Volcanic ash soils in Andean ecosystems: unravelling organic matter distribution and stabilisation

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Modelling vertical organic matter distribution in a volcanic ash soil in the Ecuadorian páramo: impact of soil volume change

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Abstract

Volcanic ash soils contain very large stocks of soil organic matter (SOM) per unit area. Consequently, they constitute potential sources or sinks for the greenhouse gas CO₂ that are of global importance and thus merit special attention. Because a large fraction of SOM is generally stored in the subsoil, a thorough understanding of the processes affecting the vertical distribution of SOM is needed to properly predict impacts of climate change and/or land use change on soil organic carbon stocks. Soil faunal bioturbation (‘bioturbation’) is often cited as the dominant process influencing the vertical distribution of SOM. An additional but often overlooked process that affects the vertical distribution of SOM is soil volume change. Soil volume change may influence depth-dependent processes such as bioturbation. We previously investigated the role of bioturbation in volcanic ash soils under grassland vegetation in the northern Ecuadorian Andes and hypothesised that bioturbation has shifted upwards in time in response to soil thickening. In the current investigation, we determined the extent of soil volume change with a geochemical mass balance involving immobile element concentrations. Furthermore, we tested our hypothesis with a one-dimensional partial differential equation model. Our results show that soil volume change is a major soil forming process in the volcanic ash soil studied. SOM accumulation resulted in more than a tripling of initial soil thickness within 4800 years, from ~20 cm to 77 cm. Our modelling exercise confirmed that an upward shifting bioturbation zone in response to soil thickening is indeed plausible. We conclude that soil volume change cannot be ignored when modelling soil organic carbon dynamics in SOM-rich soils such as volcanic ash soils.

Keywords

soil organic carbon, model, vertical distribution, bioturbation, volcanic ash soil, volume change
Introduction

Because soil organic matter (SOM) constitutes the largest pool of terrestrial organic carbon, soils are potential sources or sinks of the greenhouse gas CO₂ that are of global importance (Eswaran et al. 1993; Batjes 1996; Swift 2001; Lal 2004). This is reflected in global models for carbon cycling by incorporating SOM dynamics. Most models of SOM dynamics focus on the topsoil (< 25 cm depth) and lack spatial dimensions (Elzein & Balesdent 1995; Smith et al. 1997; Jenkinson et al. 2008). However, a large fraction of SOM is stored in the subsoil (Batjes 1996), where its stability against decomposition is supposedly higher. Thus, a thorough understanding of the processes affecting the vertical distribution of SOM is needed to properly predict impacts of climate change and/or land use change on soil organic carbon stocks (Elzein & Balesdent 1995; Jobbágy & Jackson 2000; Jenkinson et al. 2008). The vertical distribution of SOM in volcanic ash soils merits special attention, because volcanic ash soils (mainly Andosols) contain very large stocks of SOM per unit area (Eswaran et al. 1993; Batjes 1996; Lal 2004; Tonneijck et al. 2008b). Consequently, the impact of climate change and land use change on SOM in volcanic ash soils may be particularly strong (Veldkamp 1994; Rhoades et al. 2000).

The vertical distribution of SOM in soils is determined by 1) input - above and belowground - of litter, 2) decomposition and 3) vertical transport. In the case of volcanic ash soils tephra deposition also influences the vertical distribution of SOM. With respect to the vertical transport of SOM, soil faunal bioturbation (further referred to as ‘bioturbation’) is often cited as a major process (Anderson 1988; Lavelle 1988; Rasse et al. 2006). Elzein & Balesdent (1995) demonstrated in a modelling study that bioturbation is the dominant mode of vertical transport, relative to leaching, in a range of soil types. Leaching of SOM is rather insignificant in volcanic ash soils because of large metal-to-SOM ratios (Aran et al. 2001; Dahlgren et al. 2004). Generally, bioturbation is modelled with a diffusion equation of which the diffusion constant is assumed to either be uniform or to decrease with depth (O’Brien & Stout 1978; Elzein & Balesdent 1995; Bruun et al. 2007). However, in many soils the actual bioturbation pattern may be much more complex because of the presence of different groups of soil faunal species operating at different depths (Anderson 1988; Lavelle 1988; Lee & Foster 1991; Tonneijck & Jongmans 2008).

An additional process that may affect the vertical distribution of SOM is soil volume change. Soil volume changes during soil formation because of e.g. chemical element loss upon weathering, SOM incorporation and biological activity (Brimhall & Dietrich 1987; Chadwick et al. 1990; Salvador-Blanes et al. 2007). These soil forming processes all affect the dry bulk density of the soil by changing the mean solid soil particle density and/or the porosity (Lee & Foster 1991; Blanco-Canqui et al. 2006; Rühlmann et al. 2006) and thus may cause the soil to collapse or to thicken depending on their relative importance (Salvador-Blanes et al. 2007). Volume change influences soil forming processes that are related to soil depth, such as weathering, decomposition, bioturbation and rooting. While this effect is taken into
account in soil genesis models (Chadwick et al. 1990; Salvador-Blanes et al. 2007), to our knowledge it was not previously taken into account in models dealing specifically with soil organic carbon dynamics. Still, the effect of soil volume change on the vertical distribution of SOM may be substantial, particularly in the case of SOM-rich soils. Soil volume change can be calculated with a geochemical mass balance approach involving immobile element concentrations (e.g. Ti, Al, Zr) and soil dry bulk density, provided that parent material characteristics are reasonably well known (Chadwick et al. 1990). In soil carbon models, soil volume change can effectively be taken into account by predicting soil dry bulk density from SOM content, since SOM content explains most of the variation in soil dry bulk density in many soil types (e.g. De Vos et al. 2005; Heuscher et al. 2005).

