived from forest-to-pasture conversions show that MRT does not only depend on soil properties but also on pasture age (Figure 4-4). This shows the limitation of the single pool model in calculation of MRT and is probably responsible for the high estimate of MRT in Maquipucuna compared to Mindo.

Our finding that recently formed pasture-derived soil C was less stable than the old forest soil C pool (soil C_3-C) can probably explained by the difference in accumulation between C_3 and C_4 soil C. Forest-derived soil C has accumulated over a much longer period of time than pasture-derived soil C. If only a small fraction of

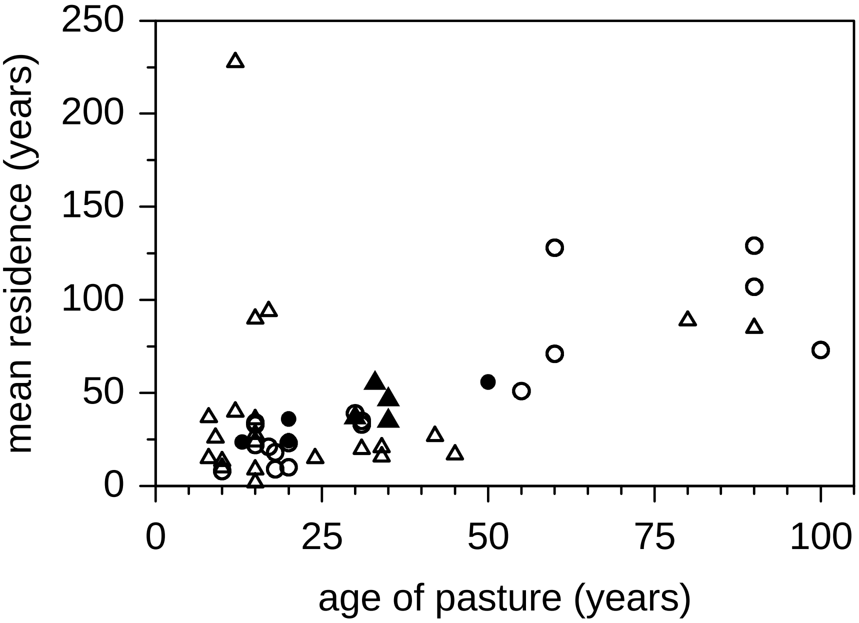

Figure 4-4: Mean residence times of forest-derived soil C in the topsoil of pastures in the humid tropics in: volcanic ash soils (circles) and others (triangles). If possible, turnover times were calculated after equation 1 and 2 in Chapter 4. Data originate from this study (black symbols) and from: Veldkamp, 1994; Townsend et al., 1995; Osher et al., 2003; Rhoades et al., 2000; Powers and Veldkamp, 2005; (volcanic ash soils); Desjardins et al., 1994; Feigl et al., 1995; Koutika et al., 1997; Desjardins et al., 2004; Powers and Veldkamp, 2005; Schwendenmann and Pendall, 2006; (open symbols). Note, high turnover times in young pastures are probably due to considerable C_3 (herbs and bushes) input.

soil C_4-C is stabilized, few decades of pastures are not sufficient to form a significant stable soil C_4-C pool. Although volcanic ash soils stabilize a lot of soil C, the turnover of pasture-derived carbon in secondary forests of volcanic ash soils was so fast that it completely disappeared in the bulk soil after few decades of secondary forests. Also fractionation of the aggregates into light and heavy fractions did not result in any soil C fractions containing pasture-derived carbon (chaprter 5). While the C storage in volcanic ash soils is very high, the stabilization of recently incorporated C is apparently very slow and the available binding sites for carbon probably become saturated. Apparently, Al-humus complexes and non-crystalline hydroxides are only important for stabilization at time scales longer than a few decades. In Hawaii, 10 to 15 years of secondary forests on former sugar cane fields resulted in a decrease of 22% to 42% C_4-derived soil C in the top 0.1 m of volcanic ash soils. This led to the conclusion that the majority of soil C_4–C was lost within the first years of secondary forests; while only a small part moved to slower cycling pools (Bashkin & Binkley, 1998).

4.6 Concluding remarks

Our study in the humid tropics of Ecuador showed that in the soils that we studied, total soil organic carbon levels were controlled by parent material (mineralogy) and texture, while aggregation and land use was less important. The combination of Al-humus complexes and non-crystalline hydroxides was more effective in carbon storage in volcanic ash soils than the silt+clay content in sedimentary soils. However, the stability of recently incorporated (pasture-derived) soil C was higher in sedimentary soils than in volcanic ash soils. Thus the mean residence time of recently incorporated organic carbon depends on clay mineralogy and is longer in soils dominated by smectite than in volcanic ash soils. In both soil types, the turnover of recently incorporated soil C was relatively fast compared to the total soil C. The implications of these results are that the presence of soil C stabilization processes, does not necessarily mean that recent incorporated soil C will also be effectively stabilized. Furthermore, carbon sequestration in soils through land use or land management changes is based mainly on the increase of labile soil C fractions and this will only be effective as long as the land use and it's management remains unchanged. In addition these fractions may respond very sensitively to climate change and thus represent a quite insecure carbon sink.

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Appendix A, Table A1: Total dry matter yield, soil C storage (g kg^{-1}), soil C concentration (g kg^{-1} sandfree aggregates), C/N, and δ^{13}C ($^{o}/_{oo}$) of water stable aggregates in sedimentary soils and volcanic ash soils of natural forest (nf), pasture (ps) and secondary forest (sf) soils. Values are given as mean and SD (n=4).

Site	Use	Aggregates (µm)	Yield (%)	Soil C (g kg^{-1} soil)	Soil C (g kg^{-1} sandfree aggregates)	C/N	δ^{13}C ($^{o}/_{oo}$)
Sedimentary soils							
Tazones	nf	8000-2000	65 (1.8)	17.6 (4.0)	36.8 (4.6)	9.0 (0.4)	-26.6 (0.4)
		2000-250	19 (4.3)	6.6 (3.1)	48.7 (8.7)	10.0 (0.4)	-27.2 (0.4)
		250-53	5 (1.9)	1.0 (0.1)	53.9 (2.8)	11.3 (1.2)	-27.9 (0.3)
		<53	11 (4.2)	4.0 (1.3)	38.7 (3.5)	9.4 (0.6)	-26.9 (0.4)
	ps	8000-2000	60 (1.9)	11.0 (1.6)	30.3 (4.7)	9.8 (1.1)	-19.7 (0.8)
		2000-250	11 (2.6)	1.8 (0.4)	28.5 (5.3)	10.9 (0.8)	-19.5 (0.7)
		250-53	12 (1.2)	1.2 (0.2)	53.6 (8.5)	11.2 (0.7)	-19.4 (0.8)
		<53	16 (1.4)	4.7 (0.3)	28.8 (0.8)	9.1 (0.5)	-19.8 (0.5)
	sf	8000-2000	62 (10.9)	13.3 (5.6)	27.7 (4.8)	9.6 (1.1)	-24.2 (0.9)
		2000-250	11 (2.2)	2.7 (1.3)	38.6 (14.8)	9.7 (0.7)	-25.0 (0.5)
		250-53	9 (5.4)	1.1 (0.2)	36.6 (9.0)	9.8 (1.5)	-26.3 (0.8)
		<53	17 (6.5)	4.6 (1.6)	27.5 (4.4)	9.2 (1.0)	-24.3 (0.8)
Penas	nf	8000-2000	60 (6.9)	13.3 (10.0)	36.8 (7.0)	10.0 (0.4)	-27.0 (0.3)
		2000-250	20 (10.1)	6.7 (3.9)	41.7 (5.6)	10.3 (0.7)	-27.0 (0.5)
		250-53	7 (2.1)	1.7 (0.8)	46.2 (2.0)	10.0 (1.0)	-27.7 (1.4)
		<53	12 (6.9)	3.5 (1.2)	31.0 (6.3)	9.2 (0.5)	-26.8 (0.2)
	ps	8000-2000	62 (3.6)	11.5 (3.0)	28.3 (5.1)	9.9 (0.3)	-20.0 (0.8)
		2000-250	11 (0.5)	1.7 (0.8)	31.8 (15.8)	10.5 (0.7)	-19.7 (0.8)
		250-53	8 (1.3)	1.0 (0.1)	57.3 (11.4)	12.4 (0.9)	-19.6 (0.4)
		<53	19 (1.6)	4.2 (0.7)	22.7 (3.8)	9.5 (0.7)	-20.3 (0.5)
	sf	8000-2000	67 (1.7)	21.0 (2.3)	32.8 (2.9)	9.4 (0.2)	-24.0 (0.7)
		2000-250	20 (1.8)	7.8 (1.1)	41.2 (8.1)	10.5 (1.0)	-25.0 (0.8)
		250-53	2 (0.4)	1.0 (0.2)	51.4 (nd)	10.0 (nd)	-26.3 (nd)
		<53	6 (0.8)	1.9 (0.4)	32.4 (4.8)	9.3 (0.0)	-24.5 (0.6)
Chonta Duro	nf	8000-2000	65 (5.5)	22.8 (6.6)	36.3 (10.4)	10.7 (1.9)	-26.4 (0.1)
		2000-250	16 (6.1)	6.2 (3.9)	38.3 (9.3)	10.7 (1.4)	-26.6 (0.4)
		250-53	3 (0.6)	1.0 (0.2)	36.7 (nd)	11.2 (nd)	-27.5 (nd)
		<53	15 (4.5)	4.3 (0.4)	30.3 (9.1)	9.2 (1.4)	-26.2 (0.4)
	ps	8000-2000	74 (4.0)	23.3 (5.3)	32.3 (6.0)	9.7 (0.8)	-19.6 (0.6)
		2000-250	10 (1.6)	3.5 (0.9)	35.5 (3.7)	9.7 (1.0)	-19.0 (0.6)
		250-53	2 (0.5)	0.9 (0.2)	43.2 (nd)	9.7 (nd)	-18.5 (nd)
		<53	13 (3.2)	3.5 (0.6)	27.7 (3.0)	8.3 (1.0)	-19.2 (0.7)
	sf	8000-2000	68 (4.3)	20.2 (4.2)	30.7 (4.9)	9.2 (0.9)	-25.9 (0.3)
		2000-250	17 (1.4)	5.7 (0.6)	35.0 (4.3)	9.6 (0.6)	-26.2 (0.3)
		250-53	3 (0.3)	1.0 (0.1)	42.7 (nd)	10.3 (nd)	-26.8 (nd)
		<53	11 (2.6)	3.3 (0.8)	30.0 (4.3)	9.2 (0.5)	-25.9 (0.2)

Appendix A, continiung: **Table A1**

Site	Use	Aggregates (μm)	Yield (%)	Soil C (g kg^{-1} soil)	Soil C (g kg^{-1} sandfree aggregates)	C/N	δ^{13}C ($^{o}/_{oo}$)
Sedimentary soils							
Minas	nf	8000-2000	65 (9.0)	31.8 (5.3)	48.0 (3.5)	11.1 (0.9)	-26.0 (0.3)
		2000-250	27 (7.7)	12.2 (2.6)	53.2 (4.5)	11.8 (1.3)	-27.2 (2.2)
		250-53	3 (0.6)	1.4 (0.3)	62.2 (nd)	10.8 (nd)	-26. (nd)
		<53	6 (0.6)	2.7 (0.3)	49.9 (1.8)	11.1 (0.7)	-26.0 (0.2)
	ps	8000-2000	74 (5.1)	30.6 (3.8)	42.8 (2.4)	10.2 (0.9)	-20.5 (0.6)
		2000-250	16 (3.3)	8.2 (1.9)	51.8 (4.9)	10.4 (1.0)	-19.7 (0.9)
		250-53	2 (0.4)	1.5 (0.3)	79.2 (nd)	11.4 nd	-17.8 (nd)
		<53	7 (2.3)	3.5 (0.5)	44.7 (3.2)	10.1 (0.5)	-19.7 (1.3)
	sf	8000-2000	79 (3.8)	35.2 (3.5)	45.6 (3.0)	11.4 (0.7)	-24.0 (0.7)
		2000-250	15 (3.8)	7.5 (2.2)	51.1 (6.3)	11.8 (1.0)	-24.2 (1.0)
		250-53	1 (0.1)	0.7 (nd)	68.2 (nd)	12.0 (nd)	-28.8 (nd)
		<53	6 (1.5)	2.7 (0.5)	42.9 (4.7)	10.6 (0.9)	-23.7 (0.8)
Volcanic ash soils							
Mindo	nf	8000-2000	31 (4.4)	19.9 (5.8)	183.4 (20.6)	13.8 (0.7)	-27.1 (0.3)
		2000-250	44 (1.5)	21.3 (5.7)	199.7 (3.4)	14.1 (0.7)	-27.3 (0.3)
		250-53	17 (2.9)	8.3 (2.1)	190.6 (25.4)	14.6 (1.0)	-27.5 (0.4)
		<53	7 (1.2)	11.6 (0.7)	159.0 (14.9)	13.9 (0.9)	-27.0 (0.2)
	ps	8000-2000	33 (4.5)	22.6 (5.9)	152.4 (3.2)	12.6 (1.5)	-17.7 (1.1)
		2000-250	42 (4.3)	16.3 (4.3)	167.0 (34.0)	12.0 (0.5)	-18.0 (1.0)
		250-53	17 (2.3)	7.2 (1.4)	155.7 (46.2)	13.8 (1.6)	-18.5 (1.0)
		<53	7 (1.1)	10.8 (1.2)	149.6 (9.7)	12.1 (0.5)	-19.0 (1.2)
	sf	8000-2000	34 (3.9)	24.6 (7.7)	199.8 (38.9)	14.4 (0.6)	-27.7 (0.6)
		2000-250	43 (1.7)	16.9 (1.9)	184.2 (54.0)	14.6 (0.8)	-27.6 (0.4)
		250-53	16 (1.9)	8.0 (1.1)	198.1 (13.7)	14.1 (0.8)	-27.8 (0.4)
		<53	6 (1.1)	10.3 (1.5)	164.7 (17.3)	13.5 (0.6)	-27.4 (0.5)
Maquipucuna	nf	8000-2000	41 (5.1)	25.7 (6.9)	150.5 (17.9)	14.6 (1.9)	-27.2 (0.5)
		2000-250	38 (2.0)	16.2 (5.0)	138.8 (27.7)	14.3 (2.7)	-27.4 (0.6)
		250-53	13 (3.7)	5.9 (1.8)	159.4 (30.0)	13.9 (1.5)	-27.7 (0.5)
		<53	8 (2.5)	10.6 (4.4)	131.6 (20.8)	12.5 (1.0)	-27.2 (0.4)
	ps	8000-2000	40 (2.5)	25.2 (6.0)	137.9 (14.9)	12.8 (1.7)	-16.9 (1.9)
		2000-250	36 (2.3)	16.6 (6.5)	160.8 (48.5)	12.6 (2.0)	-16.8 (2.3)
		250-53	19 (4.8)	8.4 (2.2)	133.5 (34.5)	12.7 (1.2)	-16.5 (1.8)
		<53	10 (3.3)	11.8 (3.9)	112.4 (6.1)	11.8 (0.6)	-16.8 (1.7)
	sf	8000-2000	32 (7.1)	16.3 (4.1)	130.8 (9.9)	13.0 (0.9)	-27.1 (0.2)
		2000-250	34 (1.8)	12.4 (2.1)	152.6 (44.1)	13.1 (0.7)	-27.2 (0.1)
		250-53	21 (4.3)	7.6 (1.0)	139.1 (11.6)	12.3 (0.1)	-27.4 (0.1)
		<53	11 (2.4)	11.9 (2.5)	112.5 (3.4)	11.8 (1.0)	-27.1 (0.3)

Appendix A, continiung: **Table A1**

Site	Use	Aggregates (µm)	Yield (%)	Soil C (g kg^{-1} soil)	Soil C (g kg^{-1} sandfree aggregates)	C/N	$\delta^{13}C$ $({}^{o}/_{oo})$
Volcanic ash soils							
Pedro Viciente	nf	8000-2000	45 (5.0)	51.3 (7.6)	169.1 (5.5)	15.4 (1.1)	-28.0 (0.3)
		2000-250	22 (2.9)	27.3 (2.2)	187.3 (12.6)	15.8 (1.3)	-28.4 (0.4)
		250-53	16 (2.7)	9.9 (1.2)	184.1 (12.6)	16.4 (1.0)	-28.7 (0.2)
		<53	17 (1.9)	22.8 (2.7)	136.7 (7.9)	15.0 (1.0)	-28.3 (0.4)
	ps	8000-2000	48 (9.1)	35.3 (9.0)	120.4 (10.7)	12.2 (0.1)	-25. (0.8)
		2000-250	24 (3.2)	17.0 (3.4)	119.0 (24.3)	12.5 (0.4)	-25.9 (0.7)
		250-53	15 (6.2)	5.6 (1.9)	104.2 (8.9)	12.7 (0.5)	-26.1 (0.7)
		<53	12 (6.1)	12.8 (8.3)	105.0 (14.1)	12.6 (1.6)	-26.1 (0.5)
	sf	8000-2000	47 (6.7)	40.5 (6.6)	138.1 (15.9)	14.2 (1.0)	-28.1 (0.1)
		2000-250	26 (3.0)	24.0 (4.2)	152.8 (22.0)	14.8 (1.1)	-28.4 (0.4)
		250-53	15 (1.9)	7.0 (1.7)	152.8 (15.6)	15.2 (0.6)	-28.6 (0.2)
		<53	14 (1.1)	15.3 (4.8)	124.3 (8.9)	13.1 (0.3)	-28.0 (0.3)
Pitzara	nf	8000-2000	44 (4.0)	56.4 (20.0)	171.2 (29.2)	14.3 (0.6)	-27.8 (0.2)
		2000-250	31 (3.9)	44.3 (11.5)	185.5 (39.5)	14.5 (0.9)	-28.0 (0.1)
		250-53	13 (2.6)	10.9 (1.9)	180.7 (32.6)	15.4 (0.8)	-28.2 (0.3)
		<53	12 (0.3)	18.7 (3.2)	160.7 (31.3)	14.6 (0.7)	-27.8 (0.3)
	ps	8000-2000	45 (4.9)	48.1 (10.6)	134.7 (9.1)	13.3 (1.0)	-23.6 (0.7)
		2000-250	35 (3.4)	41.1 (6.1)	151.9 (17.7)	13.6 (1.2)	-23.1 (0.5)
		250-53	11 (2.9)	8.5 (2.4)	132.7 (4.0)	13.8 (1.2)	-23.2 (0.7)
		<53	6 (3.5)	6.9 (3.5)	108.2 (5.0)	12.6 (1.4)	-23.8 (0.6)
	sf	8000-2000	50 (9.6)	53.8(13.5)	136.5 (8.8)	13.4 (1.3)	-27.7 (0.2)
		2000-250	30 (5.1)	37.7 (4.4)	155.2 (7.9)	14.2 (1.2)	-27.6 (0.2)
		250-53	11 (3.0)	9.1 (1.7)	163.0 (8.1)	14.7 (0.9)	-28.0 (0.1)
		<53	9 (3.0)	11.9 (3.2)	126.8 (9.5)	12.4 (0.6)	-27.5 (0.2)

5 Soil C in Density Fractions*

5.1 Abstract

Our knowledge of effects of land use changes and soil types on the storage and stability of different soil organic carbon (SOC) fractions in the tropics is limited. We analyzed the effect of land use (natural forest, pasture, secondary forest) on SOC storage (depth 0-0.1 m) in density fractions of soils developed on marine Tertiary sediments and on volcanic ashes in the humid tropics of Northwest Ecuador. The origin of organic carbon stored in free light (<1.6 g cm^{-3}) fractions, and in two light fractions (LF) occluded within aggregates of different stability, were determined by means of $\delta^{13}C$ natural abundance. Light occluded organic matter was isolated in a first step after aggregate disruption by shaking aggregates with glass pearls (occluded I LF) and in a subsequent step by manual destruction of the most stable microaggregates that survived the first step (occluded II LF). SOC storage in LFs was greater in volcanic ash soils (7.6 ± 0.6 Mg C ha^{-1}) than in sedimentary soils (4.3 ± 0.3 Mg C ha^{-1}). The contribution of the LFs to SOC storage was greater in natural forest (19.2% ± 1.2%) and secondary forest (16.6% ± 1.0%) than in pasture soils (12.8% ± 1.0%), independent of soil parent material. The amount of SOC stored in the occluded I LF material increased with increasing silt + clay content (sedimentary soils: $r = 0.73$; volcanic ash soils: $r = 0.58$) and aggregation (sedimentary soils: $r = 0.52$; volcanic ash soils: $r = 0.45$). SOC associated with occluded I LF, had the smallest proportion of new, pasture-derived carbon, indicating the stabilizing effect of aggregation. Fast turnover of the occluded II LF material, which was separated from highly stable microaggregates, strongly suggested that this fraction is important in the initial process of aggregate formation. No pasture-derived carbon could be detected in any density fractions of volcanic ash soils under secondary forest, indicating fast turnover of these fractions in tropical volcanic ash soils.

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* Soil Organic Carbon in Density Fractions of two Tropical Soil Types under Forest – Pasture – secondary Forest Land Use Changes. Paul, S., Veldkamp, E., Flessa, H. European Journal of Soil Science. (DOI: 10.1111/j.1365-2389.2007.01010.x)

5.2 Introduction

The soil organic carbon (SOC) pool represents a major part of the terrestrial carbon reservoir and plays an important role in the global carbon cycle**.** In the tropics, where 32% of the world's SOC storage is located (Jobbagy & Jackson, 2000), land use changes influence the above- and below-ground carbon stocks. While conversion of tropical forests and pastures to arable land typically decreases total SOC stocks by 40 to 60% (Guo & Gifford, 2002), conversion of forests to pastures or *vice versa* can be associated either with gains, losses or without any change of total SOC, depending on soil properties, climate, and pasture management (Detwiler, 1986; Lugo & Brown, 1993; de Koning *et al.*, 2003). These inconsistent results can be partly explained by the complexity of SOC, which consists of several pools that have a wide range of chemical properties and turnover times and consequently respond differently to land use changes.

Quantitative knowledge of stabilization and decomposition processes of SOC fractions is important so as to understand, assess and predict effects of land use changes on the storage and stability of different SOC fractions. Association of SOC with mineral particles is thought to play a key role in decomposition and stabilization processes of SOC (von Lützow et al., 2007). The amount of clay-sized mineral particles and their mineralogy are important factors controlling total SOC stocks (Feller & Beare, 1997; Six *et al.*, 2002). Density fractionation is used to separate light organic matter (light fraction (LF)) not bound to minerals and the mineral-associated organic matter (heavy fraction (HF)). Light fractions can be further fractionated according to their location within the soil matrix: the free LF located between aggregates and LF occluded within aggregates (occluded LF): Free LF consists mainly of recognizable plant debris, while occluded LF consists of more recalcitrant SOC (fewer O-alkyl and more alkyl structures) compared to the free LF (Golchin *et al.*, 1994, a,b). Moreover, SOC in free LFs, if not affected by charcoal, shows generally shorter turnover times than occluded LFs in temperate soils (von Lützow *et al.*, 2007). Differences in stability and composition of LF are supposed to result from recalcitrance and the protective mechanism of soil aggregation (Six *et al.*, 2002; John *et al.*, 2005; Yamashita *et al.*, 2006).

Light fractions generally represent only a small proportion of total SOC in biologically active soils (Gregorich et al., 2006). However, changes in carbon stocks following land use changes can be more pronounced in LF compared to bulk soil (Schwendenmann & Pendall, 2006). Information on the influence of soil properties such as clay content on the amount and stability of free and occluded LF is very limited and restricted to temperate and subtropical soils (Golchin et al., 1994b; Kölbl & Kögel-Knabner, 2004).

Our study was conducted in the humid tropics of Northwest Ecuador. In this area, forest clearing for pastures, and pasture abandonment followed by forest regrowth, are widespread. Forest regrowth on abandoned pastures has been found to increase SOC stocks in the upper 0.5 m if the secondary forests have at least 20 years to regrow (de Koning et al., 2003). Furthermore, a correlative study showed that parent material and particle-size distribution were the main factors controlling total SOC storage (Lopez et al., 2005). Using a combination of SOC quantification in soil density fractionation and $\delta^{13}C$ determination, our goal was to trace the origin and stability of SOC in density fractions under forest – pasture – secondary forest land use changes on tropical soils of different parent material (Marine Tertiary sediments and volcanic ashes). More specifically, we wanted to test the following hypotheses: i) Conversion of forest to pasture leads to a reduction in LF, and afforestation of former pasture leads to an increase in LF. Relative changes in LFs are more pronounced than changes in total SOC. ii) The great carbon storage in volcanic ash soils is caused by the interaction of organic matter with mineral surfaces: the amount of SOC stored in LFs is independent of soil parent material, while greater carbon storage is found in the HF of volcanic ash soils. iii) The amount of occluded LF increases with soil aggregation, but the amount of free LF is independent of aggregation. iv) The free LF shows a shorter turnover than the occluded LF independent of soil parent material. v) Stability of pasture-derived carbon in soil density fractions is less in volcanic ash soils than in soils formed in marine Tertiary sediments due to high carbon loads on mineral surfaces and rapid turnover of organic matter in volcanic ash soils.