We previously investigated the effect of tephra deposition and bioturbation on the vertical distribution of SOM in volcanic ash soils under tropical montane grassland (páramo) vegetation in the northern Ecuadorian Andes. These soil profiles consist of a thick current soil in a tephra deposit superimposed on a SOM-rich paleosol in a preceding tephra deposit (Tonneijck et al. 2008a). We observed a progressive downward increase in SOM from the relatively SOM-poor subsoil of the current soil into the SOM-rich top of the paleosol, further referred to as the ‘overprinted zone’. Bioturbation by two different groups of soil faunal species, operating predominantly in either the topsoil or the subsoil, was found to be responsible for this vertical distribution of SOM (Tonneijck & Jongmans 2008). The great abundance of bioturbation features throughout the overprinted zone seemingly conflicts with the gradual increase in SOM content with depth in that zone. In view of the magnitude of bioturbation in the overprinted zone, one would have expected SOM in the entire overprinted zone to be homogenised. Therefore, we hypothesised that bioturbation must have shifted upwards over time in response to soil thickening, rendering deeper positions in the soil out of reach of bioturbation (Tonneijck & Jongmans 2008).

The aims of this research were 1) to determine the extent of soil volume change and 2) to test our hypothesis of the effect of soil thickening on bioturbation, i.e. upward shifting, for a volcanic ash soil under páramo vegetation in northern Ecuador. To reach our aims we calculated soil volume change using a geochemical mass balance approach and we conducted a ‘proof of concept’ by testing our hypothesis with a one-dimensional partial differential equation model that was constructed specifically for this purpose.

**Description of study area and sites**

The study area is located in the nature protection area of Guandera Biological Station in northern Ecuador, near the border with Colombia (Figure 1.1). For the current study, we selected a site (G7, N 0°35’48”/ W 77°41’25””) at 3860 m a.s.l. that has been covered by páramo vegetation for the last millennia (Bakker et al. 2008). Dominant species in the páramo are bunch-grass *Calamagrostis effusa* KUNTH (STEUD.) and stem rosette *Espeletia pycnophylla* CUATREC. The páramo belongs to the globally leading Tropical Andes
biodiversity ‘hotspot’ (Myers et al. 2000). Mean annual precipitation is around 1900 mm and mean annual temperature ranges from 12 °C at 3000 m a.s.l. to 4 °C at 4000 m a.s.l. Both precipitation and temperature show little seasonal variation. The soil climate is isomesic and perudic.

The soil profile was formed in three tephra deposits of Holocene age, with similar mineral assemblage (Tonneijck et al. 2008a). The timing of the last tephra deposit is estimated at 2779 cal BC (Tonneijck et al. 2008a), thus resulting in ~4800 years of soil formation. Related to this tephra stratigraphy the soil contained a current soil, a paleosol and a second heavily truncated or immature paleosol, each at least 40 cm thick. The main focus of this research was on the current soil profile. Aboveground litter was mostly present as hanging dead material in the tussock grasses or on the stem rosettes rather than in a litter layer. Between the current soil and the first paleosol an overprinted zone with transitional organic carbon contents, grain size distribution and chemical element ratios was present. In the soil horizon designations we used ‘1/2’ as a prefix to indicate this overprinted zone. A thin placic horizon was present at the boundary between the first and second paleosol, which is ascribed to a strong textural contrast hindering drainage of the otherwise well drained soils. The soil classified as an Andosol according to the World Reference Base (FAO 2006).

Materials and methods

First we describe sampling and laboratory procedures. Then the method to determine the extent of soil volume change with a geochemical mass balance approach involving immobile elements is outlined in a separate section. In the subsequent section the construction of the dynamic model to test our hypothesis of an upward shifting bioturbation zone is discussed.

Sampling and laboratory procedures

The datasets used for geochemical mass balance calculations and modelling were presented by Tonneijck et al. (2008a) and Tonneijck & Jongmans (2008). We briefly discuss the sampling and laboratory procedures here. We took bulk soil samples for physical and chemical analyses and ring samples for soil dry bulk density estimation and undisturbed box samples (with dimensions of 7 cm height x 5 cm width x 4 cm depth) for the preparation of thin sections in the same soil pit at regular depths but respecting horizon boundaries. Additionally, we took undisturbed vertical soil samples (monoliths) using one or two metal gutters of 75 cm height x 5 cm width x 4 cm depth. For additional estimation of organic carbon contents, samples were cored from the monoliths by means of a corer of 0.75 cm diameter. All samples were stored at 2 °C under field moist conditions.

Total carbon was measured with a VarioEL (Elementar) CNS auto-analysrer. Total carbon equals organic carbon, since carbonates were absent. We assumed that SOM content equals twice the amount of total organic carbon content according to Van Reeuwijk (2002) and we
use both terms interchangeably. Soil dry bulk density was determined by weighing oven-dried volumetric samples (105 °C, until constant weight > 24 h). Contents of the immobile elements Ti and Al were estimated with a Perkin Elmer Optima 3000 XL ICP-OES in ground, dried and heated (900 °C) bulk samples (n = 4 for current soil and top of overprinted zone and n = 13 for the reference material) after destruction in a hot HF/H₂SO₄ mixture.