5.3 Material & Methods

5.3.1 Site Description

Our sites were located in Northwest Ecuador. Four sites had soils developed from volcanic ashes, and covering a gradient of weathering with different silt + clay contents and different amounts of iron and aluminium oxides (Table 5-1). These soils were classified as Hapludands (Soil Survey Staff, 1998). Soils of the other four sites were developed from marine Tertiary sediments and differed in clay content (Table 5-1). These soils were classified as Haplustepts and Paleudalfs (Soil Survey Staff, 1998). The clay fraction in soils developed from marine Tertiary sediments was dominated by smectite with a marginal contribution of illite, chlorite, and kaolinite. In comparison with our volcanic ash soils, these soils contained less iron and aluminium oxides (Table 5-1). In the following, we call soils developed from marine Tertiary sediments ‘sedimentary soils’ and soils developed from volcanic ashes ‘volcanic ash soils’. At each site, we selected a ‘natural forest’ (= nf) plot, a pasture (= ps) plot, which was dominated by C_4 grasses, and a secondary forest or tree plantation plot. Secondary forests formed on abandoned pastures due to natural succession without management. Plantations were established on former pastures by planting trees. As there were no differences in SOC stocks between secondary forests and plantations (de Koning et al., 2003), these sites were grouped and analyzed together (we call these sites ‘secondary forest’ (= sf)). At each plot, we selected four sampling points along a 50m transect. Sampling depth was 0-0.1 m since we expected that effects of land use changes on soil C stocks and on aggregation would be most pronounced in the topsoil (Desjardins et al., 1994). In addition, fine roots were sampled (0-0.1m depth) in four replicates at each plot by means of a root corer. Roots were separated by hand from the soil, dried (40°C) and analysed for carbon content and $\delta^{13}C$.

5.3.2 Soil Analysis

Particle-size distribution (<2 µm (clay), 2-53 µm (silt), >53 µm (sand)) of the sedimentary soils was determined by sieving and the pipette method with sodium pyrophosphate as a dispersing agent (Hartge & Horn, 1989). As the determination of clay content for soils derived from volcanic ashes reveals ambiguous results due to incomplete dispersion (Nanzyo et al., 1993), we did not determine these clay contents. The silt+clay content was determined by difference from the amount of sand. Selective dissolution of bulk soil samples was done with acid ammonium-oxalate extraction of aluminium (Al_o) and iron (Fe_o) (Schwertmann, 1964 modified, 4 hours shaking instead of 2 hours), and pyrophosphate extraction of aluminum (Al_p); McKeague, 1967). Fe and Al concentrations in these extracts were measured by inductively coupled plasma emission spectroscopy (Flame-ICP, Spectro Analytical Instruments, Kleve, Germany). Total C and N contents of soil samples and roots were measured with an automated C and N analyzer (Elementaranalysator CNS, Vario EL, Elementar, Hanau, Germany) after milling the samples with a ball mill (Retsch PM 4000, Haan, Germany). At one site (Minas) soil samples were treated with HCl (3 mol l^{-1}) to remove inorganic carbon. SOC stocks (Mg C ha^{-1}) were calculated from bulk SOC concentration (g C kg^{-1} soil) and bulk density (Mg m^{-3}) for the upper 0.1m depth layer. Stocks were corrected for land-use specific differences in bulk density (Veldkamp, 1994). Carbon stored in aggregates or density fractions were calculated in the same way. SOC concentrations of individual density fractions were reported on a mass basis (g C kg^{-1} soil) and used for the correlation of silt and clay and Mean Weight Diameter (MWD) with LFs. The MWD of water-stable aggregates was calculated as:

$$MWD = \sum_{\mathrm{i}=1}^{n} \bar{x}_{\mathrm{i}} \times w_{\mathrm{i}}\,, \tag{5-1}$$

where $\bar{x}_{\mathrm{i}}$ is the mean diameter of each size fraction, and w_{i} is the proportional weight of the corresponding size fraction (Kemper & Rosenau, 1986).

5.3.3 Density Fractionation of Soil Aggregates

The procedure to obtain density fractions of SOC is summarized in Figure 5-1. Macroaggregates (250-8000 µm) and microaggregates (53-250 µm) used for density fractionation were obtained by wet sieving (Elliot, 1986). In brief, a moist soil sample (<8000 µm; equivalent to 100 g air dried soil) was submersed in distilled water for 5 minutes on top of a sieve (<250 µm aperture) and the sieve was moved 50 times by hand 3 cm up and down. Aggregates of 8000-250 µm were collected and sieving of the fraction <250 µm was repeated with a sieve of 53 µm aperture. Aggregate size classes were dried, weighed and analyzed for total SOC content. We put 7.5 g of air-dried macro- and micro-aggregates in a centrifuge tube together with 0.04 litres sodium polytungstate solution (SPT; Sometu, Berlin, Germany) with a density of 1.6 g cm^{-3}. The tube was gently shaken by hand. After 30 minutes sedimentation, the solution was centrifuged for 1 hour at 5100 ***g***. The supernatant, including floating particles, was filtered (polyamide membrane filters, pore size: 0.45µm) under vacuum and washed with distilled water to gain the free LF. To break down aggregates, we added SPT and 18 glass pearls to the residue and shook the test tube for 18 hours at a frequency of 120 movements per minute (Balesdent et al., 1991; John et al., 2005, modified: we increased the number of glass pearls from 10 to 18 and increased the used frequency from 60 to 120 movements per minute as many aggregates survived the original protocol). Then the soil solution was centrifuged for 1 hour at 5100 ***g*** and the supernatant with floating material was filtered and washed to gain the occluded LF (we will call this fraction 'occluded I LF'). The residue that contained the most stable microaggregates that survived this procedure was washed four times with distilled water and then sieved (<53 µm) until all aggregates >53 µm were broken. The aggregates were destroyed by gently pressing the aggregates against the mesh using a dough scraper. Both fractions (>53 µm and <53 µm) were dried at 40°C. The fraction >53 µm contained visible plant remains and was therefore again treated with 1.6 g cm^{3} SPT solution as described above and a third LF (we will call this fraction 'occluded II LF') was attained. All LFs were freeze dried.

As the LFs (free LF, occluded I LF and occluded II LF) of microaggregates contributed only between 0.4% and 3.5% of total SOC, we added the density fractions of macro- and micro-aggregates for most of the analyses (Table 5-3; Table 5-4; Figure 5-2; Figure 5-3).

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Table 5-1: General soil characteristics (soil organic carbon (SOC), soil bulk density (BD), Mean Weight Diameter (MWD), clay and sand content, aluminium extracted by pyrophosphate (Al_p) and acid-oxalate (Al_o), and iron extracted by acid-oxalate (Fe_o)) and land use history of the different sites and land uses (means (n=4) and standard error; nf =natural forest; ps=pasture; sf= secondary forest). Significant differences between sites within one land use are indicated by different letters.

Site	Land use	Age of land use / years		SOC / Mg ha^{-1}		SOC / g kg^{-1}		BD / g cm^{-3}		MWD / mm		Clay		Sand		Al_p		Al_o		Fe_o	
												/ g kg^{-}									
Sedimentary soils		ps	sf																		
Tazones	nf			30.8^{a}	(3.2)	30.8^{a}	(3.8)	0.96^{d}	(0.14)	3.5^{b}	(0.1)	287^{a}	(45)	269^{bc}	(64)	0.2^{a}	(0.0)	1.3^{a}	(0.1)	1.0^{a}	(0.1)
(0.7N; 79.8W)	ps	35^{e}		19.4^{a}	(0.8)	20.2^{a}	(0.8)	1.30^{c}	(0.06)	3.2^{b}	(0.0)	324^{a}	(54)	377^{c}	(29)	0.3^{a}	(0.1)	0.8^{a}	(0.0)	2.5^{ab}	(0.4)
	sf	21^{f}	14^{g}	21.8^{a}	(2.9)	21.7^{a}	(3.1)	1.19^{d}	(0.12)	3.3^{cd}	(0.3)	360^{a}	(79)	266^{b}	(86)	0.2^{a}	(0.1)	0.9^{a}	(0.1)	1.9^{a}	(0.2)
Penas	nf			28.4^{a}	(3.1)	28.7^{a}	(3.5)	1.00^{d}	(0.12)	3.2^{b}	(0.1)	369^{b}	(30)	190^{b}	(51)	0.2^{a}	(0.1)	1.1^{a}	(0.1)	1.9^{ab}	(0.1)
(1.1N; 79.1W)	ps	30		19.3^{a}	(2.2)	19.3^{a}	(2.1)	1.44^{c}	(0.10)	3.2^{b}	(0.1)	293^{a}	(35)	340^{bc}	(32)	0.3^{a}	(0.2)	0.5^{a}	(0.0)	1.7^{a}	(0.3)
	sf	20	10	34.5^{cd}	(1.6)	34.4^{ab}	(1.6)	0.93^{bc}	(0.09)	3.8^{de}	(0.0)	532^{b}	(26)	40^{a}	(9)	0.5^{a}	(0.2)	1.6^{a}	(0.1)	3.2^{ab}	(0.5)
Chonta Duro	nf			31.1^{a}	(4.9)	35.1^{a}	(5.5)	0.89^{b}	(0.07)	3.5^{b}	(0.1)	592^{c}	(30)	37^{a}	(3)	0.3^{a}	(0.1)	1.4^{a}	(0.1)	3.7^{cd}	(0.5)
(0.9N; 79.4W)	ps	35		29.2^{ab}	(3.4)	33.0^{ab}	(1.9)	0.93^{b}	(0.07)	3.8^{c}	(0.1)	607^{b}	(58)	27^{a}	(1)	1.1^{a}	(0.9)	1.3^{a}	(0.3)	4.7^{cd}	(0.6)
	sf	20	17	26.9^{ab}	(4.8)	30.4^{a}	(2.7)	0.96^{bc}	(0.05)	3.6^{de}	(0.1)	603^{bc}	(17)	35^{a}	(2)	0.5^{a}	(0.3)	1.1^{a}	(0.1)	3.1^{ab}	(0.5)
Minas	nf			34.3^{a}	(3.0)	49.6^{a}	(1.5)	0.69^{b}	(0.11)	3.6^{b}	(0.2)	622^{c}	(33)	33^{a}	(5)	0.3^{a}	(0.1)	1.5^{a}	(0.1)	2.8^{bc}	(0.4)
(0.9N; 79.6W)	ps			30.4^{ab}	(1.1)	44.0^{bc}	(1.6)	0.85^{b}	(0.02)	3.9^{c}	(0.1)	619^{b}	(37)	39^{a}	(17)	0.6^{a}	(0.4)	1.6^{ab}	(0.1)	3.5^{bc}	(0.7)
	sf	20	10	33.3^{cd}	(3.1)	48.2^{bc}	(2.3)	0.79^{b}	(0.03)	4.1^{e}	(0.0)	639^{c}	(22)	17^{a}	(6)	0.5^{a}	(0.2)	1.6^{ab}	(0.1)	1.5^{a}	(0.3)
Volcanic ash soils																					
Mindo	nf			36.1^{ab}	(6.0)	62.3^{a}	(6.3)	0.57^{ab}	(0.12)	2.1^{a}	(0.1)	nd[h]		655^{d}	(38)	4.9^{b}	(0.9)	5.5^{b}	(1.0)	3.6^{cd}	(0.7)
(0.0N; 78.8W)	ps	20		37.0^{b}	(3.4)	60.5^{cd}	(8.1)	0.81^{b}	(0.07)	2.2^{a}	(0.1)	nd		624^{d}	(61)	3.3^{b}	(0.5)	4.4^{bc}	(0.7)	3.8^{bc}	(0.6)
	sf	5	23	33.7^{cd}	(1.3)	59.0^{c}	(2.3)	0.63^{ab}	(0.13)	2.2^{ab}	(0.1)	nd		664^{d}	(30)	4.3^{b}	(0.4)	5.0^{bc}	(0.4)	4.2^{bc}	(1.7)
Maquipucuna	nf			38.0^{ab}	(2.3)	60.9^{a}	(6.2)	0.64^{ab}	(0.10)	2.5^{a}	(0.1)	nd		597^{d}	(32)	4.7^{b}	(0.6)	8.2^{c}	(0.4)	4.5^{d}	(0.6)
(0.1N; 78.7W)	ps	50		39.0^{bc}	(7.8)	63.3^{cd}	(5.6)	0.62^{a}	(0.06)	2.3^{a}	(0.1)	nd		560^{d}	(134)	4.4^{bc}	(0.5)	7.3^{c}	(0.9)	5.4^{de}	(1.0)
	sf	30	20	29.6^{abc}	(3.2)	46.5^{bc}	(5.0)	0.78^{b}	(0.10)	2.1^{a}	(0.2)	nd		622^{d}	(47)	4.4^{bc}	(0.3)	8.3^{c}	(1.1)	5.1^{cd}	(0.4)
Pedro Viciente	nf			52.7^{bc}	(3.1)	114.7^{b}	(2.9)	0.46^{a}	(0.04)	2.5^{a}	(0.1)	nd		323^{c}	(26)	7.3^{c}	(0.4)	10.1^{c}	(1.3)	5.9^{e}	(0.9)
(0.1N; 79.0W)	ps	13		33.8^{b}	(1.8)	73.7^{d}	(4.0)	0.61^{a}	(0.07)	2.7^{ab}	(0.2)	nd		383^{c}	(30)	6.3^{c}	(0.8)	16.4^{d}	(3.0)	6.5^{e}	(0.3)
	sf	8	15	38.0^{c}	(0.9)	86.6^{d}	(4.3)	0.57^{a}	(0.02)	2.7^{abc}	(0.2)	nd		372^{c}	(24)	8.4^{c}	(1.1)	17.3^{d}	(3.3)	6.5^{d}	(0.7)
Pitzara	nf			60.2^{c}	(4.0)	129.8^{b}	(7.6)	0.48^{ab}	(0.06)	2.6^{a}	(0.1)	nd		262^{bc}	(75)	10.8^{d}	(1.5)	19.0^{d}	(2.4)	6.8^{e}	(0.4)
(0.3N; 79.2W)	ps	20		50.8^{c}	(3.2)	106.2^{e}	(6.8)	0.50^{a}	(0.05)	2.7^{ab}	(0.2)	nd		219^{b}	(38)	8.6^{d}	(2.2)	21.7^{e}	(1.4)	6.7^{e}	(0.3)
	sf	10	10	55.4^{d}	(1.5)	116.2^{e}	(3.1)	0.45^{a}	(0.05)	2.9^{bc}	(0.2)	nd		217^{b}	(11)	8.4^{d}	(0.6)	26.7^{e}	(1.6)	6.2^{d}	(0.1)

[e] pastures were established after clearing of natural forest; [f] duration of pasture before the site was changed to secondary forest; [g] secondary forests were established on former pastures; [h] nd not determined due methodical difficulties in dispersion in volcanic ash soils.

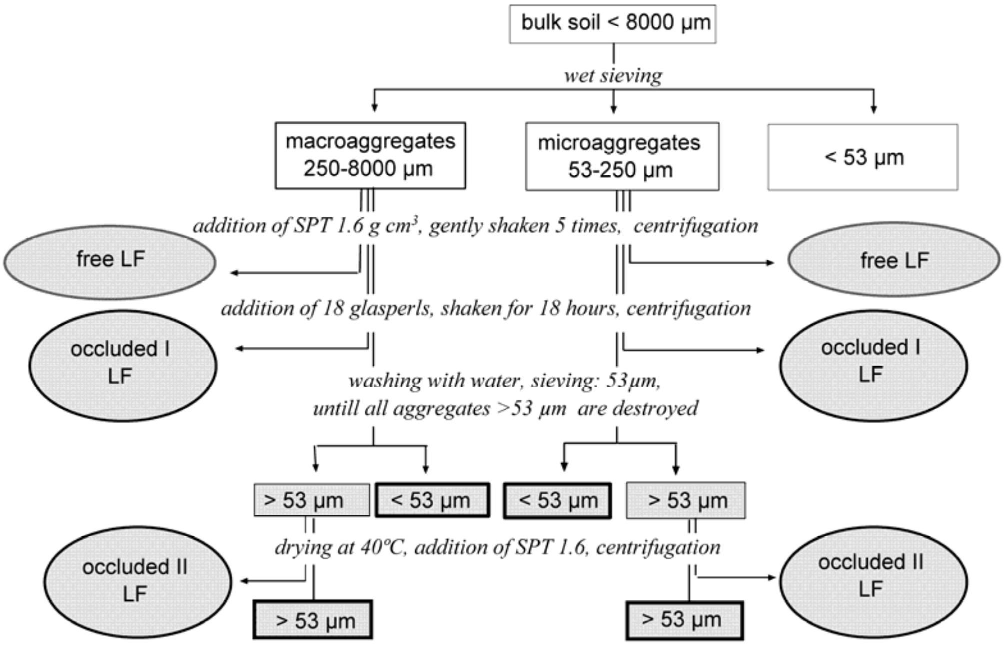

Figure 5-1: Applied fractionation scheme of aggregate fractionation followed by density fractionation. White boxes represent bulk soil and aggregate size fractions, grey ovals represent LFs and grey boxes represent the HFs.

5.3.4 Isotope Analyses

The $^{13}C/^{12}C$ isotope ratio was measured with an isotope ratio mass spectrometer (IRMS, Finnigan MAT, DELTA^{plus}, Bremen, Germany) at the Center of Stable Isotopes Research and Analysis, University of Göttingen. Samples for isotopes analysis were dried and milled. The $^{13}C/^{12}C$ isotope ratios are expressed as $\delta^{13}C$ values:

$$\delta^{13}C\ (‰) = [(R_{sam} / R_{std}) - 1] \times 10^3, \quad (2)$$

with R_{sam} = $^{13}C/^{12}C$ isotope ratio of the sample and R_{std} = $^{13}C/^{12}C$ isotope ratio of the reference standard V-PDB (Vienna PeeDee Belemnite). The proportion of SOC derived from pasture vegetation (= pasture-derived SOC = C_4–SOC) was calculated according to (Balesdent & Mariotti, 1996):

$$f = (\delta_{sam} - \delta_{ref}) / (\delta_{vegsam} - \delta_{vegref}), \quad (3)$$

where f is the proportion of pasture-derived SOC in the sample, δ_{sam} is the measured $\delta^{13}C$ value of the pasture topsoil sample or of the secondary forest topsoil, δ_{ref} is the $\delta^{13}C$ value of the corresponding sample from the natural forest as C_3 reference soil, and δ_{vegsam} are the $\delta^{13}C$ values of fine roots collected from the topsoil of the pastures or from the topsoil of secondary forests, and δ_{vegref} are the $\delta^{13}C$ values of fine roots collected from the topsoil of the natural forests. We used the $\delta^{13}C$ values of fine roots in this calculation because all A horizons of the pasture were intensively rooted and we assume that the pasture-derived SOC in these horizons originated mainly from grass roots.

5.4 Results

5.4.1 Influence of Soil Type and Land Use on Soil Organic Carbon in Density Fractions

For all sites, the majority of total SOC was associated with the HF <53 µm (Table 5-2). The amount of carbon stored in the HF was greater in volcanic ash soils (23.2 ± 1.1 Mg ha^{-1}) than in sedimentary soils (15.8 ± 0.8 Mg ha^{-1}; means calculated from Table 5-3). The relative contribution of the LF to total SOC was slightly less for sedimentary soils (14.0% ± 0.9%) than for volcanic ash soils (17.6% ± 0.9%; means calculated from Table 2). Land use influenced the relative contribution of the density fractions to total SOC storage independently of soil parent material. Under natural forest, the relative contribution of LF to total SOM was greater (sedimentary soils: 17.1% ± 1.5%; volcanic ash soils: 21.1% ± 1.8%) than under pasture (sedimentary soils 11.8% ± 1.5%; volcanic ash soils: 13.9% ± 1.3%). Secondary forest regrowth on former pastures led to an increase of LF in sedimentary soils: 15.8% ± 1.3%. In contrast, SOC storage in LF did not differ between secondary forests and pastures in volcanic ash soils (17.4% ± 1.3%, Table 5-2). There was only one site (Penas) where this general influence of land use on SOC partitioning among soil density fraction was not found. The amount of carbon stored in the HF >53 µm, that consisted of sand particles, was in all cases negligible (<0.03% of total SOC, data not shown). In volcanic ash soils, total carbon storage in LFs (7.6 ±0.6 Mg ha^{-1}) was almost two fold the sedimentary soils (4.3 ± 0.3 Mg ha^{-1}; means calculated from Table 5-3).

Further, the absolute amount of carbon stored in different density fractions was influenced by land use type: in sedimentary soils the free LF contained more carbon under natural forest (1.1 ± 0.2 Mg ha^{-1}) than under secondary forest (0.7 ± 0.1 Mg ha^{-1}) and pasture (0.4 ± 0.1 Mg ha^{-1}, means calculated from Table 3). In the occluded I LF, more carbon was stored under natural forest (4.2 ± 0.5 Mg ha^{-1}) and secondary forest (3.7 ± 0.5 Mg ha^{-1}) than under pasture (1.8 ± 0.3 Mg ha^{-1}). In contrast, under pasture more carbon was stored in the occluded II LF (0.6 ± 0.1 Mg ha^{-1}) compared to natural forests (0.1 ± 0.0 Mg ha^{-1}). One exception was the Chonta Duro site, where no differences were found between land use types. More carbon was stored in the HF of natural forest (20.0 ± 1.7 Mg ha^{-1}) and secondary forest (16.6 ± 1.6 Mg ha^{-1}) compared to pasture (12.6 ±1.8 Mg ha^{-1}; means calculated from Table 3). Also, here again, land use did not influence the carbon storage at the site Chonta Duro.

In volcanic ash soils, a similar order of soil density fractions with respect to SOC storage was found: more SOC was stored in the free LF under forest (natural forest: 2.1 ± 0.4 Mg ha^{-1}, secondary forest 1.9 ± 0.3 Mg ha^{-1}) than under pasture (0.9 ± 0.1 Mg ha^{-1}). Carbon storage in the occluded I LF was grater under natural forest

Table 5-2a: Dry matter yield and soil organic carbon (SOC) storage of macro- and microaggregates (expressed as contribution to total soil C in 1 kg soil), carbon storage in free light, occluded I light, and occluded II light fractions of micro- and macroaggregates of volcanic ash soils under different land use (means (n=4) and standard error; nf =natural forest; ps=pasture, sf= secondary forest).

							Heavy fraction		Light fractions					
Site	Land use	Aggregate size	Dry matter yield		SOC		HF < 53µm		Free LF		Occluded I LF		Occluded II LF	
		/ µm	/ %		/ Mg C ha^{-1}		/ % of SOC in bulk soil							
Mindo	nf	250-8000	75	(2)	20.3	(3.6)	40.4	(1.1)	4.6	(1.0)	12.1	(1.0)	0.9	(0.2)
	nf	53-250	17	(1)	4.7	(0.7)	10.6	(1.5)	1.2	(0.1)	0.9	(0.1)	0.3	(0.2)
	ps	250-8000	75	(1)	22.2	(2.9)	49.5	(8.6)	2.4	(0.6)	11.7	(0.6)	2.6	(0.8)
	ps	53-250	17	(1)	4.1	(0.4)	9.4	(0.6)	0.5	(0.0)	1.0	(0.0)	0.7	(0.4)
	sf	250-8000	77	(1)	23.7	(2.7)	39.3	(2.9)	5.9	(0.5)	12.1	(0.5)	0.7	(0.2)
	sf	53-250	16	(1)	4.6	(0.3)	9.7	(1.1)	1.4	(0.1)	2.0	(0.1)	0.1	(0.0)
Maquipucuna	nf	250-8000	78	(3)	25.8	(1.0)	45.3	(5.2)	3.0	(0.4)	16.9	(0.4)	0.3	(0.0)
	nf	53-250	13	(2)	3.7	(0.6)	6.2	(0.8)	0.9	(0.3)	2.1	(0.3)	0.1	(0.0)
	ps	250-8000	76	(2)	26.6	(4.0)	49.2	(2.5)	1.7	(0.2)	4.9	(0.2)	2.9	(0.6)
	ps	53-250	19	(2)	5.4	(0.7)	11.8	(0.8)	0.2	(0.0)	0.6	(0.0)	0.4	(0.3)
	sf	250-8000	67	(4)	18.3	(1.8)	45.2	(4.0)	2.8	(0.1)	7.2	(0.1)	0.2	(0.0)
	sf	53-250	21	(2)	4.8	(0.3)	14.0	(2.5)	0.8	(0.2)	1.5	(0.2)	0.2	(0.1)
Pedro Viciente	nf	250-8000	67	(2)	36.1	(2.9)	34.8	(4.5)	2.0	(0.7)	16.7	(0.7)	0.6	(0.1)
	nf	53-250	16	(1)	4.5	(0.2)	5.9	(0.7)	0.9	(0.2)	1.5	(0.2)	0.2	(0.0)
	ps	250-8000	72	(6)	24.0	(2.8)	54.9	(4.9)	1.0	(0.2)	6.3	(0.2)	2.1	(0.2)
	ps	53-250	15	(3)	2.6	(0.4)	6.5	(0.9)	0.2	(0.1)	0.4	(0.1)	0.2	(0.0)
	sf	250-8000	72	(2)	29.6	(1.8)	42.7	(6.6)	1.9	(0.2)	9.4	(0.2)	0.4	(0.1)
	sf	53-250	15	(1)	3.2	(0.4)	5.7	(0.3)	0.8	(0.1)	1.1	(0.1)	0.2	(0.0)
Pitzara	nf	250-8000	75	(1)	46.6	(3.9)	51.7	(3.5)	4.1	(1.3)	12.8	(1.3)	0.1	(0.0)
	nf	53-250	13	(1)	5.1	(0.2)	6.3	(1.1)	1.1	(0.5)	1.1	(0.5)	0.1	(0.0)
	ps	250-8000	80	(3)	44.9	(3.9)	62.2	(0.9)	3.0	(0.6)	10.8	(0.6)	1.8	(0.3)
	ps	53-250	11	(2)	4.2	(0.5)	6.9	(0.8)	0.2	(0.0)	0.6	(0.0)	0.2	(0.0)
	sf	250-8000	80	(3)	43.7	(2.6)	54.6	(4.1)	5.1	(1.2)	13.9	(1.2)	0.2	(0.0)
	sf	53-250	11	(2)	4.4	(0.4)	5.9	(0.6)	0.6	(0.2)	1.3	(0.2)	0.1	(0.0)

[a] nd= not determined due to insufficient sample size.