**Geochemical mass balance calculation**

For the calculation of soil volume change, we used the strain equation similar to Brimhall & Dietrich (1987) and Chadwick et al. (1990):

\[
\varepsilon_i(x, t_{end}) = \frac{b \rho_{s,w} C_{i,r}}{b \rho_{s,w}(x, t_{end}) C_{i,w}(x, t_{end})} - 1
\]

Equation 6.1

Where \(\varepsilon_i(x, t_{end})\) is strain (cm/cm³), or change in thickness at \(t_{end} = 4800\) (y) over initial thickness at \(t_0 = 0\) (y) due to soil formation, at depth \(x\) (cm) with subscript \(i\) referring to strain determination by use of an immobile strain index element. Depth \(x\) is defined relative to the soil surface \(x_{top}\), with positive values below the soil surface, which is common in soil science (FAO 1991). Depth \(x\) is time-dependent due to soil volume change, which we do not explicitly mention in the equations for reasons of readability. Furthermore, \(b \rho_{s,r}\) and \(b \rho_{s,w}\) represent the soil dry bulk density (g/cm³) of the reference material (subscript \(r\)) and weathered material (subscript \(w\)) respectively and \(C_{i,r}\) and \(C_{i,w}\) represent the mass percentage (%) of immobile element \(i\) in the reference material and weathered material respectively. Note that \(b \rho_{s,r}\) and \(C_{i,r}\) are not depth-dependent. We used the relatively unweathered second paleosol as reference material, which is justified because the tephra deposit it was formed in likely originated from the same volcanic source as the last tephra deposit as evidenced by their similar Ti/Al ratios and similar mineral assemblage (Tonneijck et al. 2008a). To account for natural variability in this reference material, minimum and maximum strain values were obtained by using the standard deviations of \(b \rho_{s,r}\) (\(n = 8\)) and \(C_{i,r}\) (\(n = 13\)).

We used linear regressions to interpolate strain at a given soil depth \(x\) (Figure 6.1a and b):

\[
\varepsilon_i(x, t_{end}) = ax + b
\]

Equation 6.2

Parameters ‘\(a\)’ and ‘\(b\)’ are presented in the captions of Figure 6.1a and b. The \(r^2\) of these linear regressions exceeded 0.92 in all cases. In the overprinted zone, mixing of the relatively SOM-poor current soil with the SOM-rich paleosol caused somewhat higher strain values. Therefore, applying linear regressions represents a conservative estimate of strain in the subsoil.
Figure 6.1  Strain versus sample depth (cm) computed with a) Ti as immobile index element or b) Al as immobile index element.

- = minimum strain, with $\varepsilon_{\text{Ti},w} = -0.0366 x + 3.6625$ and $\varepsilon_{\text{Al},w} = -0.0355 x + 3.7852$
- = maximum strain, with $\varepsilon_{\text{Ti},w} = -0.0535 x + 5.8227$ and $\varepsilon_{\text{Al},w} = -0.0428 x + 4.6948$
× = average strain, with $\varepsilon_{\text{Ti},w} = -0.0447 x + 4.7069$ and $\varepsilon_{\text{Al},w} = -0.0393 x + 4.2301$

To calculate the initial thickness at $t_0$ of the entire current soil, i.e. before volume change, we applied the following equation, using equation 6.2:

$$L(x, t_0) = \frac{L(x, t_{\text{end}})}{1 + \varepsilon(x, t_{\text{end}})} = \frac{1}{1 + ax + b}$$

$$L_{\text{current}}(t_0) = \int_{x_{\text{top}}}^{x_{\text{current}}} \frac{1}{1 + ax + b} \, dx = \left[ \frac{\ln(ax + b + 1)}{a} \right]_{x_{\text{top}}}^{x_{\text{current}}}$$

With $L(x, t_0)$ representing the initial thickness (cm) of a layer and $L(x, t_{\text{end}})$ representing the thickness of this layer after soil formation which we arbitrarily set at 1 cm. The total observed thickness of the entire current soil at $t_{\text{end}}$ is 77 cm and referred to as $L_{\text{current}}(t_{\text{end}})$, being the thickness from the mineral soil surface ($x_{\text{top}}$) up to the middle of the overprinted zone ($x_{\text{current}}$), see Figure 6.3. $L(x, t_0)$ was integrated from $x_{\text{top}}$ to $x_{\text{current}}$ to obtain the initial thickness of the entire current soil i.e. $L_{\text{current}}(t_0)$, see Figure 6.3. We computed minimum and maximum $L_{\text{current}}(t_0)$ using minimum and maximum strain values.

Correct application of this technique depends on immobility of at least one element. Therefore, we used Ti and Al as probable immobile elements to allow for an evaluation of internal consistency. Furthermore, immobility of an element can be checked against another supposedly immobile element and vice versa, by calculating its transport (Chadwick et al. 1990) with:
Where \( \tau_j(x, t_{\text{end}}) \) is the mass fraction of mobile element \( j \) added or subtracted to the system. To account for natural variability in the reference material, transport was calculated using minimum and maximum strain values.