(7.6 ± 0.9 Mg ha^{-1}) than under secondary forest (5.0 ± 0.7 Mg ha^{-1}) and pasture (3.6 ± 0.5 Mg ha^{-1}; means calculated from and Table 5-3). In pasture soils, the occluded II LF was, with 1.1 ± 0.1 Mg ha^{-1}, in the same range as the free LF material and considerably more than in secondary and natural forest soils (0.2 to 0.3 ± 0.0 Mg ha^{-1}). Land use did not influence the total SOC storage in the HF of volcanic ash soils (Table 5-3).

In volcanic ash soils, the amount of SOC stored in free LFs was positively correlated with clay + silt (r = 0.41; Figure 2), while the occluded I LF correlated with clay + silt (r = 0.58; Figure 2), and with MWD (r = 0.45). The amount of SOC associated with the HF correlated with clay + silt (r = 0.85) and MWD (r = 0.63). In

Table 5-2b: Dry matter yield and soil organic carbon (SOC) storage of macro- and microaggregates (expressed as contribution to total soil C in 1 kg soil), carbon storage in free light, occluded I light, and occluded II light fractions of micro- and macroaggregates of sedimentary soils under different land use (means (n=4) and standard error; nf =natural forest; ps=pasture, sf= secondary forest).

Site	Land use	Aggregate size	Dry matter yield		SOC		Heavy fraction HF < 53µm		Light fractions Free LF		Occluded I LF		Occluded II LF	
		/ µm	/ %		/ Mg C ha^{-1}		/ % of SOC in bulk soil							
Tazones	nf	250-8000	84	(3)	27.7	(4.6)	45.3	(3.3)	3.1	(0.1)	14.5	(0.1)	0.2	(0.1)
	nf	53-250	5	(1)	0.8	(0.3)	1.8	(0.5)	0.5	(0.1)	1.1	(0.1)	0.1	(0.0)
	ps	250-8000	71	(1)	12.2	(0.7)	42.2	(3.0)	1.3	(0.2)	4.1	(0.2)	2.4	(0.4)
	ps	53-250	12	(1)	1.2	(0.1)	3.3	(0.4)	0.7	(0.1)	0.8	(0.1)	0.8	(0.1)
	sf	250-8000	73	(6)	15.3	(3.3)	52.6	(6.4)	2.4	(0.4)	9.9	(0.4)	1.5	(0.2)
	sf	53-250	9	(3)	0.8	(0.3)	2.4	(0.6)	0.7	(0.2)	0.9	(0.2)	0.1	(0.0)
Penas	nf	250-8000	80	(4)	23.2	(4.0)	67.5	(6.3)	5.1	(2.4)	10.4	(2.4)	0.4	(0.2)
	nf	53-250	7	(1)	1.6	(0.2)	3.5	(0.8)	0.8	(0.1)	0.9	(0.1)	0.1	(0.0)
	ps	250-8000	73	(2)	13.2	(1.8)	40.5	(2.5)	1.9	(0.2)	11.4	(0.2)	3.8	(0.5)
	ps	53-250	8	(1)	1.0	(0.0)	2.6	(0.3)	1.1	(0.1)	0.8	(0.1)	0.8	(0.1)
	sf	250-8000	87	(1)	28.8	(1.6)	44.3	(2.4)	2.0	(0.3)	10.8	(0.3)	1.1	(0.2)
	sf	53-250	2	(0)	1.0	(0.1)	1.9	(0.2)	0.5	(nd)[a]	0.6	(nd)	0.0	(nd)
Chonta Duro	nf	250-8000	81	(3)	25.5	(4.5)	43.3	(5.5)	1.6	(0.3)	8.2	(0.3)	0.6	(0.3)
	nf	53-250	3	(0)	0.9	(0.1)	1.7	(0.4)	0.3	(0.1)	0.8	(0.1)	0.0	(0.0)
	ps	250-8000	84	(2)	23.7	(2.6)	50.2	(4.8)	1.0	(0.5)	3.0	(0.5)	0.5	(0.1)
	ps	53-250	2	(0)	0.8	(0.1)	2.2	(0.4)	0.1	(nd)	0.2	(nd)	0.1	(nd)
	sf	250-8000	85	(2)	23.0	(2.1)	51.8	(4.0)	1.5	(0.4)	8.5	(0.4)	0.4	(0.1)
	sf	53-250	3	(0)	0.9	(0.1)	2.6	(0.3)	0.7	(0.1)	0.1	(0.1)	0.0	(0.0)
Minas	nf	250-8000	91	(1)	30.1	(2.4)	68.2	(2.9)	2.8	(0.8)	16.4	(0.8)	0.1	(0.0)
	nf	53-250	3	(0)	1.0	(0.1)	1.7	(0.2)	0.3	(nd)	0.8	(nd)	0.0	(nd)
	ps	250-8000	91	(1)	26.8	(0.8)	66.5	(2.7)	1.5	(0.5)	9.0	(0.5)	1.1	(0.2)
	ps	53-250	2	(0)	1.0	(0.1)	2.5	(0.2)	0.1	(nd)	0.7	(nd)	0.0	(nd)
	sf	250-8000	93	(2)	29.5	(1.6)	65.2	(3.3)	2.2	(0.2)	18.4	(0.2)	0.8	(0.1)
	sf	53-250	1	(0)	0.5	nd	(nd)		(nd)		(nd)		(nd)	

[a] nd= not determined due to insufficient sample size.

sedimentary soils, we found no correlation of SOC stored in the free LF with clay + silt. The amount of C stored in occluded I LF material increased with increasing silt + clay (r = 0.44; Figure 2), and MWD (r = 0.37; P <0.01). Excluding the Chonta Duro site increased r considerably (silt + clay: r = 0.73; MWD: r = 0.52). Finally, the amount of carbon stored in the HF material correlated with silt + clay (r = 0.65; Figure 5-2) and MWD: (r = 0.56). Also here, exclusion of the Chonta Duro site improved correlations (silt + clay: r = 0.83; MWD: r = 0.61).

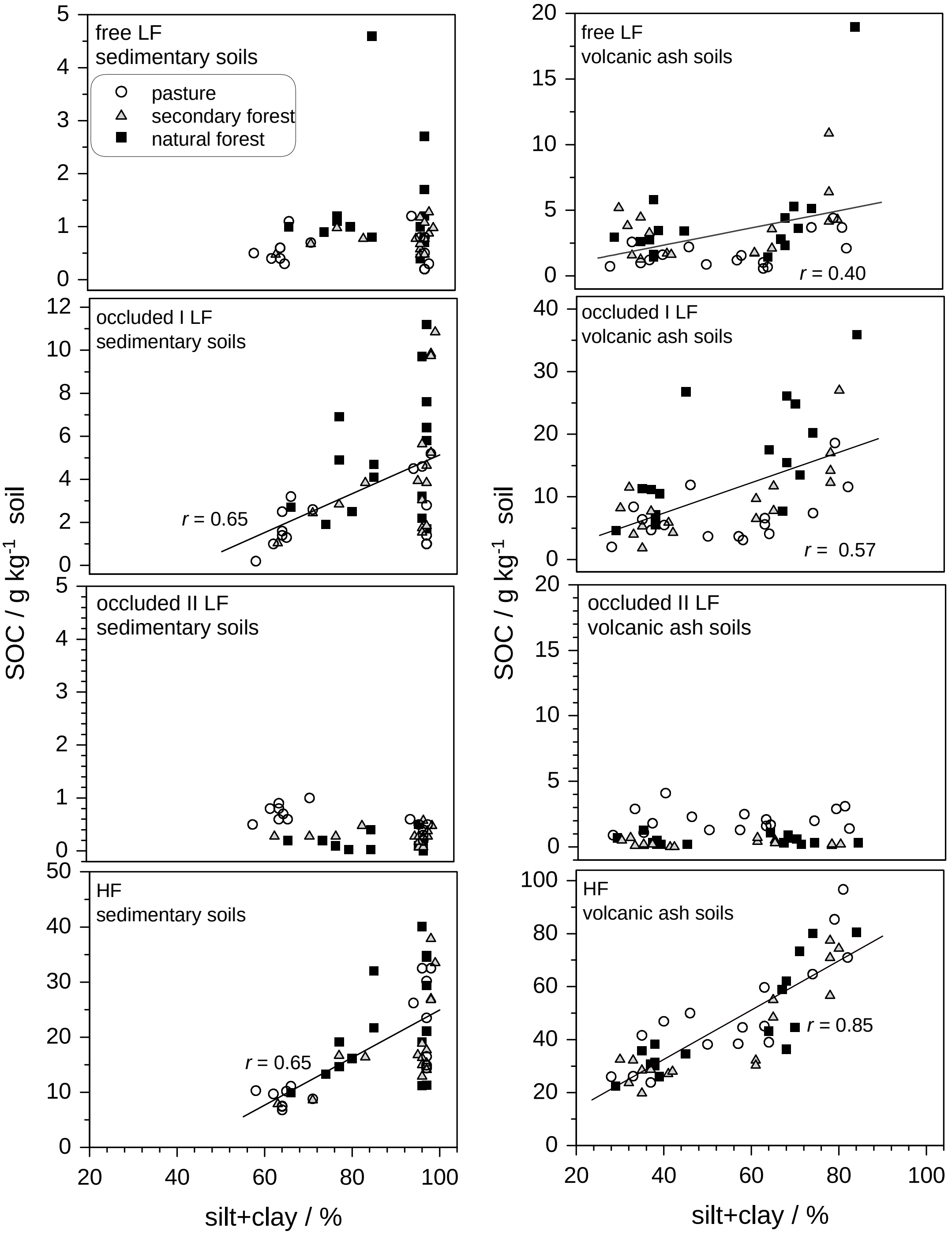

Figure 5-2: Relation of SOC concentrations in free LF, occluded I LF, occluded II LF and HF with silt+clay content of volcanic ash and sedimentary soils of different land use types.

5.4.2 C/N Ratio of Density Fractions

The C/N ratios in the HF material were influenced by soil type and land use. In sedimentary soils, C/N ratios were smaller than in volcanic ash soils, and generally smaller in pasture than in natural forest soils (sedimentary soils: pasture 7.9, natural forest 8.2; volcanic ash soils: pasture 12.0, natural forest 14.2; means calculated from Table 5-4). In contrast, C/N ratios of occluded I LF depended neither on soil parent material nor on land use. In addition, C/N ratios of occluded I LF were greater (14.2 to 25.4) than those of the HF. In the pasture sites of the volcanic ash soils, C/N ratios of the occluded II LF (17.8 to 25.8) were greater than those of the free LF (15.6 to 21.8) and of the occluded I LF (14.2 to 20.8). Sites of volcanic ash soils with much sand (Mindo and Maquipucuna) had smaller C/N ratios compared to sites with less sand (Pedro Viciente and Pitzara; Table 5-4).

5.4.3 δ^{13}C Values and Partitioning of Pasture-derived Carbon in Density Fractions

Under natural forest and secondary forest, fine roots had small δ^{13}C values (-28.7 to -30.9‰), while pasture roots had large δ^{13}C values (-11.2 to -14.1‰; Table 5-3). The δ^{13}C values of HF under natural forests were slightly less in volcanic ash soils (-27.2 to -28.2‰) than in sedimentary soils (-25.7 to -27.1‰; Table 5-3).

In pasture, SOC associated with occluded II LF had the greatest contribution of new, pasture-derived carbon, which was followed by free LFs, HFs and occluded I LFs (Figure 5-3). In the pasture at the Minas site, the calculated contribution of pasture-derived carbon in the occluded II LF was 110% due to an exceptionally small δ^{13}C value in the occluded II LF in natural forest (Table 5-3). For the same reason, we calculated a relatively high contribution of pasture-derived carbon for the secondary forest of the Minas site in the occluded II LF, which highlights the limits of the ^{13}C natural abundance approach. The greatest contribution of pasture-derived carbon in the sedimentary soils under secondary forest was generally associated with the HF. In volcanic ash soils, no C_4 carbon could be detected in any density fraction of the secondary forest.

Table 5-3. Mean C/N ratios and $\delta^{13}C$ values (n=4, and standard error) of SOC in different soil density fractions (free LF, occluded I LF , and occluded II LF and HF) and $\delta^{13}C$ value of fine roots of sedimentary soils and volcanic ash soils under natural forest (nf), pasture (ps) and secondary forest (sf).

		Light fractions			Heavy fraction		Light fractions			Heavy fraction
Site	Use	Free LF	Occluded I LF	Occluded II LF	HF <53µm	Roots	Free LF	Occluded I LF	Occluded II LF	HF <53µm
		C/N				$\delta^{13}C$ / $^{o}/_{oo}$ V-PDB				
Sedimentary soils										
Tazones	nf	nd[a]	17.8 (0.9)	nd	8.1 (0.1)	-28.9 (0.1)	-28.2 (0.3)	-28.6 (0.3)	-28.3 (0.2)	-27.0 (0.2)
	ps	nd	18.4 (0.6)	nd	7.9 (0.3)	-13.9 (0.6)	-19.9 (0.5)	-23.5 (0.1)	-16.2 (0.2)	-19.9 (0.5)
	sf	nd	17.1 (1.0)	nd	7.7 (0.4)	-29.2 (0.3)	-27.8 (0.2)	-27.1 (0.3)	-28.0 (0.1)	-24.6 (0.3)
Penas	nf	nd	20.6 (1.2)	nd	8.2 (0.1)	-28.6 (0.5)	-28.9 (0.3)	-29.0 (0.3)	-29.0 (0.5)	-27.1 (0.2)
	ps	nd	16.8 (1.6)	nd	8.2 (0.2)	-13.9 (0.6)	-20.8 (0.3)	-23.4 (0.2)	-18.2 (0.6)	-19.9 (0.3)
	sf	nd	19.2 (3.0)	nd	7.1 (0.3)	-29.1 (0.2)	-28.4 (0.2)	-26.8 (0.2)	-27.1 (0.1)	-24.0 (0.3)
Chonta Duro	nf	nd	20.0 (0.9)	nd	7.7 (0.2)	-28.6 (0.4)	-28.4 (0.3)	-28.4 (0.2)	-29.1 (0.7)	-26.7 (0.1)
	ps	nd	14.7 (0.7)	nd	7.3 (0.2)	-13.0 (0.4)	-18.5 (1.4)	-23.0 (0.3)	-18.1 (0.3)	-19.3 (0.4)
	sf	nd	24.3 (11.3)	nd	7.1 (0.3)	-28.0 (0.3)	-28.1 (0.1)	-28.4 (0.1)	-27.5 (0.1)	-26.1 (0.1)
Minas	nf	nd	18.8 (0.5)	nd	8.6 (0.2)	-28.7 (0.1)	-27.8 (0.2)	-27.8 (0.1)	-30.9 (0.4)	-25.7 (0.2)
	ps	nd	20.9 (0.4)	nd	8.1 (nd)	-13.6 (0.2)	-19.9 (2.0)	-23.0 (0.3)	-14.3 (0.4)	-20.2 (0.3)
	sf	nd	20.7 (2.0)	nd	8.0 (0.2)	-28.1 (0.4)	-25.9 (0.7)	-26.3 (0.4)	-24.6 (1.1)	-23.1 (0.4)
Volcanic ash soils										
Mindo	nf	19.3 (1.2)	18.7 (0.6)	nd	13.8 (0.3)	-29.1 (0.2)	-28.6 (0.1)	-28.2 (0.1)	-28.4 (0.1)	-27.2 (0.1)
	ps	15.6 (0.8)	14.2 (0.7)	17.8 (2.1)	11.9 (0.6)	-11.2 (0.0)	-17.9 (1.0)	-20.5 (0.8)	-14.0 (0.2)	-18.3 (0.3)
	sf	16.7 (1.2)	17.7 (1.9)	nd	13.5 (0.3)	-28.7 (0.3)	-28.4 (0.2)	-28.4 (0.2)	-28.4 (0.3)	-27.4 (0.1)
Maquipucuna	nf	18.5 (1.5)	18.6 (1.9)	nd	12.1 (0.2)	-29.1 (0.1)	-28.6 (0.3)	-28.4 (0.2)	-29.1 (0.0)	-27.1 (0.1)
	ps	18.7 (0.4)	14.3 (1.0)	21.0 (7.1)	11.9 (0.7)	-11.7 (0.2)	-14.7 (0.8)	-18.1 (1.1)	-13.0 (0.4)	-17.3 (0.9)
	sf	17.0 (1.4)	16.8 (0.7)	nd	11.4 (0.2)	-28.8 (0.1)	-28.7 (0.0)	-28.5 (0.1)	-28.7 (0.0)	-26.9 (0.0)
PedroViciente	nf	24.3 (0.7)	20.2 (0.5)	nd	14.6 (0.4)	-30.2 (0.2)	-29.2 (0.3)	-29.2 (0.2)	-29.0 (0.2)	-28.2 (0.1)
	ps	19.0 (1.0)	19.2 (0.7)	23.4 (0.4)	11.7 (0.5)	-16.2 (0.4)	-24.5 (1.0)	-27.8 (0.2)	-22.2 (1.3)	-26.2 (0.3)
	sf	24.6 (1.0)	25.4 (1.5)	nd	13.2 (0.3)	-30.1 (0.2)	-29.1 (0.4)	-29.7 (0.1)	-29.4 (0.2)	-28.0 (0.1)
Pitzara	nf	18.2 (0.9)	19.9 (0.8)	nd	14.2 (0.3)	-30.0 (0.2)	-28.6 (0.2)	-28.9 (0.1)	-29.4 (0.1)	-27.8 (0.2)
	ps	21.8 (4.0)	20.8 (2.6)	25.8 (2.1)	12.5 (1.0)	-14.1 (0.8)	-22.4 (1.0)	-26.3 (0.3)	-16.1 (0.3)	-23.7 (0.4)
	sf	24.4 (3.7)	20.3 (12.0)	nd	12.0 (0.5)	-28.2 (0.1)	-28.6 (0.1)	-28.7 (0.1)	-28.9 (0.0)	-27.5 (0.0)

[a] nd= not determined due to insufficient sample size.

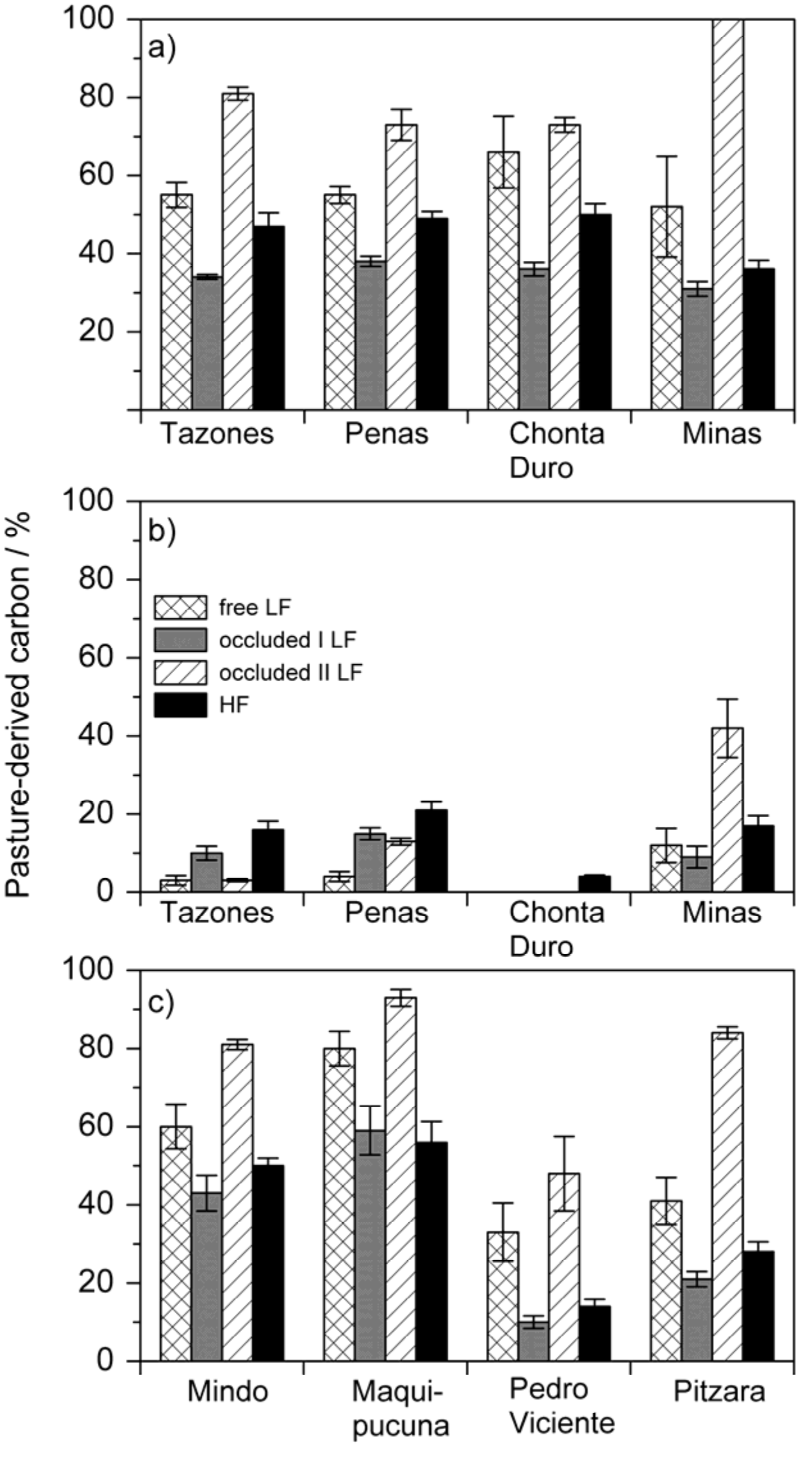

Figure 5-3: Proportion of pasture-derived carbon in density fractions of a) pastures and b) secondary forests of sedimentary soils and c) pastures of volcanic ash soils. Calculated pasture-derived carbon in the pasture at Minas was overestimated (110%) due to a low $\delta^{13}C$ value for the occluded II light fraction in natural forests compared to root litter input (Table 5-3). For the same reason relatively high pasture-derived carbon was calculated for secondary forest of Minas in the occluded II light fraction. In the secondary forest of Chonta Duro no pasture-derived carbon was detected in the light fractions. There was no pasture-derived carbon in volcanic ash soils under secondary forest.

5.5 Discussion

5.5.1 Effects of Soil Type and Land Use on Soil Organic Carbon Distribution among Soil Density Fractions

Conversion of forest to pasture resulted in a decline in the amount of SOC stored in the LF material independent of soil parent material**.** A reduction in SOC storage in the LF has also been found in other studies under contrasting soil types and climates (e.g. John et al., 2005; Dalal et al., 2005). A recent review showed that the relative proportions of SOC stored in the LF (<1.9 g cm^{-3}) can vary from 1.8 to 55.4% (mean 10.1%) in grasslands and from 0.3 to 74% (mean 16.0%) in forests (Gregorich et al., 2006). In general, soils with a considerable microbial activity and easily available plant residues and soils with little plant residue input have small proportions of LF. Response of changes in SOC storage in the HF depended on soil parent material: smaller total carbon stocks in sedimentary soil under pasture could be related to smaller carbon stocks of both LFs and HFs. In contrast, in volcanic ash soils, a decline of carbon stocks under pasture was only related to smaller carbon stocks in the LFs and not in HFs.