**Dynamic modelling**

**General model structure**

The soil profile is described by a vector where each element represents a soil layer, with an initial thickness of 5 cm. For pragmatic reasons we assume that layers have a unit area of 1 cm\(^2\). During soil formation each layer is subject to volume change as explained in the introduction and therefore layer thickness is variable in time. The upper boundary of the system is the soil surface \((x_{\text{top}})\) and the lower boundary is chosen just above the placic horizon \((x_{\text{base}})\).

The model uses time steps of five years. We start our model run \((t_0 = 0 \text{ y})\) at the moment of the last tephra deposition, i.e. before formation of the current soil and overprinted zone. The timing of the last tephra deposit is estimated at 2779 cal BC (Tonneijck et al. 2008a), thus resulting in \(\sim4800\) years \((t_{\text{end}})\) of soil formation. It should be noted that due to mixing of the top of the paleosol with the subsoil of the current soil, it has become impossible to obtain an accurate timing of the event of tephra deposition with radiocarbon dating and this timing should thus be regarded as a ‘best guess’.

Organic carbon mass and mineral mass are the state variables. We use mass based units rather than volume based units, because volume changes during simulation. The fluxes are determined by diffusion and decay equations, which are discussed in the following sections.

**Variable layer thickness**

Geochemical mass balance calculations (see Results section) showed that soil volume increase due to SOM incorporation is by far the dominant process in the soil profile studied. Therefore, we used an empirical relation between organic carbon content and soil dry bulk density as based on data of páramo soils from the same study area (Tonneijck et al. 2008a, \(r^2 = 0.98\)) to recalculate soil dry bulk density of a layer at depth \(x\) and year \(t\):

\[
\rho_{s,w}^b(x,t) = c e^{d f_{OC}(x,t)}
\]

**Equation 6.5**

With \(c = 0.9247 \text{ gcm}^{-3}\) and \(d = -5.497\) and \(f_{OC}(x,t) = \text{fraction of organic carbon g}^{-1}\). 

\[
\tau_j(x, t_{\text{end}}) = \frac{\rho_{s,w}^b(x, t_{\text{end}}) c_{j,w}(x, t_{\text{end}})}{\rho_{s,w}^b c_{j,r}} (c_{i}(x, t_{\text{end}}) + 1)
\]

Equation 6.4
We opted for this specific empirical relation rather than published general relations, since the latter were demonstrated to systematically underestimate soil dry bulk density when applied to soil types and/or areas other than those calibrated (De Vos et al. 1995). Because of the exponential nature of the relation between organic carbon and soil dry bulk density we assume that this relation reflects the combined effect of all soil forming processes and not only of SOM incorporation.

Soil dry bulk density is subsequently used to recalculate the thickness of a layer at depth x and year t according to the following equation:

$$L(x, t) = \frac{m_b(x, t)}{\rho_{s,w}(x, t)U}$$  \hspace{1cm} \text{Equation 6.6}

With $L(x, t) =$ the thickness of a layer; $m_b(x, t) =$ the sum of mineral and SOM mass (g), of that layer and $U =$ unit area (cm$^2$). Integrating $L(x, t)$ from $x_{top}$ to $x_{base}$ gives $L_{tot}(t)$ for the entire soil profile. In order to keep the layers from growing uncontrollably, layer splitting is introduced. Layers that grow beyond a thickness threshold of 10 cm are divided into two equally thick layers, while taking into account the slope of the organic fraction with depth to reduce the effect of numerical errors.

**Input**

Organic carbon enters the soil as aboveground (shoots) and belowground (roots) litter. The annual rate of aboveground litter production was assumed to be constant during the model period and calibrated, since long term data is not available. We assumed that the aboveground to belowground litter ratio equaled the aboveground to belowground biomass ratio (Hofstede & Rossenaar 1995). Rooting is typically superficial in the páramo with ~80 % of root biomass located in the first 10 cm of soil (Hofstede & Rossenaar 1995), which was also observed in the soil profile studied (Tonneijck & Jongmans 2008). In accordance we assumed root litter input to decrease exponentially with depth x, in line with Elzein & Balesdent (1995), according to the following equation:

$$I_{oc_{-r}}(x) = R \cdot I_{oc_{-s}} \cdot \frac{e^{-g \cdot x}}{g}$$  \hspace{1cm} \text{Equation 6.7}

With $I_{oc_{-r}}(x) =$ organic carbon input by root litter (gy$^{-1}$); $R =$ shoot litter to root litter ratio; $I_{oc_{-s}} =$ organic carbon input by shoot litter (gy$^{-1}$); and $g =$ a distribution parameter which is chosen such that 80 % of the total root litter input is contained in the top 10 cm of the soil. As plants grow on the soil surface, rooting depth should be defined relative to the soil surface.
Organic carbon stocks are exceptionally high in the páramo soils of the study area, because SOM is protected against decomposition by various mechanisms including the formation of organo-metallic complexes (Tonneijck et al. 2008b), which is a typical feature of volcanic ash soils (Shoji et al. 1993; Dahlgren et al. 2004). Analysis of the molecular composition of SOM in the soil profile studied showed that its composition was dominated by aliphatic compounds of primary (plant-derived) origin (Nierop et al. 2007). Because aliphatic compounds are only present in limited amounts in plants, their relative enrichment in the soil indicates severe transformation of other primary OM compounds. Therefore, we assume that decomposition of easily decomposable plant material is so fast that it does not affect the organic carbon-depth profile at the time scale of our model and only resistant plant material (RPM) enters the mineral soil. We assumed that 10% of the litter consists of RPM, being a rough estimate based on the molecular composition of SOM and aboveground litter in the soil profile studied (Nierop et al. 2007).