Afforestation of former pasture almost doubled the SOC stocks in the LF of sedimentary soils. Similar results have been found in a Brazilian Oxisol where more SOC was stored in the LF under afforestation plots compared to grasslands (de Alcantara et al., 2004). In contrast, in volcanic ash soils, we could not detect differences in total SOC storage of LF between secondary forests and pastures. The limited amount of studies investigating SOC dynamics in soil fractions during afforestation makes it difficult to identify factors controlling changes in SOC of LFs.

The major part of SOC was stored in the HF independent of soil parent material, which was also found by previous studies (Gregorich et al., 2006; von Lützow et al., 2007). This is explained by strong interactions between minerals of the clay fraction and organic matter. The greater carbon concentrations found in volcanic ash soils are generally explained by the large specific surface area of allophane in combination with large amounts of non-crystalline compounds (Saggar et al., 1996; Feller & Beare, 1997; Six et al., 2002). Apart from the strong interaction of organic matter with mineral surfaces in volcanic ash soils, larger amounts of LF also contribute to the elevated carbon concentrations found in these soils.

5.5.2 Effect of Aggregation on Soil Organic Carbon Distribution among Density Fractions

For both soil types, we found larger amounts of SOC stored in the occluded I LF with increasing silt+clay content. Similar results were found by Kölbl & Kögel-Knaber (2004) for temperate arable soils. The correlation of SOC in occluded LF with particle-size distribution may result from the effect of clay-sized material on aggregate formation and stability. Strong aggregation leads to stronger physical protection of occluded LF inside aggregates. This conclusion is supported by the correlation of MWD with the amount of occluded I LF in both soil types. Within our volcanic ash soils, greater C/N ratios of the occluded I LF were observed at sites with large amounts of silt + clay and strong aggregation. This may indicate that aggregation stabilizes less-decomposed material. Using ^{13}C NMR analysis, Kölbl & Kögel-Knabner (2004) found that the degree of degradation of free and occluded LFs decreased with greater clay contents.

The amount of free LF showed no correlation with the MWD and was independent of aggregation. In agricultural soils, Kölbl & Kögel-Knaber (2004) also observed no correlation of the amount of free LF with clay content. In soils with much biological activity, the amount free LF mainly depends on the decomposition rate, which is controlled by the primary recalcitrance of litter (von Lützow et al., 2006).

5.5.3 Partitioning of Pasture-derived Carbon among Density Fractions

Isolated LFs were heterogeneous in terms of their stability: in both soil types the free LF contained more recently incorporated carbon than the occluded LF. This has been also found for temperate agricultural soils (von Lützow et al., 2007) and tropical Oxisols (Golchin et al., 1995; Roscoe & Buurman, 2003). In our sedimentary soils after 30-35 years of pasture, 34-48% of free LF carbon was derived from C_3 vegetation and supposed to originate mainly from the original forest. This value is relatively large for a fraction usually considered as labile, but it is in the same range as found for other tropical pastures (Roscoe & Buurman, 2003; Schwendenmann & Pendall, 2006). Forest-derived charcoal, which is commonly found under tropical pastures, has been used to explain these slow turnover times of SOC in free LFs (Skjemstad et al., 1990).

The occluded I LF was the fraction with the smallest proportion of pasture-derived carbon, independent of soil parent material. Similar results were found in an Australian Oxisol after 35 years of pasture, where 38% of SOC in the occluded LF originated from C_4 grasses of the pasture (Golchin et al., 1995). An even longer pasture period (83 years) did not increase the C_4 contribution in this fraction (Golchin et al., 1995). Slow turnover of occluded LF can thus be explained by i) accumulation of recalcitrant organic matter and ii) physical protection from decomposition in soil aggregates.

5.5.4 Occluded II Light Fraction – Organic Core of Initial Aggregate Formation

Oades & Waters (1991) have postulated that plant debris forms the organic core of newly developed microaggregates. We have strong indications that the fraction that we call occluded II LF, which was separated from very stable microaggregates, represented such aggregate cores. Golchin et al. (1994a) developed a conceptual model to link the turnover of organic matter with its chemical composition and aggregate stability: Particulate organic matter entering the soil from roots or litter is first colonized by microbes to form organo-mineral particles. These plant fragments are encrusted and then form the nucleus of water-stable aggregates. These cores consist of fresh, relatively unaltered plant material. These newly formed aggregates are very stable as mucilage and metabolites stabilize the whole aggregate. Due to the intimate association of plant fragments with minerals these newly formed aggregates were not destroyed by ultrasonic dispersion and therefore are recovered in density fraction of 1.8 to 2.0 g cm^{-3}. Accordingly, the occluded LF (1.8-2.0 g cm^{-3}) showed the second greatest contribution of recently incorporated carbon after the free LF >1.6 g cm^{-3} in two Australian Oxisols (Golchin et al., 1995). The occluded II LF in our study was isolated from the most stable microaggregates that were not destroyed after 18 hours of shaking with glass pearls. Only after manual destruction of these aggregates, was the occluded II LF released. We therefore assume that this fraction represents the cores of the initial stage of aggregate formation. This assumption is supported by the greatest pasture-derived carbon content and largest C/N ratio in this fraction. In addition, microscopy revealed that occluded II LF consisted mainly of cellular plant structures.

The greater contribution of occluded II LF to total SOC under pasture compared to forest soils may be explained by the much greater root density in the upper 0.1 m of pasture soils. The results suggest that the fraction of occluded II LF was favoured by aggregate formation around the debris of fine young roots. Although pasture soils contained more very stable microaggregates with occluded II LF, this did not result in much SOC storage in total occluded LF (occluded I LF + occluded II LF).

5.5.5 Light Fractions as Sensitive Indicator for Land Use Changes?

Changes in carbon storage were more pronounced in LFs compared to whole soils. While deforestation and pasture establishment reduced total SOC storage in the upper 0.1 m by 20%, less than 50% of the SOC stored in LFs of natural forest was found in the LF of pasture soils. The occluded II LF displayed the strongest reduction in SOC storage and the fastest turnover rates due to the afforestation of pastures. Although occluded I LF in pasture soils had relatively slow turnover rates, it responded to deforestation with a considerable reduction in SOC storage, supporting the idea that LFs are more sensitive to land use changes than total SOC (Gregorich et al., 2006). This reduction was partly reversible by forest regrowth. However, the effect of reduced LFs on total soil organic carbon storage and stabilization processes in the long term remains unclear.

5.6 Conclusion

We found that independent of soil parent material, deforestation and pasture establishment reduced SOC storage in free and occluded LFs. By afforesting the former pasture, the amount SOC stored in LFs increased, but the natural forest values were not reached in all cases. Changes in SOC stocks were more pronounced in the LFs compared to bulk soil. Thus, LFs can be used as an early indicator for SOC changes induced by land use changes. Our results show that land use change affects not only total SOC stocks but also the partitioning of carbon to different functional SOC fractions. Furthermore the correlation of aggregation with the amount of occluded I LF and its slow turnover supported the hypothesis that SOC is stabilized within aggregates in both soil types. Finally, the fast turnover and large contribution of pasture-derived carbon in the occluded II LF, which was separated from very stable microaggregates, strongly suggested that this fraction is important in the initial process of aggregate formation.

The large amount of LFs in volcanic ash soils showed that considerable SOC storage in volcanic ash soils is not solely due to great storage of silt + clay-associated organic matter, but also due to greater storage in LFs. Recently incorporated pasture-derived SOC was less stabilized in the volcanic ash soils compared to sedimentary soils: the pasture-derived SOC that accumulated during up to 30 years of pasture use was not transferred to a stable or passive SOC fraction in volcanic ash soils. This implies instability of recently incorporated pasture-derived SOC that is bound to minerals, maybe because all high affinity sites were already occupied with organic matter. In contrast, the mineral surfaces of sedimentary soils formed stronger interactions with recently incorporated pasture-derived SOC.

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6 Soil C in Chemically Isolated Fractions*

6.1 Abstract

Quantitative knowledge of pool sizes and rates of formation of stable soil organic matter (SOM) is essential for the understanding and prediction of the function of soils in the global carbon cycle. However, until now knowledge of effects of different soil types on the storage of stable SOM is limited, especially in the tropics. We compare the amount of mineral-associated SOM resistant to different chemical fractionation in soils of different parent material and mineralogical composition (volcanic ashes - dominated by short-range-order aluminosilicates and marine Tertiary sediments - dominated by smectitic clays) in the humid tropics of Northwest Ecuador. Using ^{13}C isotope analyses we traced the origin of soil organic carbon (SOC) in mineral-associated soil fractions resistant to treatment with HCl, NaOCl, and $Na_4P_2O_7$ under pasture (C_4) and secondary forest (C_3). Prior to chemical fractionation, the light particulate SOM was removed by density fractionation to gain the mineral-associated SOM. NaOCl was the most efficient treatment in reducing SOC content in the residuum by 94% in soils developed in marine Tertiary sediments and 82% in soils derived from volcanic ashes, followed by HCl (55%) and $Na_4P_2O_7$ treatment (26% soils derived from marine Tertiary sediments / 46% soils derived from volcanic ashes). SOC concentration in all residual fractions strongly correlated with initial concentrations of mineral-associated SOC and was higher in natural forest soils than in pasture soils. HCl treatment was nearly ineffective in preferentially removing recently incorporated SOC. In contrast, proportion of pasture-derived SOC in residual fraction of NaOCl and in the extracts of $Na_4P_2O_7$ was halved following the chemical treatment. This suggests that forest-derived SOC was more closely associated with the mineral phase than recently incorporated pasture-derived SOC. However, isotope data revealed that recently incorporated SOC did not contribute to a long-term stabilized SOM pool in these soils, but in soils derived from marine Tertiary sediments. Thus, the outcome of these fractionation methods is sensitive to soil type which makes interpretation challenging and precludes any generalisation to other soils types or climates.

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6.2 Introduction

Globally, soils contain about 75% of the terrestrial organic carbon pool of which 32% are located in the tropics (Jobaggy and Jackson, 2000). Decomposition of soil organic matter (SOM) contributes to important fluxes of the global carbon cycle. SOM is a complex and heterogeneous mixture of plant- and microbial-derived compounds mainly associated with the mineral phase, which differs in mean residence time from month to centuries. This has lead to conceptual models where SOM is described in multiple pools with different stabilities and functions. Current models of SOM dynamics all include a passive pool having mean residence times from several hundred to thousands of years (Falloon and Smith, 2000). Due to its long-term stability, this SOM pool remains almost unaffected by land use changes on a decadal timescale, but is important as long-term sink for SOM. The following mechanisms may contribute to the long-term stabilization of SOM in soils: i) selective preservation of recalcitrant compounds, which are stable against biochemical decay due to their structure (e.g. aromatic or aliphatic compounds); ii) interactions between organic and inorganic substances, including e.g. ligand exchange and polyvalent cation bridges (Sollins et al., 1996; von Lützow et al., 2006). Other stabilization mechanisms, as the occlusion of SOM by aggregation reduces the spatially accessibility for microbes and enzymes, but are not considered to be important for long-term stabilization (Six et al., 2002; von Lützow et al., 2006).

Quantitative knowledge of the amount, stability and stabilization mechanisms of passive SOM pools is necessary to understand, assess, and predict long-term effects of land-use or climatic changes on the storage, stability and functionality of SOM. Various approaches have been introduced to determine the partitioning of SOM into different pools characterized by different turnover times and stability (Baldock et al., 2004). These approaches include base and acid hydrolysis, oxidative degradation of organic matter, destruction of mineral phases, density fractionation, and a combination of chemical and physical fractionation methods. However, at present there is no general accepted method to isolate a passive SOM pool or SOM pool stabilized by a specific mechanism (von Lützow et al., 2007). Moreover, knowledge about the stability and functionality of the isolated SOM fraction is scarce. In addition, our understanding of mineral-associated SOM fractions and mean residence time in different soil types is limited, especially in tropical soils, as most SOM fractionations were conducted on soils of temperate climate (Plante et al., 2004, Eusterhues et al., 2005; Helfrich et al., 2007; Zimmermann et al., 2007; Follet et al., 2007).

For the present study we tested three chemical fractionation techniques, which are assumed to isolate a distinct SOM pool according to their effect on SOM degradation, and applied this on soils from different parent material in the humid tropics of Ecuador. The most widely used method to gain a more stable SOM fraction is treatment with HCl which breaks bonds sensitive to acid hydrolysis (Six et al., 2002; Paul et al., 2006). In addition, inorganic binding partners are dissolved, which brings SOM in solution. Acid hydrolysis preferentially removes young, easily biodegradable compounds (e.g. proteins, polysaccharides) while more recalcitrant biomacromolecules (e.g. long chain alkyls, waxes, aromatics) are left behind (Leavitt et al., 1996; Paul et al., 2006). Thus, the non-hydrolysable fraction is proposed to represent a recalcitrant pool, which is a meaningful estimate for the passive pool in SOC models like Century (Parton et al., 1987). In most temperate soils the non-hydrolysable SOC was found to be about 1200 years (mean ^{14}C age) older than bulk SOC (Paul et al., 2006).

Other methods to isolate stable SOM pools use oxidative treatments like NaOCl to imitate natural oxidative processes in soils and to leave behind mineral-protected organic material (Mikutta et al., 2005; Kaiser and Guggenberger, 2007). An increase in mean ^{14}C ages of 75 to 1800 years after NaOCl treatment was found in a range of acidic subsoil samples from temperate and tropical forests (Kleber et al., 2005).

$Na_4P_2O_7$ treatment extracts SOM complexed by polyvalent cations as well as SOM attached to mineral surfaces (Shoji et al., 1993; Kaiser and Zech, 1996). The remarkably close correlations of SOM with pyrophosphate-soluble Al in volcanic ash soils are often explained with stabilization of SOM through Al-humus complexes and non-crystalline hydroxides. Aluminium-humus complexes are related to long-term stabilization of SOM (Torn et al., 1997).

In the humid tropics of Northwest Ecuador, long-term stabilization of SOM in soils derived from volcanic ashes has been explained by the formation of metal-humus complexes and allophanes, whereas in soils with smectitic clay minerals SOM appeared to be stabilized primarily through sorption to clay (López-Ulloa et al., 2005). On a selection of these sites, the mean residence time of recently incorporated SOC depended on clay mineralogy and was longer in soils dominated by smectite than for soils dominated by short-range-order aluminosilicates (Chapter 4). Furthermore, density fractionation of water-stable aggregates revealed that about 85% of SOC was associated with minerals in volcanic ash and sedimentary soils (Chapter 5).

In the present study, our objectives were i) to quantify the amount of mineral-bound SOM resistant to three chemical fractionation techniques (treatment with HCl, NaOCl, and $Na_4P_2O_7$) in soils of different parent material and mineralogical composition (volcanic ashes - dominated by short-range-order aluminosilicates and marine Tertiary sediments - dominated by smectitic clays); ii) to determine if SOM storage in these fractions depends on land-use (natural forest, pasture, secondary forest); iii) to evaluate these methods in terms of their ability to separate older forest-derived SOC from recently incorporated pasture-derived SOC. We combined chemical fractionation of mineral-associated SOM with ^{13}C isotope analyses on soil samples from natural forest, pastures and secondary forest sites that had undergone C_3-C_4-C_3 vegetation changes in the humid tropics of Northwest Ecuador.

6.3 Materials & Methods

6.3.1 Site Description

Our sites were located in Northwest Ecuador which has a humid tropical climate. Four sites had soils developed from volcanic ashes and varied in silt + clay content (35-79%). The clay mineralogy is characterized by the presence of allophane (de Koning et al., 2003). These soils were classified as Hapludands. Soils of the other four sites were developed from marine Tertiary sediments and differed also in silt + clay content (62-83%). These soils were classified as Haplustepts and Paleustalfs (Soil Survey Staff, 1998). X-ray diffraction of clay fraction of sedimentary soils revealed that sedimentary soils were dominated by smectite with marginal contribution of illite, chlorite, and kaolinite. At each site, we selected a natural forest plot (which we call ‘natural forest’ (=nf)), a pasture plot (=ps), and a secondary forest or tree plantation plot. Pasture plots had been established after cutting and burning natural forest. Pastures were dominated by C_4 grasses (*Paspalum dilatatum* Poir., *Panicum maximum* Jaqc., *Cynodon plectostachyus* (K. Schum.) Pilger. Secondary forests formed on abandoned pastures due to natural succession without management, whereas the plantations were established on former pastures by planting trees. As there were no differences in SOC contents between secondary forests and plantations (de Koning et al., 2003), these sites were grouped and analyzed together (we call these sites ‘secondary forest’ (=sf)). Soil samples and root samples (down to 0.1 m depth) were taken at each site (n = 4). General soil characteristics and land use history are described in Table 6-1. A more detailed site description and soil characteristics were given in chapter 4.

6.3.2 Soil Analysis

Particle size distribution of soils derived from marine Tertiary sediments was done after Hartge and Horn (1989). As the determination of clay content for allophane containing soils reveals ambiguous results due to incomplete dispersion (Nanzyo et al., 1993), we did not determine the clay content in soils derived from volcanic ashes. Sand content (particles >53 µm) was determined by dispersion with sodium pyrophosphate and wet sieving at 53 µm. Selective dissolution was done using acid ammonium-oxalate extraction of aluminium (Al_o) and iron (Fe_o), and pyrophosphate extraction of aluminum (Al_p; Buurman et al., 1996). Total C and N of all soil fractions were measured using an automated C and N analyzer (Vario EL, Elementar, Hanau, Germany).

6.3.3 Chemical Fractionation

Prior to chemical fractionation, density fractionation was applied to all soil aggregates >53 µm to remove light particulate SOM to gain the mineral-associated SOM. Air-dried aggregates (7.5 g) were put in a centrifuge tube together with 40 ml sodium polytungstate solution (SPT; Sometu, Berlin, Germany) with a density of 1.6 g cm^{-3}. Aggregates were destroyed by adding 18 glass pearls to the residue and shaking the test tube for 18 hours at a frequency of 120 movements per minute and by gently pressing the aggregates against the mesh using a dough scraper (chapter 5). After 30 minutes of sedimentation, the solution was centrifuged for 1 hour at 5100 g. The residue was washed four times with distilled water and sieved (53 µm). The fraction < 53µm that contain mainly mineral-associated SOM served as starting material for all chemical fractionation methods.

Acid hydrolysis was carried out according to Plante et al. (2006). Briefly, 0.5 g soil (fraction < 53µm) was refluxed with 25 ml of 6M HCl for 16 hours. The HCl resistant SOM was washed with distilled water (soil: water ration: 1:80) until free of acid and freeze-dried. The sodium hypochlorite procedure was modified after Siregar et al. (2005). In brief, 1 g of soil (fraction < 53µm) was placed in 50 ml bottles and treated four times with 20 ml of 6 % NaOCl (pH 8) for a total of 24 hours. Afterwards, the NaOCl resistant soil was washed twice with 20 ml 1 M NaCl and distilled water until electrical conductivity was < 50µS. Extraction with pyrophosphate was done after Buurman et al. (1996). Briefly, 0.5 g of soil (fraction < 53µm) was shaken for 18 hours in 50 ml (soils derived from marine Tertiary sediments) or 100 ml (soils derived from volcanic ashes) 0.1M $Na_4P_2O_7$ (pH 10). Samples were centrifuged (1 hour at 5100 g) and supernatant were filtered (polyamide membrane filters, pore size: 0.45µm) and extracts were analysed for Al by inductively coupled plasma emission spectroscopy (Flame-ICP, Spectro Analytical Instruments, Kleve, Germany). For this measurement samples were diluted (1:10) and 100µl HNO_3 was added. The $Na_4P_2O_7$ residuum was washed with distilled water (soil to water ratio: 1:80) and dried at 40 °C.

6.3.4 Isotope Analyses

The $^{13}C/^{12}C$ isotope ratio was measured using an isotope ratio mass spectrometer (IRMS, Finnigan MAT, DELTAplus, Bremen, Germany) at the Center for Stable Isotopes Research and Analysis, University of Göttingen. Carbon isotope ratios were expressed as $\delta^{13}C$ ‰ (V-PDB). The proportion of SOC derived from pasture vegetation (= C4-SOC) was calculated according to Balesdent and Mariotti (1996):

$$f = (\delta_{sam} - \delta_{ref}) / (\delta_{pasture} - \delta_{forest}), \qquad (6\text{-}1)$$

where f is the proportion of pasture-derived SOC in the sample, δ_{sam} is the measured

$\delta^{13}C$ value of the topsoil sample, δ_{ref} is the $\delta^{13}C$ value of the corresponding sample from the natural forest as C_3 reference soil, and $\delta_{pasture}$ and δ_{forest} are the $\delta^{13}C$ values of fine roots collected from the topsoil of pastures and forests, respectively. Proportions of pasture-derived SOC after chemical fractionation were calculated under the assumption that isotopic shifts between untreated soil and chemical fraction observed in the natural forest occur analogous in the pasture. Note, in case of the $Na_4P_2O_7$ extraction, $\delta^{13}C$ was additionally measured on the extract as $\delta^{13}C$ differences to the bulk soil were more pronounced than in the residuum.

6.3.5 Statistical Analyses

Statistical analyses were carried out using ANOVA and multiple comparisons among land use types and parent material were conducted using least significant difference test at $P \leq 0.05$ if not indicated otherwise. Pearson correlation was used to assess the relationships of SOC in residual fractions to initial SOC content of mineral-associated fractions. All statistical analyses were carried out using the STATISTICA 6.1 software package (StatSoft Inc., Tulsa, Oklahoma, USA).

6.4 Results

6.4.1 Mineral-associated Soil Organic Carbon

Mineral-associated SOC concentrations of soils derived from volcanic ashes (range from 87 to 143 g kg^{-1}) were 3 to 4 times higher than in soils developed from marine Tertiary sediments (range from 21 to 44 g kg^{-1}, Table 6-2). Deforestation and pasture establishment was generally associated with losses of mineral-associated SOC and a decrease in C/N ratio independent of soil parent material (Table 6-2). In soils derived from marine Tertiary sediments, regrowth of secondary forest did not alter mineral-associated SOC concentrations. This was also found for soils derived from volcanic ashes at Pitzara and Maquipucuna, while at Mindo and Pedro Viciente higher mineral-associated SOC concentrations were found in secondary forest than in pasture soils. After 30 to 35 years of pasture on soils derived from marine Tertiary sediments, 40-50% of the mineral-associated SOC originated from pasture vegetation (Figure 6-1). After 13 to 50 years of pasture in soils derived from volcanic ashes, 15-57% of the mineral-associated SOC was pasture-derived. On soils derived from marine Tertiary sediments, forest regrowth for 10 to 17 years after pasture reduced the pasture-derived SOC to 3-19%, while no pasture-derived SOC was detected in any secondary forest of soils derived from volcanic ashes (Figure 6-2).

Table 6-1: General soil characteristics of the bulk soil (soil organic carbon (SOC) content; Aluminium extracted by pyrophosphate (Al_p) and acid-oxalate (Al_o), iron extracted by acid-oxalate (Fe_o)) and land use history of the different sites and land uses (means (n=4) and standard deviation in parentheses; nf =natural forest; ps=pasture, sf= secondary forest).

Site	Land use	Age of land use		SOC		Clay		Sand		Al_p		Al_o		Fe_o	
		— years —		g kg^{-1}											
Sedimentary soils		ps[a]	sf[b]												
Tazones	nf			30.8	(6.4)	287	(45)	269	(64)	0.2	(0.0)	1.3	(0.1)	1.0	(0.1)
	ps	35		20.2	(1.7)	324	(54)	377	(29)	0.3	(0.1)	0.8	(0.0)	2.5	(0.4)
	sf	21[c]	14	21.7	(7.2)	360	(79)	266	(86)	0.2	(0.1)	0.9	(0.1)	1.9	(0.2)
Penas	nf			28.7	(7.0)	369	(30)	190	(51)	0.2	(0.1)	1.1	(0.1)	1.9	(0.1)
	ps	30		19.3	(4.2)	293	(35)	340	(32)	0.3	(0.2)	0.5	(0.0)	1.7	(0.3)
	sf	20[c]	10	34.4	(3.2)	532	(26)	40	(9)	0.5	(0.2)	1.6	(0.1)	3.2	(0.5)
Chonta Duro	nf			35.1	(10.9)	592	(30)	37	(3)	0.3	(0.1)	1.4	(0.1)	3.7	(0.5)
	ps	35		33.0	(3.8)	607	(58)	27	(1)	1.1	(0.9)	1.3	(0.3)	4.7	(0.6)
	sf	20[c]	17	30.4	(5.4)	603	(17)	35	(2)	0.5	(0.3)	1.1	(0.1)	3.1	(0.5)
Minas	nf			49.6	(2.9)	622	(33)	33	(5)	0.3	(0.1)	1.5	(0.1)	2.8	(0.4)
	ps	33		44.0	(3.2)	619	(37)	39	(17)	0.6	(0.4)	1.6	(0.1)	3.5	(0.7)
	sf	20[c]	10	48.2	(4.5)	639	(22)	17	(6)	0.5	(0.2)	1.6	(0.1)	1.5	(0.3)
Volcanic ash soils															
Mindo	nf			62.3	(12.5)	nd[b]		655	(38)	4.9	(0.9)	5.5	(1.0)	3.6	(0.7)
	ps	20		60.5	(16.3)	nd		624	(61)	3.3	(0.5)	4.4	(0.7)	3.8	(0.6)
	sf	5[c]	23	59.0	(4.7)	nd		664	(30)	4.3	(0.4)	5.0	(0.4)	4.2	(1.7)
Maquipucuna	nf			60.9	(12.5)	nd		597	(32)	4.7	(0.6)	8.2	(0.4)	4.5	(0.6)
	ps	50		63.3	(11.2)	nd		560	(134)	4.4	(0.5)	7.3	(0.9)	5.4	(1.0)
	sf	30[c]	20	46.5	(10.0)	nd		622	(47)	4.4	(0.3)	8.3	(1.1)	5.1	(0.4)
Pedro Viciente	nf			114.7	(5.9)	nd		323	(26)	7.3	(0.4)	10.1	(1.3)	5.9	(0.9)
	ps	13		73.7	(8.0)	nd		383	(30)	6.3	(0.8)	16.4	(3.0)	6.5	(0.3)
	sf	8[c]	15	86.6	(8.5)	nd		372	(24)	8.4	(1.1)	17.3	(3.3)	6.5	(0.7)
Pitzara	nf			129.8	(35.3)	nd		262	(75)	10.8	(1.5)	19.0	(2.4)	6.8	(0.4)
	ps	20		106.2	(11.8)	nd		219	(38)	8.6	(2.2)	21.7	(1.4)	6.7	(0.3)
	sf	10[c]	10	116.2	(6.3)	nd		217	(11)	8.4	(0.6)	26.7	(1.6)	6.2	(0.1)

[a] pastures were established after clearing of natural forest

[b] secondary forests were established on former pastures

[c] duration of pasture before the site was changed to secondary forest

Table 6-2: Soil organic carbon (SOC) content and C/N ratios of soil fraction <53 µm and the residual fraction treatment with HCl, NaOCl and $Na_4P_2O_7$ of different sites and land use types (nf =natural forest; ps=pasture, sf= secondary forest), means and standard deviation.