**Decay**

RPM is decomposed according to a one compartment model, where the decay rate is assumed to be first order and therefore directly proportional to the organic carbon mass of a layer:

\[
\frac{\partial m_{OC}(x,t)}{\partial t} = -k(x)m_{OC}(x,t)
\]

Equation 6.8

With \(m_{OC}(x,t)\) = mass of organic carbon (g) and \(k(x)\) = a decay constant (y\(^{-1}\)). We assume that this decay constant \(k(x)\) is proportional to bioturbation (equation 6.10 and 6.11), because we previously found that microbial decomposition predominantly takes place in the litter layer rather than in the mineral soil, while soil fauna may further transform SOM in the mineral soil (Tonneijck et al. 2008b).

**Organic carbon transport**

Vertical transport of dissolved OM by leaching can be assumed insignificant in volcanic ash soils, because of the large metal-to-SOM ratios that strongly limit its mobility (Aran et al. 2001; Dahlgren et al. 2004). Moreover, we did not find evidence of SOM illuviation (coatings or radiocarbon age inversions) in the soil studied. Tonneijck & Jongmans (2008) demonstrated previously that bioturbation is the main process responsible for SOM transport in the soils studied. Change in mass of organic carbon for a layer due to transport by bioturbation is modelled with the diffusion equation, similar to Elzein & Balesdent (1995):

\[
\frac{\partial m_{OC}(x,t)}{\partial t} = D(x)\frac{\partial^2 m_{OC}(x,t)}{\partial x^2}
\]

Equation 6.9

With \(D(x)\) = the diffusion coefficient (cm\(^2\) y\(^{-1}\)) of that layer, see also equation 6.10.
Bioturbation patterns

Micromorphological data (Tonneijck & Jongmans 2008) showed that bioturbation was caused by two groups of soil faunal species producing clearly distinct pedofeatures. Bioturbation features of the first group were concentrated in the topsoil and decreased in abundance with depth, while contrary bioturbation features of the second group increased with depth and were most abundant in the subsoil. Because fresh bioturbation features of both species groups were present up to the soil surface we concluded that both species groups are currently active (Tonneijck & Jongmans 2008). To represent this observed bioturbation pattern in the model we used a function based on two Gaussian-shaped kernels to describe the diffusion coefficient D with depth x:

\[
D(x) = D_A \cdot e^{-(x^2)/w_A} + D_B \cdot e^{-(x-x_b)^2}/w_B \quad \text{for } D(x) \geq h
\]

\[
D(x) = 0 \quad \text{for } D(x) < h
\]

Equation 6.10

With \(D_A\) = the height of the first Gaussian kernel (cm\(^2\)y\(^{-1}\)); \(w_A\) = a parameter (cm\(^{-1}\)) influencing the width of the first kernel; \(D_B\) = the height of the second Gaussian kernel (cm\(^2\)y\(^{-1}\)); \(w_B\) = a parameter (cm\(^{-1}\)) influencing the width of the second Gaussian kernel, \(x_b\) = the depth of \(D_B\) (cm) and \(h\) = a D(x) beyond which the value of the kernels is set to zero. To test our hypothesis of an upward shifting bioturbation zone in response to soil thickening, equation 6.10 is defined relative to the soil surface. We assume that the páramo vegetation immediately colonised the last tephra deposit and also that the soil faunal community immediately colonised this tephra deposit according to this bioturbation pattern.

As explained previously, the decay constant \(k\) from equation 6.8 is proportional to bioturbation as represented by equation 6.10 through:

\[
k(x) = qD(x)
\]

Equation 6.11

With \(q\) = a conversion parameter (cm\(^2\)).

Initial settings

The last tephra deposit buried a pre-existing tephra deposit in which a paleosol was present. The presence of this paleosol influences the vertical distribution of organic carbon in the current soil due to bioturbation, and must therefore be taken into account in our model. Because of the specific vertical pattern of bioturbation and the organic carbon gradient, the direction of organic carbon transport from the paleosol is upward throughout the modelling period and consequently no organic carbon enters the paleosol. The estimate of the initial organic carbon-depth profile of the paleosol at \(t_0\) thus should compensate for loss of organic carbon due to decay and for soil volume change due to mixing. This was achieved by linearly extrapolating the currently measured organic carbon-depth profile of the paleosol up to a depth \(x\), which was calibrated. The initial thickness of the entire current soil before soil
volume change, i.e. $L_{\text{current}}(t_0)$ see Figure 6.3, covering this paleosol was calculated using a geochemical mass balance approach (equation 6.3) and we also calibrated this parameter. Comparison of the calibrated initial thickness to the calculated initial thickness represents an independent check of the extent of soil volume change.

**Model calibration**

To explore the effect of the vertical bioturbation pattern, we first calibrated the model by manually adjusting parameters related to the first Gaussian kernel (referred to as ‘bioturbation A’) while excluding the second Gaussian kernel (referred to as ‘bioturbation B’). Next, we added bioturbation B to the optimal scenario for bioturbation A. Because of soil thickening, the effect of bioturbation B could not be tested without including bioturbation A in the model. Finally, we adjusted the parameters ‘initial thickness of the entire current soil’, ‘aboveground organic carbon input’ and ‘decay’ (through conversion parameter $q$ of equation 6.11) within realistic ranges to get an optimal fit to the observed total soil thickness (up to the placic horizon) at the end of the modelling period. We used the root mean squared error between model predicted and observed organic carbon fraction i.e. $f_{oc}(x,t_{\text{end}})$ as the error criterion to be minimised.

**Results**

**Soil volume change**

Soil properties are presented in Table 6.1. Immobility of Al and Ti were checked by evaluating plots of transport of these elements calculated with strain based on Ti or Al respectively as immobile element index against strain, see Figure 6.2a and b. Immobility is established when a portion of the transport line falls within the horizontal band of ‘transport’ of the immobile index element as caused by natural variation of that element in the reference material (Chadwick et al. 1990).

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth [cm]</th>
<th>Organic C [mass %]</th>
<th>Dry bulk density [g/cm^3]</th>
<th>Soil pH_{calc} [-]</th>
<th>TiO$_2$ [mass %]</th>
<th>Al$_2$O$_3$ [mass %]</th>
</tr>
</thead>
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<tr>
<td>Ah1</td>
<td>10</td>
<td>20.1</td>
<td>0.35</td>
<td>3.92</td>
<td>0.33</td>
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<tr>
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<td>0.40</td>
<td>4.10</td>
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<tr>
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<td>47</td>
<td>12.7</td>
<td>0.42</td>
<td>4.30</td>
<td>0.43</td>
<td>13.9</td>
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<td>63</td>
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<td>0.41</td>
<td>4.34</td>
<td>0.49</td>
<td>14.7</td>
</tr>
<tr>
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<td>4.16</td>
<td>0.57</td>
<td>14.0</td>
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<td>n.d$^b$</td>
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<td>0.57</td>
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<td>154</td>
<td>2.7</td>
<td>n.d$^b$</td>
<td>4.84</td>
<td>0.67</td>
<td>19.7</td>
</tr>
<tr>
<td>3BCb</td>
<td>170</td>
<td>0.38</td>
<td>0.93</td>
<td>5.36</td>
<td>0.70</td>
<td>19.9</td>
</tr>
</tbody>
</table>

| 3BCb all| -          | 0.81 ± 1.11 (n=15)  | 0.95 ±0.04 (n=8)          | 5.11 ± 0.32 (n=15) | 0.66 ± 0.10 (n=13) | 19.31 ± 0.85 (n=13) |

$^a$ = prefix 1/2 refers to the overprinted zone, see description of study area and sites

$^b$ = not determined
Measurements show that soil volume increased throughout the current soil profile, as indicated by positive strain values of up to 4.7 in the topsoils and up to 2.1 in the subsoils. Strain decreased linearly with depth, although the subsoil samples that were located in the overprinted zone had a relatively high strain value because of mixing with the SOM-rich paleosol. The initial thickness of the entire current soil was estimated at 17 – 26 cm (average 21 cm) with Ti as immobile index element and at 20 – 24 cm (average 22 cm) with Al as immobile index element. Thus, the current soil (now 77 cm thick, up to the middle of the overprinted zone) increased 300 – 440 % in thickness relative to its initial thickness.

Figure 6.2  Transport $\tau$ (fraction, gains are positive and losses are negative) of a) Ti and b) Al computed with strain $\varepsilon$ based on Al and Ti as immobile element index respectively, against strain based on that immobile index element, for 4 samples taken from the current soil and top of the overprinted zone. Immobility is established when a portion of the transport line falls within the horizontal band of ‘transport’ of the immobile index element as caused by natural variation of that element in the reference material (Chadwick et al. 1990).

Modelling results

The model output at several moments in time and the model fit to the data (at $t_{\text{end}} = 4800$ y) are shown in Figure 6.3. The parameters used to obtain this fit are presented in Table 6.2. The model output at $t_0$ shows the initial paleosol settings. Organic carbon content was relatively high at the top of the paleosol.

Bioturbation A regulated organic carbon distribution in the current soil and the original top of the paleosol thus shaping the top of the overprinted zone (Figure 6.3, $t_{\text{end}}$), while bioturbation B shaped the organic carbon distribution at the bottom of the overprinted zone (Figure 6.3, $t_{\text{end}}$). Bioturbation A had to be slow and had to operate over a relatively large depth interval (> 60 cm), while bioturbation B had to be relatively fast and had to cover a small depth interval (12 cm) in order to represent the observations.
Figure 6.3  Modelled (—) organic carbon-depth profiles with bioturbation A and B at several moments in time (t in y). The current situation is represented by the figure for \( t_{\text{end}} = 4800 \) y and includes measurements (○) and a modelled organic carbon-depth profile without bioturbation B (---). The initial thickness of the entire current soil, i.e. \( L_{\text{current}}(t_0) \), is indicated in figure \( t_0 \) and its total thickness after soil formation, i.e. \( L_{\text{current}}(t_{\text{end}}) \), is indicated in figure \( t_{\text{end}} \).