Site		SOC								C/N							
		Mineral associated		HCl		NaOCl		$Na_4P_2O_7$		Mineral associated		HCl		NaOCl		$Na_4P_2O_7$	
		g kg^{-1}															
Soils derived from marine Tertiary Sediments																	
Tazones	nf	34	(1)	13.2	(0.1)	2.2	0.7	25.4	(0.6)	8.9	(0.2)	18.1	(1.6)	7.8	(1.1)	8.8	(0.2)
	ps	25	(1)	10.5	(0.3)	1.4	0.2	19.7	(0.8)	8.3	(0.1)	16.4	(1.0)	8.6	(1.1)	8.8	(0.2)
	sf	23	(2)	9.5	(1.0)	nd[a]		17.1	(2.2)	8.2	(0.3)	13.3	(0.6)	nd		8.7	(0.2)
Penas	nf	27	(4)	11.0	(2.1)	1.7	0.5	22.0	(5.1)	8.7	(0.2)	18.8	(2.0)	11.1	(1.2)	9.5	(0.2)
	ps	21	(2)	10.4	(1.4)	1.2	0.2	16.2	(1.7)	8.9	(0.2)	17.3	(0.9)	10.8	(2.3)	9.9	(0.3)
	sf	25	(1)	10.2	(1.0)	nd		18.3	(3.0)	7.9	(0.1)	14.4	(0.8)	nd		8.6	(0.2)
Chanta duro	nf	29	(7)	12.2	(3.1)	2.1	0.7	21.0	(4.9)	8.3	(0.2)	14.9	(0.9)	7.9	(1.6)	8.5	(0.3)
	ps	29	(3)	11.1	(1.1)	2.6	0.6	19.9	(1.3)	7.7	(0.2)	14.1	(0.9)	11.5	(2.3)	8.4	(0.4)
	sf	26	(2)	10.0	(0.9)	nd		18.1	(1.3)	7.6	(0.3)	12.3	(0.8)	nd		8.2	(0.2)
Minas	nf	44	(3)	20.2	(1.6)	2.7	0.4	34.1	(5.8)	9.0	(0.1)	16.5	(0.5)	8.3	(0.7)	8.9	(0.2)
	ps	36	(1)	17.1	(1.2)	2.2	0.2	25.8	(1.2)	8.5	(0.3)	15.3	(0.9)	9.2	(0.7)	8.8	(0.3)
	sf	36	(5)	16.0	(2.3)	nd		25.6	(6.9)	8.3	(0.2)	14.4	(0.8)	nd		8.6	(0.2)
Soils derived from volcanic ashes																	
Mindo	nf	143	(6)	65.1	(4.2)	28.9	3.2	68.5	(6.0)	14.6	(0.5)	38.8	(2.4)	30.6	(4.9)	12.2	(0.5)
	ps	112	(10)	52.9	(6.0)	21.1	2.0	66.6	(11.0)	12.3	(0.6)	27.7	(1.9)	32.3	(3.3)	11.7	(0.7)
	sf	140	(9)	55.6	(5.7)	nd		66.6	(3.1)	13.9	(0.4)	39.8	(1.3)	nd		11.6	(0.2)
Maquipucuna	nf	102	(11)	51.7	(12.4)	17.8	4.8	57.4	(9.4)	12.8	(0.7)	30.3	(2.9)	26.7	(4.4)	12.9	(0.9)
	ps	99	(7)	40.3	(6.5)	18.5	3.5	59.5	(10.5)	12.3	(0.8)	28.8	(1.5)	27.8	(4.0)	12.9	(0.8)
	sf	97	(3)	37.9	(4.2)	nd		51.9	(5.0)	11.8	(0.2)	30.0	(1.6)	nd		11.7	(0.2)
PedroViciente	nf	119	(4)	68.7	(5.4)	20.7	6.2	67.2	(3.5)	15.5	(0.9)	36.7	(3.0)	33.4	(10.8)	15.0	(0.9)
	ps	87	(18)	37.3	(11.7)	13.7	2.9	47.0	(14.3)	12.5	(0.3)	29.8	(1.8)	28.3	(3.0)	10.6	(0.5)
	sf	105	(6)	45.0	(5.6)	nd		58.0	(3.7)	13.5	(0.4)	40.1	(2.1)	nd		11.5	(0.5)
Pitzara	nf	126	(17)	56.0	(10.6)	27.7	10.4	57.5	(5.0)	14.8	(0.9)	35.5	(1.5)	32.1	(6.8)	13.6	(0.4)
	ps	94	(7)	35.4	(7.3)	17.2	1.1	52.6	(2.1)	12.9	(1.2)	33.5	(4.1)	32.6	(6.4)	13.0	(1.0)
	sf	101	(3)	39.2	(5.7)	nd		58.3	(4.3)	12.8	(0.4)	33.1	(1.6)	nd		12.5	(0.5)

[a]nd = not determined

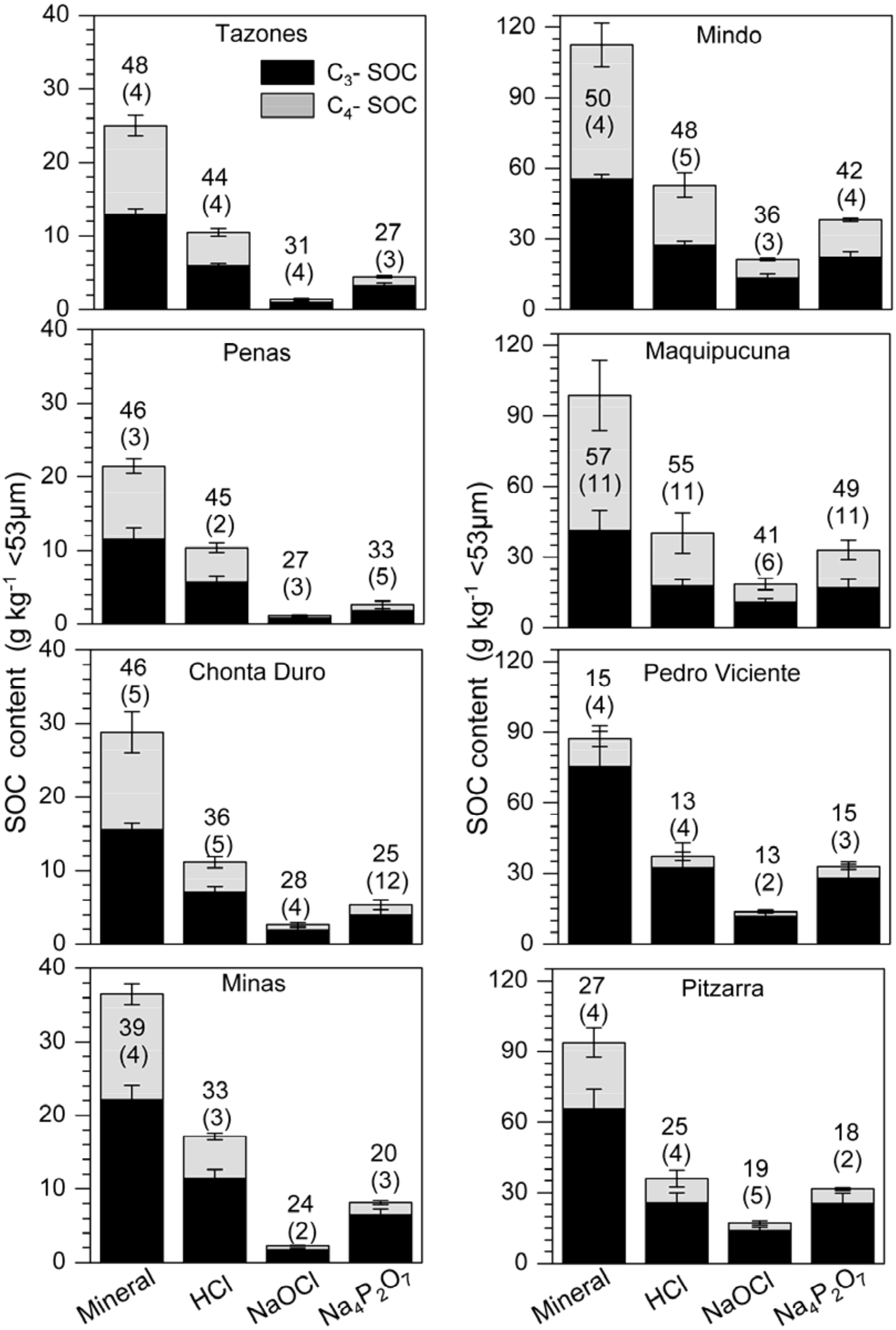

Figure 6-1: Means (n=4 and standard deviation) of pasture-derived SOC (C_4-SOC) and forest-derived SOC (C_3-SOC) in the <53µm fraction (Mineral) of pasture sites and in the residuum following chemical fractionation using HCl and NaOCl and in the extract of $Na_4P_2O_7$ treatment. The sites Tazones, Penas, Chonta Duro and Minas represent soils derived from marine Tertiary sediments, while Mindo, Maquipucuna, Pedro Viciente and Pitzara represent soils derived from volcanic ashes. Numbers represent proportion of pasture-derived SOC in fractions.

6.4.2 Treatment with HCl

About 55% of the mineral-associated SOC was lost after treatment with HCl independent of parent material (Figure 6-3). In soils derived volcanic ashes relative SOC losses were higher for pasture and secondary forest (60%) than for natural forest (48%). The exception was Mindo, where no relative differences were detected in SOC loss of pasture and natural forest soils. SOC concentration in the residuum depended on land use, with higher concentrations under natural forest than under pasture and secondary forest (Table 6-2). This effect was more pronounced in soils derived from volcanic ashes. SOC concentration after treatment correlated with initial concentrations of mineral-associated SOC (r = 0.87, p<0.01 in soils deived from volcanic ashes; r = 0.93, p<0.01 in soils derived from marine Tertiary sediments, Figure 6-4). After treatment with HCl, C/N ratio doubled (Table 2). Land use influenced the C/N ratio in the residuum of soils derived from marine Tertiary sediments: C/N ratio decreased from natural forest (17 ± 2), to pasture (16 ± 2) and secondary forest (14 ± 1; Table 6-2). At two sites of soils derived from volcanic ashes (Mindo and Pedro Viciente) C/N ratio was also influenced by land use with higher values in the forest than in pasture soils.

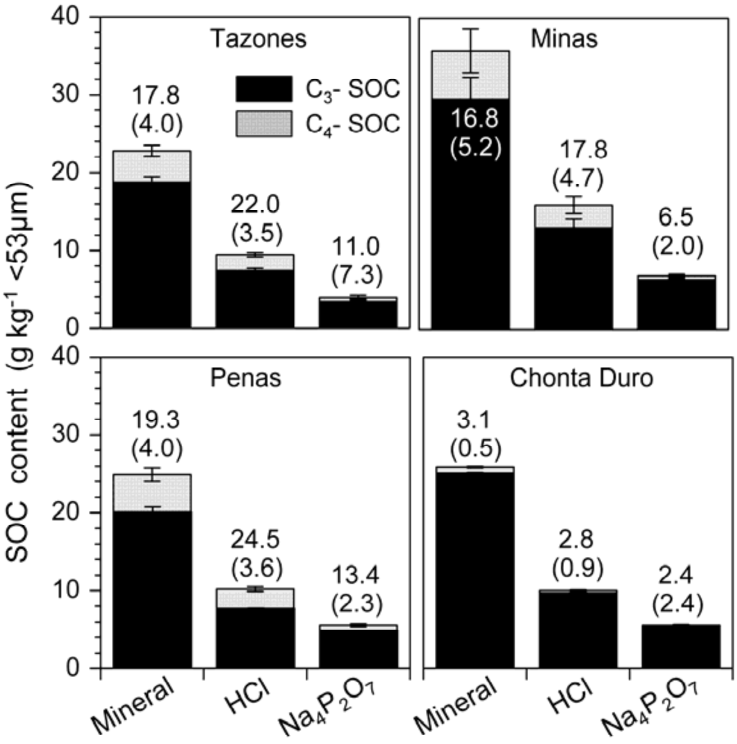

Figure 6-2: Means (n=4) and standard deviation) of pasture-derived SOC (C_4-SOC) and forest-derived SOC (C_3-SOC) in the <53µm fraction (Mineral) of secondary forest sites of soils derived from marine Tertiary sediments in the residuum following chemical fractionation using HCl and NaOCl and in the extract of $Na_4P_2O_7$ treatment. Numbers represent proportion of pasture-derived SOC in fractions (means, n=4 and standard deviation in parentheses). In none of the fractions of soils derived from volcanic ashes did we detect pasture-derived SOC.

Treatment with HCl resulted in a residue depleted in 13C (of as much as 2.1 ‰) in all natural forest soils (Table 6-3). In soils derived from volcanic ashes, mineral-associated and non-hydrolysable mineral-associated SOM did not differ in the proportions of pasture-derived SOC suggesting no preferential loss of recently incorporated SOM (Figure 6-2, Figure 6-5). In contrast, in pasture of soils derived from marine Tertiary sediments at Minas and Chonta Duro, slightly lower C4 –SOC proportions were found after acid hydrolysis (Figure 6-5). With the exception of Penas, we observed slightly higher (10%) losses of pasture-derived SOC than of forest-derived SOC in pasture soils (Figure 6-5). However, in secondary forest of soils derived from marine Tertiary sediments pasture-derived SOC proportions were not altered upon HCl treatment. Neither in the non-hydrolysable fraction nor in untreated soil could we detect the presence of C4 -SOC in soils derived from volcanic ashes under secondary forest.

6.4.3 Treatment with NaOCl

Soil mineralogical composition influenced pool size of NaOCl resistant SOM. In soils derived from volcanic ashes, which are characterised by high amounts of Al and Fe- (hydro)oxides, we found ten times higher SOC contents in residual fraction resistant to oxidation by NaOCl than in soils rich in smectite (Table 6-2). Accordingly, higher relative losses of mineral-associated SOC were found in soils derived from marine Tertiary sediments (91-94%) than in soils derived from volcanic ashes (78-83%; Figure 6-3). SOC concentration after treatment with NaOCl correlated with initial SOC concentration ($r = 0.57$, $p<0.01$ soils of volcanic ashes; $r = 0.74$, $p<0.01$ soils of marine Tertiary sediments, Figure 4) and with the amount of carbon released through $Na_4P_2O_7$ extraction ($r = 0.59$, $p<0.01$ soils of marine Tertiary sediments; $r = 0.69$, $p<0.01$ for volcanic ashes). With the exception of Chonta Duro, SOC resistant to NaOCl-treatment depended on land use, with higher SOC concentrations in natural forest than in pasture soils.

The C/N ratio of soils derived from marine Tertiary sediments was not affected by NaOCl treatment. In contrast, in soils of volcanic ashes C/N ratio increased from about 13 ± 1 to 30 ± 6 after the NaOCl treatment (Table 6-2).

NaOCl resistant SOM in natural forest was slightly depleted in ^{13}C (0.5-1.1‰) compared to the untreated SOM (Table 6-3). Proportions of pasture-derived SOC in soils of marine Tertiary sediments were reduced from between 39 and 48% in the mineral-associated SOC to between 24 and 31% in the residuum after treatment with NaOCl (Figure 6-3). Only 4% of initial pasture-derived and 9% of initial forest-derived SOC was stable against NaOCl treatment (Figure 6-1 and 6-5). With the exception of Pedro Vicente, in soils of volcanic ashes 13% of initial pasture-derived and 26% of forest-derived SOC were stable against NaOCl treatment (Figure 6-5).

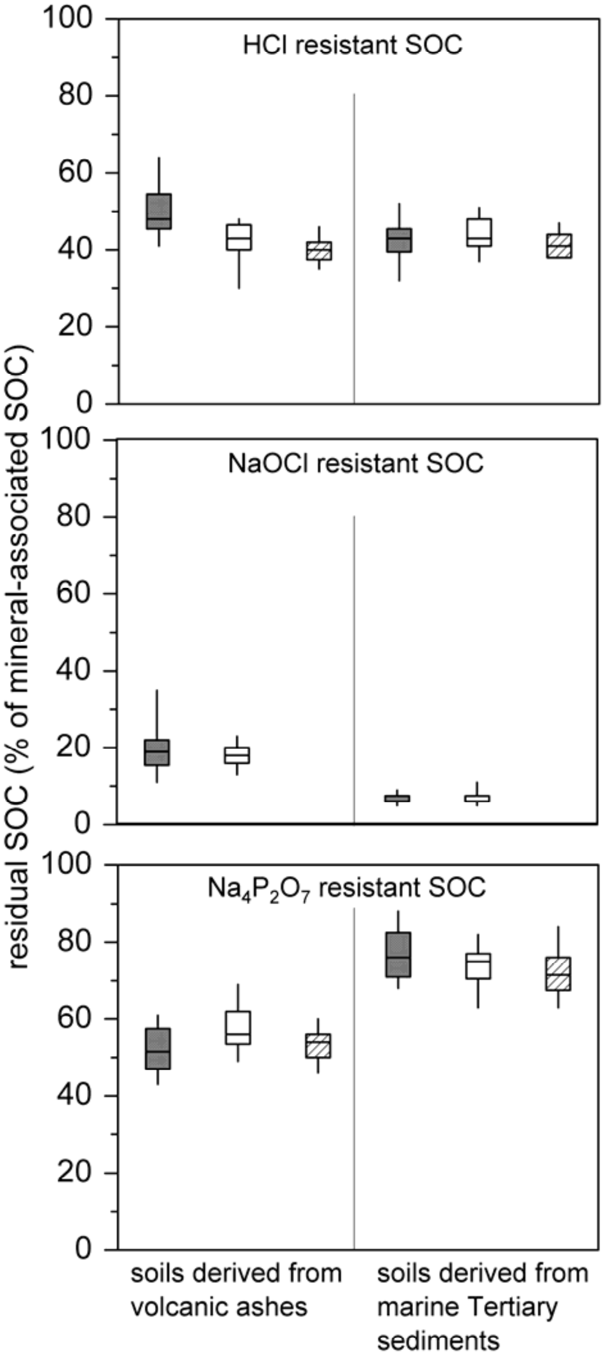

Figure 6-3: Box Plots of residual SOC (median (n=16), upper and lower quartile and extreme values) after different chemical fractionation of mineral-associated SOC in soils derived from different parent material and land use types (natural forests = grey; pasture = white; secondary forest = striped).

Table 6-3: $\delta^{13}C$ values of soil fraction <53 µm (mineral associated) and the residual fraction treatment with HCl, NaOCl and $Na_4P_2O_7$ and in the extracts of $Na_4P_2O_7$ of different sites and land use types (nf =natural forest; ps=pasture, sf= secondary forest), means and standard deviation.

Site	Use	Mineral-associated	HCl residuum	NaOCl residuum	$Na_4P_2O_7$ extract	$Na_4P_2O_7$ residuum
		‰				
Soils derived from marine Tertiary sediments						
Tazones	nf	-26.8 (0.3)	-28.9 (0.3)	-27.6 (0.4)	-24.6 (0.6)	-26.9 (0.3)
	ps	-19.6 (0.6)	-22.4 (0.6)	-23.1 (0.6)	-20.3 (0.4)	-19.9 (0.7)
	sf	-24.2 (0.6)	-25.6 (0.5)	ND[a]	-22.7 (1.1)	-24.3 (0.6)
Penas	nf	-26.7 (0.3)	-28.7 (0.3)	-27.7 (0.4)	-26.4 (0.6)	-27.1 (0.3)
	ps	-20.0 (0.5)	-22.0 (0.3)	-23.8 (0.4)	-21.5 (0.7)	-20.4 (0.5)
	sf	-23.9 (0.6)	-25.1 (0.5)	ND	-24.4 (0.3)	-24.2 (0.6)
Chonta Duro	nf	-26.3 (0.3)	-28.1 (0.3)	-27.1 (0.2)	-24.1 (0.5)	-26.4 (0.2)
	ps	-19.2 (0.8)	-22.5 (0.7)	-22.7 (0.7)	-20.2 (1.9)	-19.4 (0.8)
	sf	-25.8 (0.1)	-27.6 (0.2)	ND	-23.7 (0.4)	-26.0 (0.1)
Minas	nf	-25.8 (0.2)	-27.5 (0.3)	-26.4 (0.2)	-23.1 (1.1)	-26.0 (0.2)
	ps	-19.9 (0.7)	-22.4 (0.5)	-22.7 (0.3)	-20.1 (0.5)	-20.1 (0.6)
	sf	-23.3 (0.8)	-24.8 (0.7)	ND	-22.2 (0.3)	-23.5 (0.8)
Soils derived from volcanic ahes						
Mindo	nf	-27.2 (0.3)	-29.3 (0.4)	-28.2 (0.4)	-27.0 (0.2)	-27.5 (0.3)
	ps	-18.2 (0.7)	-20.6(0.8)	-21.7 (0.5)	-19.4 (0.7)	-17.8 (0.6)
	sf	-27.4 (0.2)	-29.3 (0.3)	ND	-27.3 (0.2)	-27.6 (0.3)
Maquipucuna	nf	-26.9 (0.3)	-28.9 (0.3)	-27.4 (0.1)	-26.7 (0.4)	-27.4 (0.3)
	ps	-17.0 (1.9)	-19.4 (2.0)	-20.3(1.1)	-18.2 (1.9)	-16.7 (1.7)
	sf	-26.9 (0.1)	-28.9 (0.1)	ND	-26.7 (0.1)	-27.2 (0.1)
Pedro Viciente	nf	-28.1 (0.3)	-30.2 (0.3)	-29.1 (0.3)	-28.0 (0.1)	-28.5 (0.2)
	ps	-26.0 (0.5)	-28.3 (0.5)	-27.2 (0.3)	-25.9 (0.4)	-26.1 (0.7)
	sf	-28.0 (0.1)	-30.2 (0.2)	ND	-27.4 (0.3)	-28.4 (0.2)
Pitzara	nf	-27.7 (0.3)	-29.6 (0.2)	-28.6 (0.8)	-27.4 (0.3)	-27.8 (0.3)
	ps	-23.5 (0.7)	-25.7 (0.8)	-25.6 (0.9)	-24.4 (0.4)	-23.1 (0.8)
	sf	-27.4 (0.2)	-29.6 (0.1)	ND	-27.3 (0.2)	-27.7 (0.2)

[a]ND = not determined

6.4.4 Treatment with $Na_4P_2O_7$

SOC loss through pyrophosphate treatment depended on parent material: relative loss of mineral-associated SOC was lower in soils of marine Tertiary sediments (26%) than in soils of volcanic ashes (45%; Figure 6-2). Concentration of mineral-associated SOC after treatment correlated with initial concentrations ($r = 0.80$, $p<0.01$ in soils of volcanic ashes; $r = 0.94$, $p<0.01$ in soils of marine Tertiary sediments). SOC concentrations in the residuum were unaffected by land use in soils of volcanic ashes, while in soils of marine Tertiary sediments higher carbon concentration were found in the residuum of natural forest than of pasture soils (except for Chonta Duro, Table 6-2). C/N ratios decreased in soils of volcanic ashes (except Maquipucuna), while C/N ratio in soils of marine Tertiary sediments increased slightly after treatment with pyrophosphate (Table 6-2).

While mineral-associated SOM in the residuum of natural forest was only slightly depleted in ^{13}C, the extracts of $Na_4P_2O_7$ were enriched in ^{13}C. The enrichment was stronger in soils of marine Tertiary sediments (0.4-2.7‰) than in soils of volcanic ashes (0.2-0.4‰; Table 3). In pasture of soils derived from marine Tertiary sediments proportions of pasture-derived SOC were 39-48% in the mineral-associated soil and 20-33% in the extract (Figure 6-1) resulting in a preferential extraction of forest-derived SOC (Figure 6-5). Accordingly, in soils of marine Tertiary sediments under secondary forest the contribution of pasture-derived SOC in the extract was about half as in the mineral-associated soil (Figure 6-2 and Figure 6-5). Similarly, in soils of volcanic ashes, more forest-derived (38-41%) than pasture-derived SOC (22-28%) was extracted (Figure 6-5). One exception was Pedro Viciente where no preferential loss of forest-derived SOC was observed (Figure 6-5). We detect no pasture-derived SOC in the $Na_4P_2O_7$ extracts of any secondary forest of soils derived from volcanic ashes.

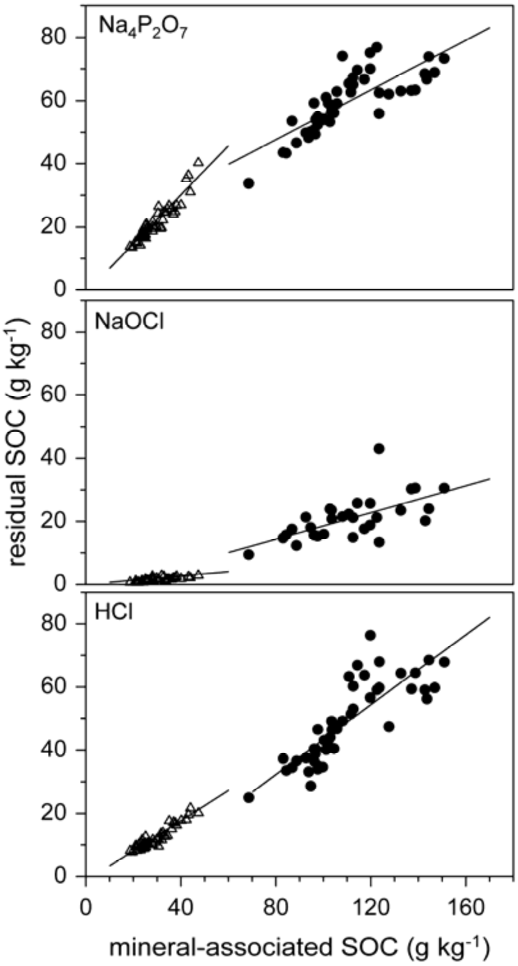

Figure 6-4: Relation of initial mineral-associated SOC and residual SOC resistant to treatment with HCl, NaOCl and $Na_4P_2O_7$ of soils derived from marine Tertiary sediments (triangles) and soils derived from volcanic ashes (circles).

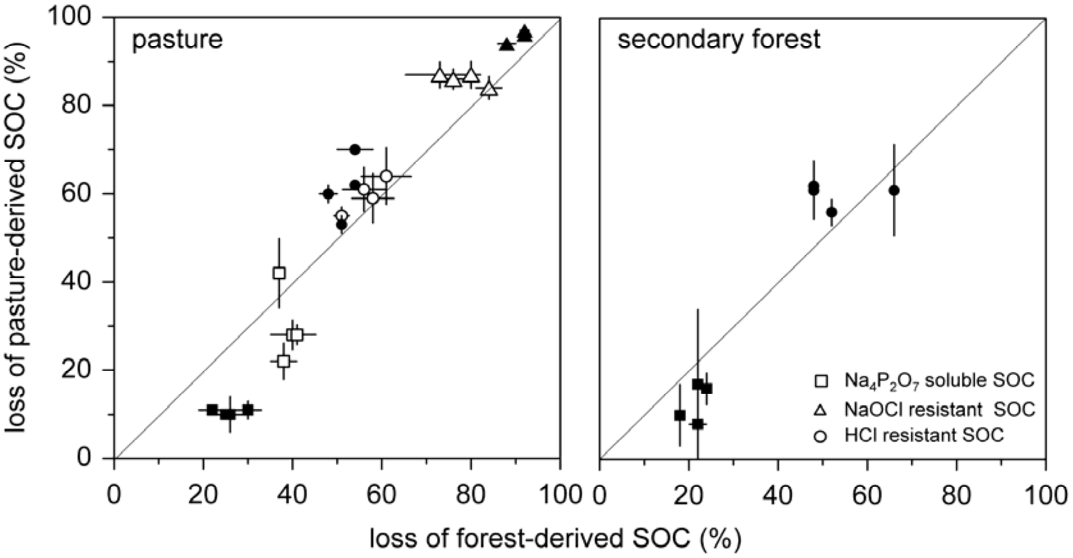

Figure 6-5: Loss of forest-derived SOC versus loss of pasture-derived SOC of soils derived from volcanic ashes (open symbols) and from marine Tertiary sediments (dark symbols; means n=4 and standard deviation) of different chemical treatments in pasture and secondary forest. In all secondary forest of soils derived from volcanic ashes no pasture-derived SOC was detected

6.5 Discussion

6.5.1 Influence of Parent Material on Soil Organic Matter Pools Resistant to Chemical Fractionation

Independent of soil mineralogical composition, 38% to 58% of the mineral-associated SOC was non-hydrolysable, which agrees with the finding of Paul et al. (2006) that 30-80% (mean 55%) of total SOC is resistant to acid hydrolysis. In contrast, the proportion of mineral-associated SOC that was resistant to treatment with $Na_4P_2O_7$ and NaOCl was higher in soils of volcanic ashes than in soils derived from marine Tertiary sediments. In our tropical topsoils, the relative amount of SOC stable against NaOCl treatment (6-22% of mineral-associated SOC) was slightly lower than what was found for temperate topsoils (15-25%; Helfrich et al., 2007) and of 12 temperate and tropical acidic subsoils (28-87%; Mikutta et al., 2006). The larger pool size of NaOCl resistant SOC found in soils derived from volcanic ashes indicates that soils rich in Al-humus complexes and non-crystalline hydroxides are more effective in stabilising SOM against chemical oxidation than soils rich in smectites. In agreement with these results, the variance of NaOCl resistant SOM could be explained to a large extent by Fe_o and Al_o in a range of temperate and tropical subsoils (Kleber et al. 2005). The higher SOM binding capacity of Al-humus complexes and non-crystalline hydroxides is also supported by higher amounts of $Na_4P_2O_7$ extractable SOC found in soils derived from volcanic ashes compared to soils of marine Tertiary sediments. Contributions of SOC extracted by $Na_4P_2O_7$ have been found to vary considerably (16-100% of total SOC) with highest values reported from sesquioxide-rich subsoils (Parfitt et al., 1999; Verde et al., 2005; Siregar et al., 2005).

Correlation of the amount of SOC extracted by $Na_4P_2O_7$ with NaOCl resistant SOC has also been observed in 12 acidic subsoils (Kleber et al., 2005). While this may suggest that NaOCl resistant SOC is partly stabilized by attachment to mineral surfaces or complexed by hydroxides, the amount of SOC extracted by $Na_4P_2O_7$ is about double the NaOCl resistant SOC, which illustrates that a part of $Na_4P_2O_7$ soluble SOC is also oxidisable with NaOCl. For 12 acidic subsoils it was shown that only a part (24-60%) of NaOCl resistant SOC could be extracted by $Na_4P_2O_7$ (Siregard et al., 2005), which suggests that the very strongly bind between SOM and allophane or other minerals cannot be released by extraction with $Na_4P_2O_7$.

The finding that acid hydrolysis isolated fixed proportions of initial SOC content suggests that the amount of non-hydrolysable SOM was mainly controlled by the chemical structure of SOM itself rather than by soil properties. In contrast, treatment with $Na_4P_2O_7$ or NaOCl isolated SOM fractions which were influenced by the mineralogical composition.

6.5.2 Influence of Land Use on Soil Organic Matter Pools Resistant to Chemical Fractionation

Our finding that the results of chemical extraction techniques dependent on land-use contradicts with the notion of a conceptual passive SOM pool, which should not be affected by short-term land use effects. From literature it is known that all used methods selectively enrich specific compounds: Acid hydrolysis by HCl leaves long chain alkyls, waxes and lignin unaffected (Barriuso et al. 1987); aliphatic structures are less reactive upon oxidation and are therefore enriched in the residuum after NaOCl treatment (Mikutta et al., 2005) and the residuum after $Na_4P_2O_7$ extraction is enriched in aliphatic organic compounds (Wattel-Koekkoek et al., 2001; Nierop et al., 2005). Accordingly, differences in composition of mineral-associated SOM between pasture and forests prior to chemical fractionation have influenced the efficiency of the different treatments to remove mineral-associated SOM. As a result, the pool sizes of residual SOM fractions are influenced by SOM of current land use and pool sizes are altered on decadal time scale following land use changes. Rapid pool size changes of non-hydrolysable SOM following afforestation or cultivation have also been reported by Paul et al. (2006) while higher SOC content in forest than in grassland/cropland following chemical oxidation with NaOCl has also been observed (Helfrich et al., 2007; Zimmermann et al., 2007).

6.5.3 C/N of Different Soil Fractions

The observed shifts in C/N ratios in particular upon the HCl treatment can be explained by selective reaction mechanisms. Since C-N bonds are often more vulnerable to hydrolysis than ordinary C-C bonds, increased C/N ratios are commonly reported after hydrolysis (Plante et al., 2006; Helfrich et al., 2007). In contrast, increasing C/N ratios after treatment with NaOCl were only observed for the volcanic ash soils, which indicate that N containing compounds are preferentially oxidised in soils with large amount of poorly crystalline Al and Fe phases. Similar results have been reported by Kleber et al. (2005). However, fixation of NH_4^+ to clay minerals can also affect C/N ratio and may mask or distort effects of preferential removal of N containing organic compounds.

6.5.4 δ^{13}C of Different Soil Fractions of Natural Forests

The observed ^{13}C depletion in natural forest after acid hydrolysis is probably the result of an accumulation of aliphatic and aromatic structures (depleted in ^{13}C) while polysaccharides (enriched in ^{13}C) are hydrolysed (Balesdent and Mariotti, 1996). Accordingly, the enrichment of aliphatic structures may also explain the observed depletion in ^{13}C in the residuum of the NaOCl treatment. Extracts of $Na_4P_2O_7$ are dominated by polysaccharides with a minor contribution of chitin, lignin, proteins and lipids, while the residuum is enriched in aliphatic organic compounds (Wattel-Koekkoek et al., 2001; Nierop et al., 2005), which may explain the observed enrichment of ^{13}C enrichment of the extracts.

6.5.5 Proportion of Pasture-derived Carbon in Different Soil Fractions

The efficiency to remove the recently incorporated pasture-derived SOM by acid hydrolysis depends on mineralogical composition. Treatment with HCl was ineffective in isolating an older SOM fraction in soils derived from volcanic ashes. In contrast, a slight preference to remove the young SOM was found in soils derived from marine Tertiary sediments. A more pronounced preferential loss of 30-50% of recently incorporated SOM after drastic acid hydrolysis was found in temperate arable soils (Poirier et al., 2006; Helfrich et al., 2007). In temperate soils the mean ^{14}C age of the non-hydrolysable fraction was found to be on average 1200 years older compared to the whole soil (Paul et al., 2006).

However, acid hydrolysis had no effect on the ^{14}C content in the topsoils of tropical Oxisols and volcanic ash soils (Trumbore, 1993; Trumbore and Zheng, 1996). One reason might be that organo-mineral complexes and the mineral assemblage in temperate soils differ from those in tropical soils. Isolating an assumed stable SOM pool according to its resistance against chemical hydrolysis is arguable since freshly plant-derived compounds such as lignin are resistant to chemical hydrolysis (Barriuso et al. 1987), but not to microbial degradation (van Bergen et al., 1997). Moreover, SOM survival in soils is not only a function of its pure biochemical recalcitrance but also due to physical protection which cannot be accounted with chemical hydrolysis altering the mineral phase (Zimmermann et al., 2007).

For the NaOCl treatment, a considerable amount of pasture-derived SOC in the NaOCl resistant fraction indicated that also recently incorporated SOM survived this treatment. In temperate arable topsoils the preferential loss of recently incorporated SOC upon NaOCl treatment was more pronounced (90-95% loss of recently incorporated maize-derived SOC and 60-72% loss of older wheat-derived SOC, Helfrich et al., 2007) compared to our tropical soils. Also here, selective enrichment (in this case of aliphatic structures) during oxidation may contribute to recently incorporated SOM in these organic-rich tropical topsoils. However, stabilization of recent SOM by minerals may also have contributed to the low age of NaOCl resistant SOM. Mikutta et al. (2006) reported that minerals protect also recent SOM against NaOCl treatment. Other oxidation procedures, e.g. H_2O_2 and $Na_2S_2O_8$, were found to be more effective in removing recently incorporated SOM in two temperate soils than treatment with NaOCl (Helfrich et al., 2007). However, the former methods affect the mineral structure, which is not the case for NaOCl (Mikutta et al., 2005).

Our results show that $Na_4P_2O_7$ was able to extract older, forest-derived SOC, but also here the extract still contained a share of pasture-derived SOC. In agreement with our results, Kaiser and Ellerbrock (2005) observed a reduced proportion of recently incorporated SOC on sites which had undergone a C_3-C_4 vegetation change. Higher mean 14C ages of about 200 to 1400 years were found in SOC extracted by $Na_4P_2O_7$ (Anderson and Paul, 1984; Wattel-Koekkoek et al., 2003, Wattel-Koekkoek and Buurman, 2004; Kaiser and Ellerbrock, 2005). However, repeated sequential extraction with NaOH and $Na_4P_2O_7$ did not lead to preferential loss of recently incorporated SOC in a temperate arable soil (Balesdent, 1996).

Forest-derived SOC was more resistant to NaOCl and more extractable by $Na_4P_2O_7$ treatment than pasture-derived SOC independent from soil parent material. This suggests that forest-derived SOM is more closely associated with the mineral phase than recently incorporated pasture-derived SOM. Therefore, the recently incorporated SOM receives less protection compared to the older, already sorbed SOM. This is in line with the finding that for a low carbon to mineral surface ratio, SOM is stronger bound to the mineral phases via multiple bonds (Kaiser and Guggenberger, 2007). Once the reactive binding sites are occupied, recently added SOM is only loosely bound and, thus, less likely to be incorporated into the long-term stabilized SOM.

The fact that in the volcanic soils derived from volcanic ashes no recently incorporated SOC could be detected in any fraction under secondary forest indicates that the pasture-derived SOC found in the chemically resistant fraction in the pasture soil was not stabilized on long-term. Thus, the non-hydrolysable fraction does not represent a stable SOM pool in the volcanic ash soils following land use change. In contrast, in soils developed from marine Tertiary sediments, recently incorporated pasture-derived SOC could be detected in chemical isolated fractions under secondary forest. Accordingly, a part of the pasture-derived SOC that survived chemical treatment in pasture soils contributed to a stabilized SOM pool in soils dominated by smectite.

Our comparison of three chemical methods showed that although in most cases there is a slight preference to isolate older SOM, the residue (in the case of NaOCl and Hydrolysis) or extract (in the case of $Na_4P_2O_7$.) still contained considerable amounts of pasture-derived SOM. In addition, SOC content in the residuum depended on land use. We therefore conclude that SOM fractions separated by HCl, NaOCl or $Na_4P_2O_7$ do not present a passive SOM pool in any of the analysed tropical topsoils. Consequently, it is also unlikely that these chemical fractions can be used to directly calibrate SOC models.

6.6 Conclusion

Independent of soil mineralogical composition, about 55% of mineral-associated SOC is resistant to acid hydrolysis indicating a similar SOM composition for the investigated soils. Contrary, the results point to an enhanced stability of mineral-bound SOM against oxidation by NaOCl for soils developed from volcanic ashes. In addition, more SOC can be extracted by $Na_4P_2O_7$ indicating the importance of Al-humus complexes in these soils. However, the disappearance of recently incorporated (pasture-derived) SOC in the secondary forest soils developed from volcanic ashes revealed that recently incorporated SOM was not long-term stabilized after land use change. The results indicate that the employed methods were not able to isolate a SOM fraction which is protected against microbial decay under field conditions. This questions the idea that SOM fractions separated by HCl, NaOCl or $Na_4P_2O_7$ do present stable SOM pools in soils derived from volcanic ashes. In contrast, for soils rich in smectite, recently incorporated SOM was partly stabilized. Thus, the outcome of these fractionation methods is sensitive to soil type which makes interpretation challenging and precludes any generalisation to other soils types or climates.

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7 Summarizing Synthesis & Conclusions

This study analysed storage and stability of organic carbon in different tropical soils. The objectives were to determine how soil properties influence soil C contents and stability in bulk soil, physically, and chemically defined soil fractions. Furthermore, the quantification of soil C changes in these fractions induced by different land-use changes (natural forest to pasture and pasture to secondary forest) was elucidated. Finally, it was evaluated whether these soil fractions represent meaningful soil C pools with respect to stabilization mechanisms. For this purpose soils in Northwest Ecuador were investigated. Investigated soils can be divided into soils which differ in key factors (soil texture and parent material (volcanic ashes and marine Tertiary sediments)) influencing storage and stabilization of soil C. Different operationally defined soil fractions were investigated: a) physical fractionation procedures: i) aggregate size classes; ii) density fractions: light fractions and the heavy, mineral-associated fraction; and b) chemical fractionation procedures of the mineral-associated fraction: treatment with i) HCl, ii) NaOCl, and iii) $Na_4P_2O_7$.

7.1 Soil C in Bulk Soil

Parent material of soils was the master variable controlling total soil C levels. Higher soil C contents (0-0.1m depth) in volcanic ash soils (47 to 130 g kg^{-1}) than in sedimentary soils (19 to 50 g kg^{-1}) showed that the combination of Al-humus complexes and non-crystalline hydroxides in volcanic ash soils were more effective in carbon storage than silt + clay contents in sedimentary soils. Besides mineralogy, soil texture influenced carbon storage, as in both soil types the content of silt + clay was positively correlated with soil C. Compared to soil type and texture, the influence of land use on soil C storage was less important. However, pasture establishment after deforestation reduced soil C storage by about 20% in both soil types. Conversely, afforestation of pastures lead to an increase in soil C contents, but within the observed time frame of a few decades the former soil C levels of natural forests were not reached in all secondary forest.

As one result of this study, the stabilization mechanism of soil C is dependent on soil type. Higher carbon contents in volcanic ash soils were attributed to both: higher storage of old forest-derived and recently incorporated pasture-derived carbon as revealed by ^{13}C data. In both soil types, mean residence times of recently incorporated pasture-derived carbon in secondary forests were considerably shorter than of forest-derived carbon in pasture soils. The mean residence time of forest-derived carbon in pastures increased from 37 to 57 years with increasing silt+clay contents in sedimentary soils; but in volcanic ash soils the mean residence times were independent from soil properties (24-56 years). However, the comparison of mean residence times of the volcanic ash soils is limited by the use of a one-pool model since different pasture ages may bias the direct comparison of mean residence times of the studied soils. Especially fast turnover rates of recently incorporated carbon were found in volcanic ash soils, where no pasture-derived carbon could be detected in any of the four studied secondary forest soils.

To understand the differences in soil C storage, mechanisms and rates of soil C stabilization of the different soils, information of pool sizes and stability of operationally defined soil C pools are necessary. Figure 7-1 summarizes the proportion of soil C stored in the operationally defined fractions to the total soil C of volcanic ash and sedimentary soils for different land use types (natural forest, pasture, and secondary forest).

7.2 Physically Defined Fractions

7.2.1 Aggregate Size Fractions

Soil was fractionated into aggregate size classes (8000-2000, 2000-250, 250-53, <53 µm) to determine the degree of aggregation in these different soil types and the role of aggregation on Soil C storage and stability. Furthermore, factors influencing aggregate formation and stabilization, especially the role of organic matter, were elucidated. In addition, the effect of sample pretreatment (wet sieving of air-dried vs moist soils) on soil C distribution into aggregate size classes was investigated.

The result of aggregate fractionation strongly depended on the applied sample pretreatment, soil type, and soil texture. Irrespective of these factors, in both soil types most of the carbon was stored in macroaggregates (>250 µm) and less than 20% (moist pretreatment) or 3% (air-dried pretreatment) of total soil C was stored in the fraction <53 µm. Soil texture influenced in both soil types the distribution of soil C into aggregate size classes. With increasing silt + clay content, a larger proportion of dry matter and soil C falls into the large size classes, i.e. aggregation (expressed as Mean Weight Diameter) increased. Similar, amounts of carbon stored in aggregate size classes increased (Figure 7-2). However, using multiple regression, soil C could not explain additional variation in Mean Weight Diameter in addition to silt + clay content. This suggested that texture played the dominant role in aggregate formation. Only in sedimentary soils, aggregation was influenced by land use, with higher aggregation in the pasture soils, which may point to soil compaction due to cattle trampling.

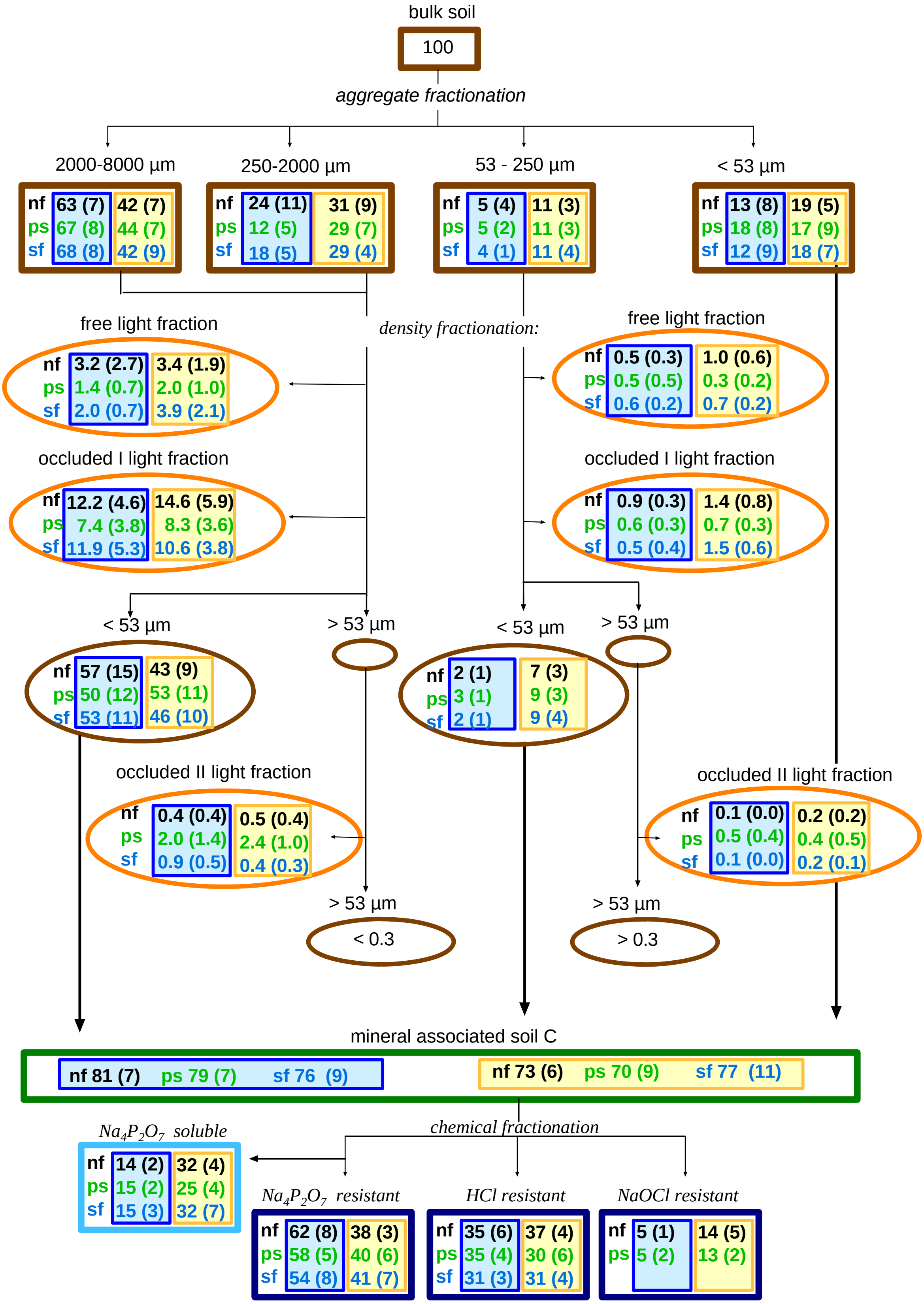

Figure 7-1: Proportion of soil C stored in the operationally defined fractions (aggregate size classes of moist pretreatment: brown box; light fractions: red ovals; heavy fraction: brown ovals; mineral-associated fraction: green box; and chemical defined fractions: blue box) to the total soil C (%) of the three land use types (nf = natural forst; ps = pasture, sf = secondary forest) of volcanic ash soils (yellowish box) and sedimentary soils (bluish box). Values present means (n=16) and standard deviation in parentheses.