Figure 6.4  Modelled organic carbon-depth profiles with bioturbation A and B and measured (○) organic carbon-depth profiles as obtained with a) \( \text{width}_A = \sim 98 \) cm and \( D_A = 0.03 \text{ cm}^2 \text{ y}^{-1} \) (— —) or \( 0.3 \text{ cm}^2 \text{ y}^{-1} \) (---), b) \( D_A = 0.1 \text{ cm}^2 \text{ y}^{-1} \) and \( \text{width}_A = 180 \) cm (---) or \( 60 \) cm (——) and c) an initial thickness of the entire current soil of \( 30 \text{ cm} \) (---) or \( 10 \) cm (——). Other parameter settings in these figures are equivalent to Table 6.2.
The effect of $D_A$ and $w_A$ describing the Gaussian kernel of bioturbation $A$ (equation 6.10) is shown in figure 6.4a and b respectively. Increasing $D_A$ at fixed $w_A$ results in homogenisation of the organic carbon-depth profile of the current soil. With a relatively low $D_A$, a large $w_A$ (i.e. small width) limits transport to a smaller distance resulting in organic carbon accumulation in the topsoil rather than the subsoil while contrary a small $w_A$ (i.e. large width) results in a more even distribution of organic carbon throughout the soil. The sensitivity of the organic carbon-depth profile to the initial thickness of the entire current soil is shown in Figure 6.4c.

Table 6.2  Model fit to the data for several parameters as compared to data reported in the literature. These ranges were used as limits for model calibration.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Fit</th>
<th>Literature data</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial thickness of the entire current soil</td>
<td>$L_{current(t_0)}$</td>
<td>[cm]</td>
<td>20</td>
<td>10 – 30</td>
<td>Geochemical mass balance calculation, this paper</td>
</tr>
<tr>
<td>Resistant plant material</td>
<td>RPM</td>
<td>[%]</td>
<td>Fixed</td>
<td>10</td>
<td>Personal communication Nierop (2008)</td>
</tr>
<tr>
<td>Turnover time $A$</td>
<td>$(1/k)$</td>
<td>[y]</td>
<td>10000</td>
<td>4500 – 170000</td>
<td>Van Dam et al. (k_p 1997) Torn et al.(1997)</td>
</tr>
<tr>
<td>Turnover time $B$</td>
<td>$(1/k)$</td>
<td>[y]</td>
<td>5000</td>
<td>4500 – 170000</td>
<td>Van Dam et al. (k_p 1997) Torn et al.(1997)</td>
</tr>
<tr>
<td>Diffusion coefficient (maximum value), bioturbation $A$</td>
<td>$D_A$</td>
<td>[cm^2 y^-1]</td>
<td>0.1</td>
<td>0.42 – 3.97</td>
<td>Elzein &amp; Balesdent (1995)</td>
</tr>
<tr>
<td>Kernel width, bioturbation $A$</td>
<td>$width_A$</td>
<td>[cm]</td>
<td>~98</td>
<td>0 – 200</td>
<td>Representing the depth of the whole soil profile</td>
</tr>
<tr>
<td>Diffusion coefficient (maximum value), bioturbation $B$</td>
<td>$D_B$</td>
<td>[cm^2 y^-1]</td>
<td>0.2</td>
<td>–</td>
<td></td>
</tr>
<tr>
<td>Kernel width, bioturbation $B$</td>
<td>$width_B$</td>
<td>[cm]</td>
<td>12</td>
<td>0 – 200</td>
<td></td>
</tr>
<tr>
<td>Depth of $D_B$</td>
<td>$x_B$</td>
<td>[cm]</td>
<td>60</td>
<td>60 – 80</td>
<td>Tonneijck &amp; Jongmans 2008</td>
</tr>
</tbody>
</table>

Discussion

Extent of volume change

We conclude that soil volume change is a major soil forming process in the volcanic ash soil studied. The current soil more than tripled in thickness over time, as based on three independent methods; namely geochemical mass balance calculations 1) with Al and 2) with Ti as immobile index element and 3) modelling of organic carbon dynamics. The narrower range in total initial soil thickness calculated with Al than calculated with Ti is due to the higher measurement accuracy of the former. Using a thicker total initial current soil in the
model resulted in dilution of the organic carbon content in the model output (Figure 6.4c), which could not be corrected for by increasing organic carbon input \( (I_{oc,s}) \) because the soil would then become too thick in total due to soil volume increase.

Figure 6.2 demonstrates that Al and Ti were indeed immobile and thus confirms the reliability of the calculations involving Ti or Al as immobile index element. In all cases a portion of the transport line falls within the horizontal band representing ‘transport’ due to natural variation of the immobile index element in the reference material (Figure 6.2a and b, Chadwick et al. 1990). Although immobile, this does not mean that Al is inert (Chadwick et al. 1990), because when released during weathering it is stabilised in situ e.g. in Al-humus complexes (Tonneijck et al. 2008b).