Organic matter as stabilising agent was of different importance in the two soil groups as the distribution of soil C among aggregate size fractions differed between the two soil groups. In sedimentary soils, both soil sample pre-treatments resulted in distinct aggregate fractions with different C content and proportion of recently incorporated soil C. In the air-dried pre-treatment the simultaneous increase of carbon concentration and the proportion of recently incorporated carbon with aggregate size supported the concept of aggregate hierarchy (Oades and Waters, 1991). Thus, wet-sieving of air-dried soil provided information of the stabilising effect of fresh organic matter on macroaggregates. Furthermore, this method separated stable macroaggregates. In contrast, wet-sieving of moist soil separated a microaggregate fraction which was characterized by a high proportion of microaggregates in an early stage of aggregate formation. Although the air-dried pre-treatment separated distinct aggregates size classes, differences were relatively small compared to the results of aggregate fractionation of temperate climate soils (Puget et al., 1995; Jastrow et al., 1996; Six et al., 2002).

In contrast to sedimentary soils, volcanic ash soils showed a different aggregate dynamic: Here, the distribution of dry matter and soil C concentration of aggregate size classes were not influenced by the soil pretreatment. Thus, it is not possible to define stable and unstable aggregates using this aggregate fractionation method in volcanic ash soils. In addition, none of the pretreatments were able to separate aggregate size fractions with distinct proportions of pasture-derived carbon. This illustrates that aggregates in volcanic ash soils are not predominantly stabilized by soil organic matter and that mineral-to-mineral bindings in these soils rich in aluminium and iron oxides are more important. Moreover, the even distribution of pasture-derived carbon among aggregate size classes may indicate that disaggregation and reformation of aggregates is probably a fast process. Land use did not alter the aggregate distribution.

In order to elucidate the consequences of the measured difference in the dominating stabilization agents between the two soil types on the stabilization of soil organic matter, it is necessary to separate organic matter according to their location within the soil matrix.

7.2.2 Density Fractions

Density fractionation of soil aggregates was used to determine the quantity and stability of i) the free light fraction located outside of aggregates with a density <1.6 g cm^{-3}, ii) an occluded I light fraction located within aggregates with a density <1.6 g cm^{-3}, iii) an occluded II light fraction located in highly stable microaggregates with a density <1.6 g cm^{-3}, and iv) the heavy fraction (density >1.6 g cm^{-3}). The total light fraction separated from aggregates >53 µm contributed 12-17% to total soil C in the sedimentary soils and 14-21% in volcanic ash soils (Figure 7-1). Similar to soil C storage in bulk soil, absolute amounts of carbon stored in light fractions of volcanic ash soils (15 g kg^{-1}) were three times higher than in sedimentary soils (5 g kg^{-1}). This result demonstrated that high soil C storage in volcanic ash soils is not solely due to high storage of silt + clay associated organic matter, but also due to higher storage in light fractions. Compared with soil types, the influence of land use on soil C storage in light fractions was less important. However, in both soil types pasture establishment after deforestation reduced soil C storage in both the free and in the occluded light fractions by about 50%. Nevertheless, the amount of light fraction was partly recovered by afforestation.

The effect of silt + clay content on the amount of soil organic carbon stored in light fractions was most pronounced in the occluded I light fraction for all land use and soil types. The correlation of soil C in the occluded I light fraction and soil texture may result from the effect of clay on aggregate formation and stability. The results of aggregate fractionation showed that silt + clay content strongly affected aggregation in both soil types. Strong aggregation leads to stronger physical protection of the occluded I light fraction inside aggregates. This conclusion is supported by strong correlation of the Mean Weight Diameter with the amount of

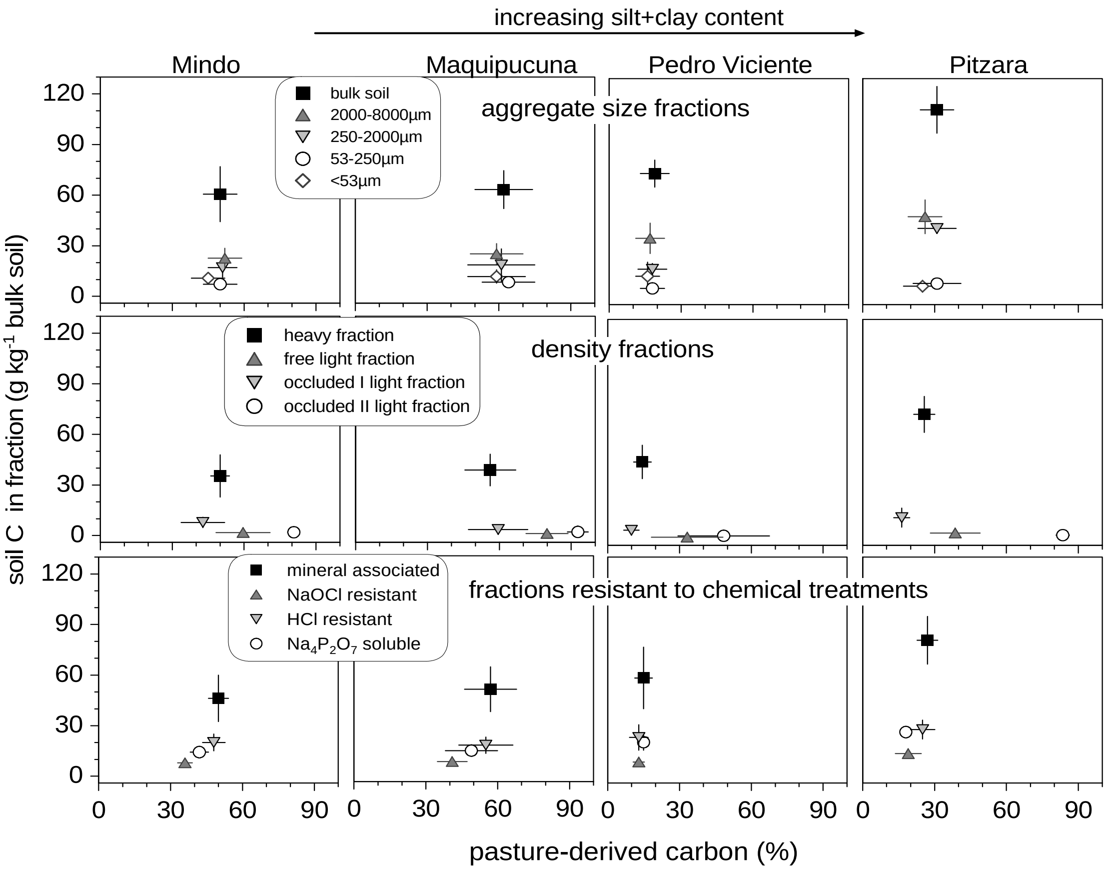

Figure 7-2a: Storage of soil C in different soil fractions (aggregate size fractions of moist pretreatment, density fractions and fractions resistant to various chemical treatments) versus the proportion of pasture-derived carbon in these fractions in pastures of volcanic ash soils. Silt + clay content, which correlates with the Alp content is increasing from Mindo to Pitzara. Values present means (n=4) and standard deviation.

occluded I light fraction in both soil types.

Isolated light fractions were heterogeneous in terms of their stability: in both soil types, the free light fraction contained more recently incorporated carbon than bulk soil and the occluded I light fraction. The slow turnover of occluded I light fraction, which contains less recently incorporated carbon as bulk soil, supports the hypothesis that soil C is stabilized within aggregates (Golchin et al., 1995). In addition, the occluded light fraction showed a higher degree of decomposition (Golchin et al., 1995; Helfrich et al., 2006). The more decomposed stage of the occluded light fraction can be seen in Figure 7-3. The fastest turnover and highest contribution of pasture-derived carbon was found in the occluded II light fraction which was separated from highly stable microaggregates. This result strongly suggested that this fraction might be involved in the initial aggregate formation. Moreover, I assume that this fraction represents plant debris forming the cores of an initial stage of aggregate formation postulated by Oades and Waters in 1991. Figure 7-3 shows that the occluded II light fraction consisted mainly of cellular plant structures.

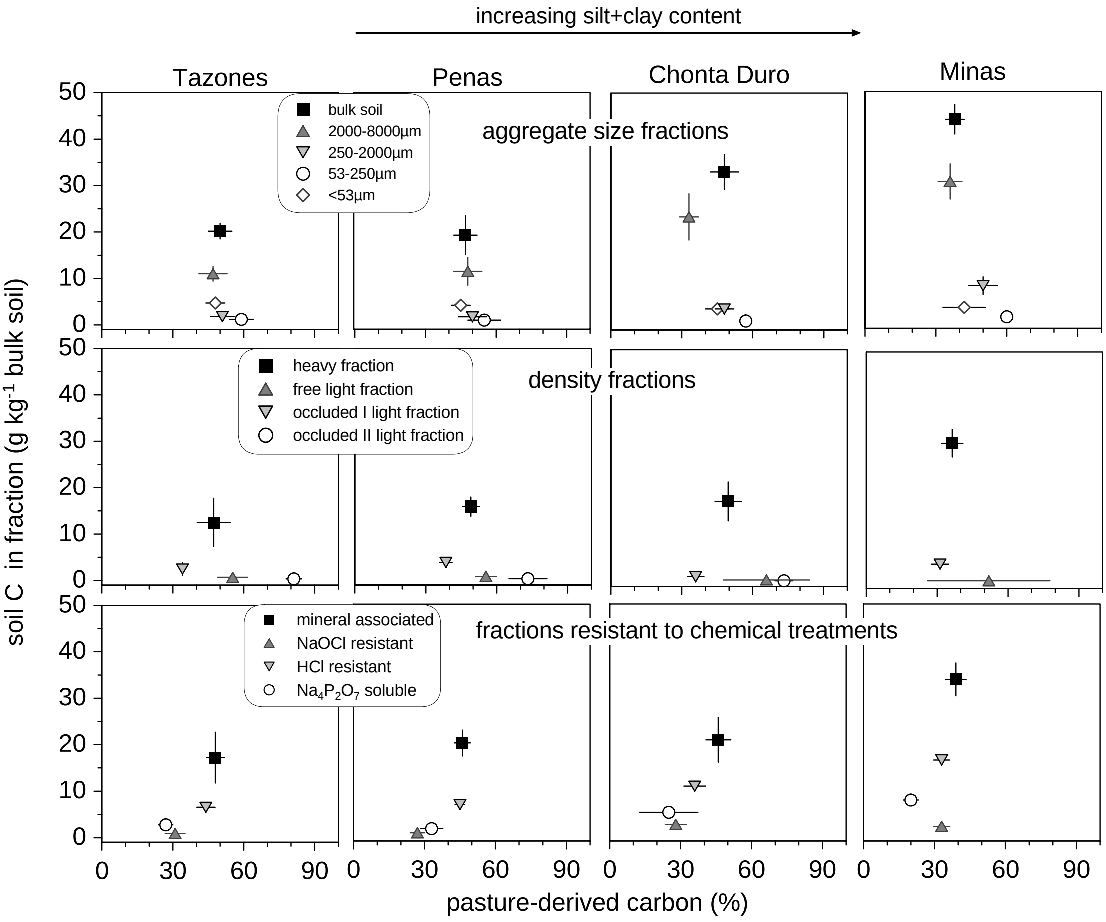

Figure 7-2b: Storage of soil C in different soil fractions (aggregate size fractions of moist pretreatment, density fractions and fractions resistant to various chemical treatments) versus the proportion of pasture-derived carbon in these fractions in pastures of sedimentary soils. Silt + clay content of individuals sites is increasing from the left side (Tazones) to the right side (Minas). Values present means (n=4) and standard deviation.

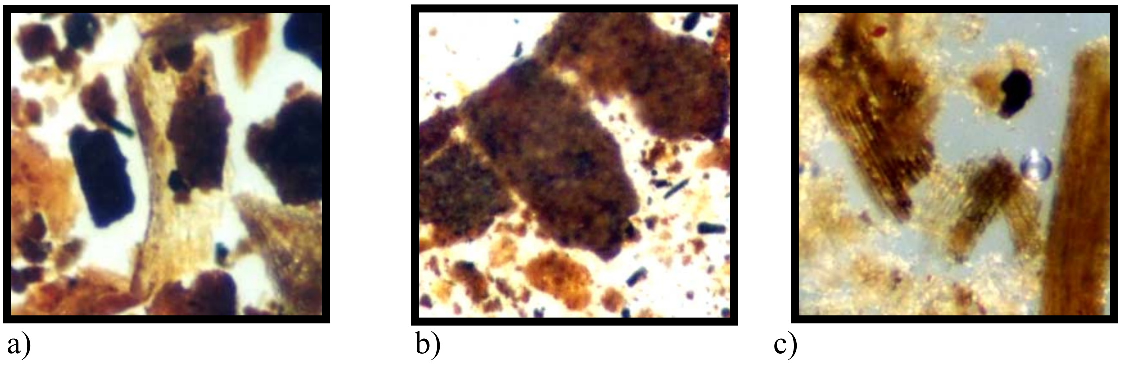
a) b) c)

Figure 7-3: Microscopic photos of a) free light fraction, b) occluded I light fraction, and c) occluded II light fraction. Scale of frame is about 1 mm.

7.3 Chemically Defined Fractions

In order to determine the chemical recalcitrance of the mineral-associated soil C, three chemical fractionation methods (treatment with HCl, NaOCl, and $Na_4P_2O_7$) were applied to the mineral-associated soil fraction (fraction <53 µm). While all chemical treatments reduced the carbon content NaOCl was the most efficient treatment: only 5% (sedimentary soils) and 14% (volcanic ash soils) of total soil C was resistant to it. About 33% of total soil C was resistant to acid hydrolysis regardless the soil type. The lowest carbon reduction was found in the residuum of $Na_4P_2O_7$ treatment with 58% (sedimentary soils) and 40% (volcanic ash soils) of total soil recovered after treatment (Figure 7-1). In both soil types, soil C concentrations in all residual fractions were strongly correlated with the initial concentrations of mineral-associated soil C. Higher carbon contents were measured in all residual fractions of natural forest than in pasture soils.

Acid hydrolysis isolated fixed proportions of initial soil C content independent on soil mineralogy. This suggests that the amount of hydrolysis resistant soil C was controlled by the chemical structure of soil organic matter itself rather than by soil properties. Moreover, low preferential loss of recently incorporated carbon in the non-hydrolysable fraction indicates that there is no close link between chemical hydrolysability and in-situ persistence of soil C in these tropical topsoils (Figure 7-2). In contrast, treatment with $Na_4P_2O_7$ or NaOCl isolated pool sizes which were controlled by soil properties, both being higher in volcanic ash soils. This indicates that complexation with hydroxymetal species and adsorption to mineral surfaces was more effective in binding soil C in volcanic ash soils than adsorption of soil C to smectitc clays in sedimentary soils. In addition, the proportions of pasture-derived carbon in the residual fraction of NaOCl and in the extracts of $Na_4P_2O_7$ were halved following the chemical treatment. This is a hint that NaOCl and $Na_4P_2O_7$ in fact separated older soil organic matter pools (Figure 7-2). However, the disappearance of recently incorporated (pasture-derived) soil C in the secondary forest soils developed from volcanic ashes revealed that recently incorporated soil organic matter was not long-term stabilized after land use change. The results indicate that the employed methods were not able to isolate a soil organic matter fraction which is protected against microbial decay under field conditions. This questions the idea that soil organic matter fractions separated by HCl, NaOCl or $Na_4P_2O_7$ do present stable soil organic matter pools in soils derived from volcanic ashes. In contrast, for soils rich in smectite, recently incorporated soil organic matter was partly stabilized. Thus, the outcome of these fractionation methods is sensitive to soil type which makes interpretation challenging and precludes any generalisation to other soils types or climates.

7.4 Summarizing Evaluation of Different Soil C Fractions

7.4.1 Which Soil C Fractions are Sensitive Indicators for Land Use Change?

Changes in carbon storage induced through land use changes were relatively small in most soil C fractions compared to the impact of soil properties. Significant differences were often only obtained through the analysis of the whole dataset and not for an individual site. If significant differences occurred at an individual site, then often differences among land use types can be seen in all isolated soil C fractions. Nevertheless, changes in carbon storage were more pronounced in light fractions compared to other soil C fractions. While pasture establishment after deforestation reduced total soil C storage by 20%, the reduction in the light fraction was more than 50%. The occluded II light fraction displayed the strongest reduction in soil C storage and also the fastest turnover rates. This was derived from an almost pure C_4 signature in the occluded II light fraction of pasture soils which vanishes after afforestation. Although the occluded I light fraction in pasture soils has relative slow turnover rates, it responds to deforestation with a considerable reduction in soil C storage. This supports the idea that light fractions are generally more sensitive to land use changes than total soil C and are therefore used as an early indicator (Gregorich et al., 2006). However, in this study time span after land use conversion comprised a few decades, therefore both the amounts of soil C was reduced and the C4 signal was already transferred to the slower cycling pools and consequently changes could also be observed in the bulk soil.

7.4.2 Which Information can be Gained from the Different Soil C Fractions about Soil C Stability and Stabilization Mechanisms?

The applied fractionation scheme resulted in soil C fractions with different stabilities (Figure 7-2a and 7-2b). Several fractions contained more recently incorporated carbon than the bulk soil. The occluded II light fraction was the youngest fraction, followed by the free light fraction, which consisted of organic material in loose association with minerals and was found outside aggregates. The free light fraction comprised about 30% more pasture-derived carbon as the bulk soil. Less than 4 % of total soil C storage was found in this fraction (Figure 7-1). Stability of this density fraction mainly depended on the primary recalcitrance of plant litter as in active top-soils the first degradation steps of plant debris is determined by its litter quality (von Lützow et al., 2006). The free light fraction was found to comprise a mixture of relatively fresh, unaltered plant debris together with a more decomposed component (Poirer et al., 2005).

Soil C in almost all isolated fractions is probably stabilized by a combination of specific stabilization mechanisms (selective preservation of recalcitrant compounds, spatial inaccessibility, or interaction with minerals). Even, if the applied fractionation methods were not specific with respect to stabilization mechanisms, it provided new insight in the importance of different mechanisms for organic carbon storage and stability: With the applied fractionation scheme, information was gained about the stabilization mechanism spatial inaccessibility, namely the protection of organic matter through aggregation. Even though organic material played a different role in the stabilization of aggregates in volcanic ash and sedimentary soils, in both soil types soil C seems to be stabilized through aggregation to a similar extent. Evidence arose from i) correlation of soil C with the degree of aggregation, ii) the increasing amount of occluded light fraction with increasing degree of aggregation, and iii) the observed older age of the occluded I light fraction. Besides the stabilization mechanism spatial inaccessibility, the selective preservation of recalcitrant compounds may also contribute to the stability of occluded I light fraction, as the occluded I light fraction was found to be more recalcitrant than the free light fraction (Golchin et al., 1995; Helfrich et al., 2006).

Furthermore, information about the processes behind the initial aggregate formation can be obtained from this fractionation scheme. Although aggregate stabilization mechanisms were different for both soil types, the initial phase of aggregate formation seemed to be valid for both soil types. The occluded II light fraction separated from highly stable microaggregates showed the highest enrichment of recently incorporated carbon compared to bulk soil in both soil types. The occluded I light fraction, which stored about 15% of total soil C, was older than both the free light fraction not occluded in aggregates and the bulk soil. However, differences in stability were relatively small. This indicates that soil C is not stabilized in long-term by aggregation.

Results from chemical fractionation procedures (treatment with NaOCl and $Na_4P_2O_7$) revealed differences in the dominating stabilization mechanism between the two soil types. About two to three fold higher carbon storage in the NaOCl resistant and $Na_4P_2O_7$ soluble soil C fraction in the volcanic ash soils revealed that interaction with minerals (complexation with hydroxymetal species and adsorption to mineral surfaces) was a more important stabilization mechanisms in volcanic ash soils than in sedimentary soils. However, similar stabilities of these fractions indicate a comparable function of these soil fractions with respect to soil C stabilization. Although chemically isolated soil C fractions were the oldest of all gained fractions, a stable soil C pool with considerably longer mean residence times than bulk soil was not gained.

None of the investigated soil fractionation methods was successful in isolating a passive soil C pool that is stabilized in long-term in these organic rich tropical topsoils. Until now, the conceptual carbon pools used in soil organic matter models still lack validation with measured operationally defined fractions with specific functions for soil C stabilization.

7.5 Outlook

Results of this study revealed that the main part of soil organic matter was associated with the mineral phase. Association of soil C with mineral particles is thought to play a key role in decomposition and stabilization processes of soil C (Christensen, 2001; von Lützow et al., 2007). However, until now knowledge about binding mechanisms of mineral-associated soil C is scarce; particularly with respect to the interrelation between mineral properties and soil organic matter qualities on the formation and stability of mineral-organic associations. With three different chemical fractionation methods it was not possible to separate a soil C pool from the mineral-associated soil C that was considerably older than bulk soil C bound to minerals. Even the most promising treatment with NaOCl, which does not alter properties of the mineral phase, still contained recently incorporated soil C. The challenge is to find a method that isolates a passive fraction altering neither the mineral phase nor the stabilized organic material. This is particularly important with respect to identify individual stabilization mechanisms between organic matter and mineral surfaces. To this end, further studies should not only be restricted to A-horizons but rather include the subsurface horizons where stabilization of organic matter is stronger. For a better understanding of involved processes detailed characterisation is indispensable for mineral surfaces, soil organic matter, and soil solution.

The natural abundance approach on bulk soil fraction was used to determine pool sizes of forest- and pasture-derived carbon and the mean residence time of old forest-derived carbon under pastures and of recently incorporated pasture-derived carbon in the secondary forests. The mean residence time is a valuable indicator for the stability of soil C. However, it remained unknown to what extend the old forest-derived soil C is still involved in the microbial cycling under pasture. Separation of specific biomarkers such as amino sugars or phospholipid fatty acids and the subsequent determination of their carbon isotope ratio may provide clues to what extent this old forest-derived carbon is still utilized by microorganisms.

This thesis focused on the storage and the stability of soil C. Recent literature suggests that carbon and nitrogen dynamics are tightly linked to each other and that N cycling influences C stabilization in the temperate regions (Berg, 2004; Waldrop et al., 2004; Knorr et al., 2005). Furthermore, evidence arose that the carbon sequestration potential is linked to the source of nitrogen. For instance, soil C stocks increased after afforestation with N-fixing trees, but not after afforestation with non N-fixing trees and N fertilization on volcanic ash soils in Hawaii (Kaye et al., 2000; Binkley et al., 2004). Regarding the C-sequestration potential in the near future and expected increasing atmospheric nitrogen deposition, especially in the tropics, it is imperative to understand the causal link between carbon and nitrogen stabilization and how additional nitrogen might influence the carbon balance.

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9 Appendix – Soil Profiles

Chonta Duro (00°55.26N, 079°25.30W; 30m NN)
Soil classification: FAO: stagnic Luvisol, Soil Taxonomy: Paleustalf

Land use: pasture; slope: 10; orientation: 360°

Horizon	depth	color[a]		texture[b]	clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				—g kg^{-1}—			g kg^{-1}		‰	————g kg^{-1}————						
Ah	0-6	10 YR	3/3	silty clay	41	7	5.7	39	8.7	-17.9	7.6	0.3	1.4	0.6	5.4	9.4	strong subangular blocky
Bt1	6-54	10 YR	4/4	clay	65	2	4.7	11	6.9	-21.3	4.5	3.5	2.3	0.7	3.2	10.3	strong angular blocky
Bt2g	54-80++	10 YR	5/6	clay	62	4	4.7	5	5.6	-23.3	2.1	2.9	2.4	0.6	3.1	19.7	weak angular blocky

Land use: secondary forest; slope: 3; orientation: 300°

Horizon	depth	color[a]		texture[b]	clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				—g kg^{-1}—			g kg^{-1}		‰	————g kg^{-1}————						
Ah	0-7	10 YR	3/3	silty clay	53	4	5.8	34	9.0	-26.2	5.7	0.2	1.1	0.7	4.3	9.4	strong subangular blocky
Btg	7-40	10 YR	4/4	clay	62	2	4.9	10	7.0	-25.0	3.4	1.3	1.6	0.7	2.9	11.2	strong angular blocky
BCg	40-80++	10 YR	6/3	silty clay loam	38	9	4.9	4	5.2	-24.8	1.5	0.3	1.8	0.7	2.9	16.1	strong angular blocky

Land use: natural forest, slope:5; orientation: 40°

Horizon	depth	color[a]		texture[b]	clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				—g kg^{-1}—			g kg^{-1}		‰	————g kg^{-1}————						
Ah	0-10	10 YR	3/2	silty clay	48	5	6.0	32	8.7	-26.5	5.1	0.1	1.3	0.8	4.4	9.8	strong subangular blocky
Btg1	10-30	10 YR	5/3	silty clay	56	4	5.4	15	7.4	-25.4	3.5	0.1	1.3	0.6	3.4	11.0	strong angular blocky
Btg2	30-60-	10 YR	4/6	clay	63	3	4.9	6	6.6	-24.8	2.5	3.6	1.6	0.6	2.3	nd	weak subangular blocky
Cg	60-90++	10 YR	5/6	silty clay	54	3	5.0	3	4.3	-24.7	1.1	0.1	1.4	0.5	1.9	16.2	weak subangular blocky

[a] according to Munsel soil colour chart (1975), [b] according to soil taxonomy (Soil Survey Staff, 1998)

Minas (00°51.86N, 079°34.24W; 190m NN)
Soil classification: FAO: stagnic Cambisol, Soil Taxonomy: Haplustepts

Land use: pasture; slope: 3; orientation: 270°

Horizon	depth	color^a	texture^b	clay	sand	pH	C	C/N	δ^{13}C	C$_p$	Al$_p$	Al$_o$	Si$_o$	Fe$_o$	Fe$_d$	aggregation
	cm			—g kg^{-1}—			g kg^{-1}		‰	———g kg^{-1}———						
Ah	0-10	10 YR 2/1	clay	62	5	7.4	74	11.7	-20.2	17.1	0.3	1.4	0.8	3.6	9.7	strong subangular blocky
AB	10-28	10 YR 4/3	clay	nd	nd	7.6	26	10.0	-22.1	7.1	0.1	1.6	1.0	4.0	13.4	strong angular blocky
Bwg	28-68	2,5 Y 5/4	clay	nd	nd	7.7	18	24.5	-23.5	1.6	0.6	1.3	1.0	2.3	16.9	strong angular blocky

Land use: secondary forest; slope: 16; orientation: 100°

Horizon	depth	color^a	texture^b	clay	sand	pH	C	C/N	δ^{13}C	C$_p$	Al$_p$	Al$_o$	Si$_o$	Fe$_o$	Fe$_d$	aggregation
	cm			—g kg^{-1}—			g kg^{-1}		‰	———g kg^{-1}———						
Ah	0-9	10 YR 2/1	clay	64	5	6.9	65	10.9	-23.7	10.6	0.5	1.7	0.8	1.5	5.2	strong subangular blocky,
AB	9-21	10 YR 4/2	clay	nd	nd	6.2	26	8.9	-23.6	6.6	1.2	1.8	0.9	1.4	6.0	strong angular blocky
Bw1	21-48	10 YR 5/3	clay	nd	nd	5.9	10	7.8	-23.5	2.9	0.7	2.1	0.9	1.6	9.6	strong angular blocky
Bw2	48-70	2,5 Y 6/3	clay	nd	nd	5.7	5	6.4	-23.2	2.1	0.8	1.9	1.0	1.3	10.0	strong angular blocky

Land use: natural forest, slope: 8; orientation: 350°

Horizon	depth	color^a	texture^b	clay	sand	pH	C	C/N	δ^{13}C	C$_p$	Al$_p$	Al$_o$	Si$_o$	Fe$_o$	Fe$_d$	aggregation
	cm			—g kg^{-1}—			g kg^{-1}		‰	———g kg^{-1}———						
Ah	0-15	7,5 YR 2,5/1	clay	62	9	6.9	51	10.9	-26.2	10.6	0.6	1.8	1.0	3.4	12.2	strong subangular blocky
AB	15-35	7,5 YR 3/2	clay	nd	nd	6.7	25	9.0	-24.6	6.2	0.5	1.9	1.0	4.3	14.7	strong angular blocky
Bwg	35-80	7,5 YR 4/6-7/8	clay	nd	nd	4.8	6	7.5	-23.6	2.8	0.3	1.8	0.6	3.3	21.5	coherent

Tazones (00°43.24N, 079°50.09W; 100m NN)
Soil classification: FAO: Eutric Cambisol; Soil Taxonomy: Haplustepts

Land use: pasture; slope: 28; orientation: 220°

Horizon	depth	color[a]		texture[b]	clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				—g kg^{-1}—			g kg^{-1}		‰	———g kg^{-1}———						
Ah	0-9	10 YR	3/1	clay loam	28	38	6.2	26	8.9	-20.0	4.4	1.2	0.9	0.6	2.4	6.4	strong subangular blocky
Bw	9-26	10 YR	4/2	clay loam	32	36	6.6	8	7.1	-22.7	2.3	0.5	1.0	0.6	1.5	7.7	strong angular blocky
BwC	26-50	10 YR	5/4	clay loam	36	30	6.3	3	6.2	-23.5	1.6	0.6	1.0	0.7	1.6	10.4	strong angular blocky
C	50-++	10 YR	5/3	clay loam	36	33	6.1	2	5.1	-23.3	0.8	0.8	0.8	0.6	1.2	8.1	coherent

Land use: secondary forest; slope: 28; orientation: 335°

Horizon	depth	color[a]		texture[b]	clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				—g kg^{-1}—			g kg^{-1}		‰	———g kg^{-1}———						
Ah	0-12	10 YR	3/2	clay loam	32	28	6.5	24	8.7	-24.1	4.4	0.6	0.9	0.5	1.1	4.4	strong subangular blocky
ABw	12-36	10 YR	4/4	clay loam	34	33	6.4	6	6.6	-23.4	2.3	0.3	0.9	0.6	0.9	8.4	strong angular blocky
BwC	36-100	10 YR	4/4	loam	25	46	6.7	3	5.4	-23.7	1.1	0.2	1.0	0.6	0.9	7.2	coherent

Land use: natural forest, slope: 7; orientation: 300°

Horizon	depth	color[a]		texture[b]	clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				—g kg^{-1}—			g kg^{-1}		‰	———g kg^{-1}———						
Ah	0-6	7,5 YR	2,5/2	clay loam	28	32	7.1	38	9.5	-27.4	5.0	0.4	1.1	0.6	1.5	3.1	strong subangular blocky
Bw	6-15	10 YR	4/3	clay loam	28	nd	6.4	14	7.7	-26.0	2.8	0.4	1.1	0.5	2.1	4.2	strong angular blocky
Cg	15-60	2,5 Y	5/4	clay loam	32	nd	5.0	4	6.6	-25.0	1.5	0.3	1.5	0.5	2.0	5.9	coherent

Penas (01°04.37N, 079°08.09W; 45m NN)

Soil classification: FAO: Eutric Cambisol, Soil Taxonomy: Haplustepts

Land use: pasture; slope: 9; orientation: 330°

Horizon	depth	color[a]	texture[b]	clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	si_o	Fe_o	Fe_d	aggregation
	cm			—g kg^{-1}—			g kg^{-1}		‰	g kg^{-1}						
Ah	0-10	10 YR 3/2	clay loam	29	27	6.4	36	10.1	-19.1	5.3	2.0	0.7	0.6	2.4	3.3	strong subangular blocky
Bwg	10-30	10 YR 3/2	clay loam	34	nd	6.5	9	7.9	-21.4	2.1	1.3	0.7	0.6	1.5	5.6	strong subangular blocky
BC	30-60	10 YR 4/2	clay	53	nd	6.1	5	6.8	-20.6	2.0	1.7	0.9	0.5	1.0	5.7	weak subangular blocky
C	60-90++	10 YR 6/8	clay	54	nd	4.8	3	5.8	-23.0	1.5	0.2	1.0	0.4	0.8	13.4	coherent

Land use: secondary forest; slope: 19; orientation: 240°

Horizon	depth	color[a]	texture[b]	clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	si_o	Fe_o	Fe_d	aggregation
	cm			—g kg^{-1}—			g kg^{-1}		‰	g kg^{-1}						
Ah	0-10	10 YR 3/3	silty clay	48	4	5.6	30	9.0	-23.2	7.4	1.4	1.5	0.6	3.4	10.8	strong subangular blocky
Bw1	10-20	10 YR 4/4	silty clay	52	nd	5.7	16	8.5	-22.6	4.1	1.2	1.6	0.7	2.7	12.8	medium subangular blocky
Bw2	20-40	10 YR 5/3	silty clay	48	nd	6.0	8	8.1	-22.2	2.8	0.2	1.5	0.7	2.0	18.8	coherent
C	40-100	10 YR 6/8	silty clay	37	nd	6.5	2	5.1	-22.8	0.9	0.1	1.2	0.6	0.8	20.7	coherent

Land use: natural forest, slope: 11; orientation: 120°

Horizon	depth	color[a]	texture[b]	clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	si_o	Fe_o	Fe_d	aggregation
	cm			—g kg^{-1}—			g kg^{-1}		‰	g kg^{-1}						
Ah	0-10	10 YR 3/3	Silty clay loam	33	15	6.0	30	9.0	-27.2	5.6	0.7	1.3	0.5	2.5	6.7	strong subangular blocky
ABw	10-30	10 YR 4/4	Silty clay loam	37	nd	5.2	13	7.9	-25.9	3.5	1.1	1.2	0.4	2.2	7.6	strong angular blocky
C	30-60	10 YR 6/8- 5/8	Silty clay loam	29	nd	4.9	4	6.9	-25.4	1.6	0.7	1.3	0.6	2.0	12.9	coherent

Mindo (00°01.45N, 078°46.16W, 1665m NN)
Soil classification: FAO: Eutric Andosol, Soil Taxonomy: Hapludands

Land use: pasture; slope: 0; orientation: -

Horizon	depth	color^a		texture^b	silt+clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				——g kg^{-1}—			g kg^{-1}		‰	——————g kg^{-1}———————						
Ah	0-5	10 YR	2/2	sandy loam	26	74	5.5	82	11.8	-17.4	25.2	1.7	6.6	0.8	8.6	5.1	medium subangular blocky
AB	5--15	7,5 YR	3/4	sand	19	81	5.6	25	12.3	-23.7	10.5	1.8	6.6	1.5	7.8	5.4	medium subangular blocky
B	15-29	10 YR	3/4	sand	14	86	5.6	14	12.2	-25.0	4.4	1.0	4.4	1.4	5.1	3.3	coherent
C	29-45	10 YR	4/4	sand	7	93	5.7	5	10.1	-24.8	2.4	0.7	3.5	1.3	4.5	1.9	coherent
Ahb1	45-90	10 YR	3/4	sandy loam	28	72	5.9	16	11.7	-23.7	5.9	1.1	6.7	2.4	5.3	4.2	coherent
Ahb2	90-100	7,5 YR	3/3	sandy loam	58	42	6.0	20	11.4	-20.2	8.1	2.9	15.2	7.0	5.9	7.2	coherent
Ahb3	100-120	7,5 YR	3/2	sandy loam	35	65	5.0	16	11.6	-19.7	7.3	2.7	18.5	8.8	6.5	6.3	coherent

Land use: secondary forest; slope: 10; orientation: 270°

Horizon	depth	color^a		texture^b	silt+clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				——g kg^{-1}——			g kg^{-1}		‰	——————g kg^{-1}———————						
Ah	0-10	10 YR	2/2	sandy loam	21	79	5.1	58	13.2	-27.2	20.3	3.6	4.0	0.4	4.6	3.6	strong subangular blocky
AB	10--20	7,5 YR	3/3	sandy loam	13	87	5.3	24	13.2	-26.7	16.2	3.8	5.0	0.6	6.2	4.1	coherent
B	20-32	5 YR	3/4	sand	6	94	5.5	11	15.1	-26.8	16.3	5.1	4.5	0.9	3.9	2.5	coherent
bAh	32-45	10 YR	3/4	sandy loam	39	61	5.7	18	12.2	-24.6	10.0	3.3	10.0	3.5	5.7	5.4	medium subangular blocky
Ahgb	45-75	10 YR	3/4	sandy loam	59	41	5.8	23	11.6	-21.5	9.5	3.2	15.1	6.5	6.4	6.0	coherent
Bb	75-100	10 YR	3/3	sandy loam	34	66	5.1	17	11.7	-21.5	7.8	2.8	16.7	7.6	4.7	5.8	coherent

Mindo

Land use: natural forest, slope: 12; orientation: 340°

Horizon	depth	color[a]	texture[b]	silt+clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm			g kg^{-1}			g kg^{-1}		‰	g kg^{-1}						
Ah	0-10	7,5YR 2,5/2	sandy loam	21	79	5.4	54	13.8	-27.4	22.5	4.2	4.8	0.5	4.5	3.7	strong subangular blocky
B	10--30	5 YR 3/4	lomy sand	5	95	5.6	8	13.9	-26.4	5.1	2.5	2.9	0.8	2.5	1.5	coherent
Ab1	30-46	10 YR 3/4	sandy loam	31	69	5.7	15	12.5	-26.4	6.9	2.9	9.4	3.3	4.4	5.8	coherent
Ahb2	46-60	10 YR 3/2	sandy loam	49	51	5.7	22	12.1	-21.6	9.4	3.6	16.9	7.1	5.8	7.2	coherent
Ahb3	60-100	10 YR 3/1	sandy loam	47	53	5.6	20	12.2	-21.7	7.1	2.8	17.0	7.5	4.4	5.5	coherent

Mauipucuna (00°07.21N, 078°37.55W, 1360m NN)
Soil classification: FAO: Eutric Andosol, Soil Taxonomy: Hapludands

Land use: pasture; slope: 13; orientation: 300°

Horizon	depth	color[a]	texture[b]	silt+clay	sand	pH	C	C/N	$\delta^{13}C$	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm			g kg^{-1}			g kg^{-1}		‰	g kg^{-1}						
Ah	0-9	7,5 YR 2,5/3	sandy loam	32	68	5.4	41	10.5	-17.5	14.1	3.8	4.8	nd	8.7	6.1	strong subangular blocky
B	9-23	7,5 YR 3/4	sandy loam	23	77	5.6	19	10.2	-22.3	7.4	2.6	6.1	2.1	7.0	6.0	medium subangular blocky
Ahb	32-47	10 YR 3/3	sandy loam	53	47	5.9	23	11.1	-21.7	9.1	3.4	13.4	5.0	5.6	6.2	strong subangular blocky
Bb	47-55	10 YR 5/3	sandy loam	76	24	5.9	13	10.9	-20.1	5.0	2.5	13.9	6.2	4.1	4.8	medium angular blocky
Ahb1	55-70	10 YR 2/2	sandy loam	47	53	6.0	29	12.1	-18.0	10.6	3.8	23.6	9.9	8.5	8.9	strong subangular blocky
Ahb2	70-110	10 YR 3/2	sandy loam	34	66	6.0	20	11.4	-20.0	7.6	3.4	18.6	8.0	4.8	5.8	strong subangular blocky
Bb	110-140	10 YR 3/2	sandy loam	29	71	6.0	14	11.6	-20.2	6.7	2.8	18.3	8.0	4.7	4.3	strong subangular blocky
Ahb	140-160	10 YR 2/1	sandy loam	34	66	5.9	24	12.5	-20.7	7.1	3.1	22.1	9.6	6.8	6.5	strong subangular blocky

Mauipucuna

Land use: secondary forest; slope: 8; orientation: 170°

Horizon	depth	color[a]		texture[b]	silt+clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				g kg^{-1}			g kg^{-1}		‰	g kg^{-1}						
Ah	0-10	7,5 YR	2,5/2	sandy loam	27	73	5.3	46	11.2	-27.5	16.4	4.1	5.9	1.4	4.6	5.0	medium subangular blocky
Bu1	10-20	7,5 YR	3/4	loamy sand	26	74	5.4	21	11.2	-25.6	11.5	4.0	9.4	2.8	4.7	4.6	medium subangular blocky
Bu2	20-40	7,5 YR	3/3	sandy loam	38	62	5.6	18	11.1	-22.4	7.4	2.9	13.5	5.3	6.5	6.8	weak subangular blocky
BC	40-80	10 YR	3/2	sandy loam	26	74	5.8	9	11.5	-21.6	3.6	1.9	11.6	5.2	3.9	3.6	coherent
C	80-100	10 YR	4/2 - 6/8	sand	13	87	5.9	4	10.3	-23.1	2.0	1.1	7.7	4.1	3.8	1.7	coherent

Land use: natural forest, slope: 22; orientation: 180°

Horizon	depth	color[a]		texture[b]	silt+clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				g kg^{-1}			g kg^{-1}		‰	g kg^{-1}						
Ah	0-10	10 YR	2,5/2	sandy loam	31	69	5.3	55	11.6	-27.4	18.4	4.4	6.6	1.5	5.2	4.8	strong subangular blocky
Ahb	10-30	7,5 YR	3/2	loamy sand	25	75	5.3	25	11.2	-25.6	11.3	3.7	15.0	5.9	6.1	4.6	strong angular blocky
Ahb	30-40	10 YR	3/2	loam	46	54	5.5	27	11.5	-21.7	12.1	4.0	9.1	2.7	4.8	7.5	mediumangular blocky
Ahb	40-55	10 YR	3/2	silty loam	55	45	5.6	27	11.6	-19.2	10.8	3.7	22.5	9.6	7.8	8.4	strong angular blocky
Bb1	55-70	10 YR	3/1	loam	55	45	5.7	21	11.5	-19.1	8.8	3.7	22.3	11.0	5.9	8.4	weak angular blocky
Bb2	70-90	10 YR	5/4	silt	41	59	5.7	13	11.3	-21.3	5.0	2.8	39.2	nd	5.5	12.3	weak angular blocky
C	90-110	7,5 YR	5/6	sandy loam	35	65	5.7	7	11.0	-23.0	2.4	2.4	31.9	nd	6.0	15.0	coherent

Pedro Viciente (00°05.65N, 079°01.51W, 690m NN)

Soil classification: FAO: Eutric Andosol, Soil Taxonomy: Hapludands

Land use: pasture; slope: 0; orientation: -

Horizon	depth	color[a]		texture[b]	silt+clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				g kg^{-1}			g kg^{-1}		‰	g kg^{-1}						
Ah	0-15	10 YR	2/2	silty clay	57	43	5.7	99	12.0	-25.6	28.5	7.7	18.1	5.4	7.4	8.8	strong subangular blocky
B	15-70	10 YR	4/3	silty clay	45	55	5.9	25	10.5	-24.0	7.0	2.9	31.0	13.9	7.4	9.6	medium subangular blocky
C	70++	10 YR	4/3	silty clay	34	66	nd	5	9.0	-23.3	2.2	1.8	20.9	11.2	3.7	4.2	coherent

Pedro Viciente

Land use, secondary forest; slope: 0; orientation: -

Horizon	depth	color^a		texture^b	silt+clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				g kg^{-1}			g kg^{-1}		‰	g kg^{-1}						
Ah	0-10	7,5YR	2,5/3	silty clay	52	48	5.1	72	13.6	-28.2	23.8	7.1	15.8	4.5	6.3	nd	strong subangular blocky
B	10-60	10 YR	4/3	silty clay	45	55	5.8	24	10.0	-24.3	9.6	3.3	39.1	18.1	7.4	9.3	strong angular blocky
C1	60-100	10 YR	4/3	sand	44	56	5.8	9	9.9	-23.6	2.0	1.7	25.8	13.3	4.2	6.1	coherent
C2	100++	10 YR	4/1	sandy loam	41	59	5.8	3	8.5	-23.8	1.0	1.2	13.1	7.6	1.9	3.5	coherent

Land use: natural forest, slope: 8; orientation: 210°

Horizon	depth	color^a		texture^b	silt+clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				g kg^{-1}			g kg^{-1}		‰	g kg^{-1}						
Ah	0-11	7,5YR	2,5/3	loam	64	36	4.7	77	13.8	-27.6	28.2	8.0	14.6	3.3	8.4	7.5	strong subangular blocky
B	11-53	10 YR	4/3	loam	58	42	5.3	28	10.6	-25.6	11.7	3.6	7.7	2.2	6.6	8.4	strong angular blocky
BC	53-90	10 YR	4/3	sandy loam	44	56	5.6	10	10.4	-24.0	2.4	2.0	23.7	10.1	5.8	5.7	coherent
C	90-105	10 YR	4/1	sand	46	54	5.6	3	9.3	-24.1	1.1	1.6	24.6	12.4	3.5	4.4	coherent
Ahb	105++	10 YR	4/3	sandy loam	46	54	5.7	17	11.3	-23.9	4.0	2.9	18.7	10.4	2.6	12.1	coherent

Pitzara (00°16.22N, 079°09.74W, 290m NN)
Soil classification: FAO: Eutric Andosol, Soil Taxonomy: Hapludands

Land use: pasture; slope: 7; orientation: 210°

Horizon	depth	color^a		texture^b	silt+clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm				g kg^{-1}			g kg^{-1}		‰	g kg^{-1}						
Ah1	0-10	10 YR	3/2	silty clay	71	29	5.3	99	12.2	-22.8	28.2	7.7	22.7	7.6	7.5	9.3	strong subangular blocky
Ah2	10-22	10 YR	4/4	silty clay	71	29	5.6	41	11.4	-25.3	16.5	5.2	32.4	12.5	8.0	10.8	strong subangular blocky
B	22-68	10 YR	4/2	sandy clay	51	49	6.0	20	10.5	-25.0	5.3	3.4	39.7	nd	6.4	10.3	strong angular blocky
C	68-80	10 YR	5/4	sandy clay	55	45	6.1	5	10.4	-24.6	1.3	1.9	23.7	13.5	3.3	5.8	coherent
Ahb	80-90	10 YR	3/4	sandy clay	47	53	6.0	23	12.2	-24.5	4.9	3.3	48.4	nd	8.7	12.8	coherent
Bb	90-100	10 YR	4/4	sandy clay	48	52	6.0	18	11.8	-24.4	4.1	3.3	51.3	nd	9.5	13.0	coherent

Pitzara

Land use, secondary forest; slope: 5; orientation: 190°

Horizon	depth	color[a]	texture[b]	silt+clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm			——g kg^{-1}——			g kg^{-1}		‰	——————g kg^{-1}——————						
Ah1	0-10	10 YR 2/2	silty clay loam	64	36	5.3	93	12.7	-27.5	24.6	7.8	29.5	11.1	6.5	9.8	strong subangular blocky
Ah2	10-25	10 YR 3/4	silty clay loam	52	48	5.7	41	10.3	-26.1	15.5	4.8	40.7	17.6	7.5	11.0	strong subangular blocky
B1	25-80	10 YR 4/4	silty clay loam	56	44	5.9	24	10.1	-25.2	6.3	3.4	42.9	nd	7.5	11.0	coherent
B2	80-120	10 YR 4/2	silty clay loam	51	49	5.8	11	10.9	-24.1	2.2	2.2	30.6	17.0	4.6	9.6	coherent

Land use: natural forest, slope: 3; orientation: 280°

Horizon	depth	color[a]	texture[b]	silt+clay	sand	pH	C	C/N	δ^{13}C	C_p	Al_p	Al_o	Si_o	Fe_o	Fe_d	aggregation
	cm			——g kg^{-1}——			g kg^{-1}		‰	——————g kg^{-1}——————						
Ah1	0-10	10 YR 3/2	silty clay loam	68	32	4.7	91	13.2	-27.9	38.8	10.1	19.8	5.8	7.1	7.4	strong rounded blocky
Ah2	10-44	10 YR 4/4	silty clay loam	67	33	4.7	28	9.9	-25.8	12.2	3.7	31.5	13.3	6.9	9.2	angular-subangular blocky
B1	44-67	10 YR 5/3	silty clay loam	50	50	5.2	18	10.0	-24.4	5.8	2.9	39.7	nd	7.0	9.7	angular blocky- coherent
B2	67-80	10 YR 5/2	silty clay loam	57	43	5.5	7	9.4	-24.1	2.2	1.9	24.6	14.2	3.5	6.2	coherent

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Curriclum Vitae

Sonja Marit Paul
geboren am 19.08.1977
in Göttingen

Wissenschaftliche Ausbildung

2004-2007	Promotionsstudium Biologische Diversität und Ökologie an der Georg-August-Universität Göttingen
1997-2003	Studium der Geoökologie an der Universität Bayreuth Abschluss: Dipl.-Geoökologin
2000-2001	Stipendiatin des EU-Socrates/Erasmus Programms: Studium der Biologie, University of York, England
1984-1997	Grundschule, Orientierungsstufe und Gymnasium in Göttingen, Abschluss: Allgemeine Hochschulreife

Veröffentlichungen:

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Erklärung

Ich versichere, dass ich die vorliegende Dissertation selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

Die den Kapiteln 3, 4, 5 und 6 zugrunde liegenden Manuskripte habe ich als Erstautorin verfasst. Ausserdem bin ich bei den vier Veröffentlichungen korrespondierende Autorin. Ein Teil der in Kapitel 3 dargestellten Daten (trockene Vorbehandlung) stammt aus der Masterarbeit von Guntars Martinson.

Ich versichere, dass ich nicht bereits anderweitig eine Dissertation eingereicht oder versucht habe, mich einer Doktorprüfung zu unterziehen.

Göttingen, den 07.06.2007

(Sonja Marit Paul)