Soil thickening is clearly the result of SOM incorporation in the mineral soil, mainly by bioturbation. Barois et al. (1998) also mentioned soil thickening in combination with SOM accumulation in the case of Mexican Andosols, but did not quantify it. Other common soil forming processes did not significantly affect soil volume in the soil studied. First, bioturbation itself did not necessarily lead to an increased porosity (Tonneijck & Jongmans 2008) and therefore could not explain the great extent of soil thickening. Second, soil collapse due to leaching of elements apparently did not counterbalance soil thickening, even though weathering of volcanic ash soils under perudic conditions is rapid. This may be explained by complexation of elements with SOM (e.g. Al, Fe) and by biocycling of elements (e.g. Si, K, P), preventing leaching. Moreover, element leaching does not necessarily lead to soil volume change (Chadwick et al. 1990). In view of the vast accumulation of SOM that is characteristic for volcanic ash soils (Shoji et al. 1993; Dahlgren et al. 2004), we expect that soil thickening is an important process for this soil type in general and probably also for other SOM-rich soils (e.g. Chernozems).

**Evaluation of parameters**

Although we used realistic ranges to calibrate the parameters of our model (see Table 6.2), there is no guarantee that there are no other combinations of parameters that would produce equal or better results. Nonetheless, we conclude that the parameter set used to obtain our model fit is a plausible one, as discussed in this section.

Diffusion constants were low compared to diffusion constants estimated by Elzein & Balesdent (1995) and Van Dam et al. (1997). However, when applying 3 times larger diffusion constants in the model this already resulted in near homogenisation of organic carbon content with depth (Figure 6.4a). Diffusion rates increase with increasing biological activity (Elzein & Balesdent 1995). In the field we indeed rarely encountered soil fauna when excavating soil pits. This observation would indeed support the low diffusion rates in the model. The abundance of bioturbation features observed using micromorphological techniques (Tonneijck & Jongmans 2008) does not necessarily contradict low diffusion rates, since it is the cumulative result of bioturbation over several millennia. Bioturbation rates
may indeed be low due to the unfavourable soil environment, i.e. perudic conditions and acidic soil pH. Because bioturbation B only covers a small vertical distance at every timestep, its final effect on the organic carbon-depth profile is minimal (Figure 6.3, \( t_{\text{end}} \)). Endogeic soil faunal species, like the ones represented by bioturbation B in the model (Tonneijck & Jongmans 2008), create extensive horizontal burrowing networks indeed resulting in SOM transport over short vertical distances only (Anderson 1988; Lee & Foster 1991).

In our model structure, decay was correlated to bioturbation (equation 6.11), because we found that microbial transformations predominantly take place in the litter layer, while in the mineral soil matrix it is the soil fauna that further transforms SOM (Tonneijck et al. 2008b). Therefore, turnover times were also low, which is in line with turnover rates generally reported for the stable pool of organic carbon in volcanic ash soils (Torn et al. 1997; Van Dam et al. 1997). Because the parameters ‘aboveground litter input’ and ‘decay’ are obviously correlated, which is a general problem when modelling organic carbon dynamics, ‘aboveground litter input’ was at the low end of the range reported in the literature (Hofstede & Rossenaar 1995; Tonneijck 1999). However, it is possible that the proportion of RPM was overestimated, which would then automatically lead to higher estimates for aboveground litter input.

**Upward shifting**

The good fit between data and model confirms (sensu Oreskes et al. 1994) that our hypothesis of an upward shifting bioturbation zone in response to soil thickening is indeed able to clarify the observed vertical distribution of SOM. Although this does not necessarily imply that our hypothesis is true, at least we show that it is plausible. It is well known that soil fauna is related to depth, because of preferred environmental conditions such as oxygen supply, water content and temperature (Lavelle 1988; Lee & Foster 1991), explaining upward shifting in response to soil thickening. In this hypothesis, organic carbon content is apparently not a limiting factor for the soil fauna represented by bioturbation B, since upward shifting implies movement towards lower organic carbon contents. Alternatively, correlating the bioturbation pattern to organic carbon content evidently results in homogenised organic carbon-depth profiles.

It is also plausible that roots have shifted upwards in response to soil thickening. This may explain the apparent paradox of the abundance of root-derived organic molecules (e.g. suberin) throughout the current soil profile (Nierop et al. 2007), while rooting was clearly superficial according to field observations and micromorphological observations (Tonneijck & Jongmans 2008).

Because soil volume change may influence depth-dependent soil forming processes, as clearly illustrated by our modelling exercise, it should be taken into account when modelling soil organic carbon dynamics, especially in the case of SOM-rich soils. This pertains to volcanic ash soils, but probably also to Chernozems and Phaeozems which are also characterised by bioturbation and carbon accumulation.
Implications

The studied soil profile contains paleoecological proxies (e.g. pollen and plant species specific organic molecules or ‘biomarkers’) that are used to reconstruct the vegetation history in the study area (Jansen et al. 2008a; Moscol Olivera & Hooghiemstra 2008). Since the use of paleoecological proxies contained in soils depends on their preservation in chronostratigraphic order, the degree and type of bioturbation is of key importance. Based on the model structure and parameter set presented in this investigation, we conclude that bioturbation may have been slow. In combination with upward shifting bioturbation, this may explain the linear increase of age with depth observed in soil profiles of the study area, including the soil profile investigated in this chapter (Tonneijck & Jongmans 2008). Therefore, in line with our previous investigations (Tonneijck et al. 2008a; Tonneijck & Jongmans 2008), the results from the present study suggest that as long as paleoecological proxies were transported through the soil profile similarly to bulk SOM, they will probably be distributed in a (crude) chronostratigraphic order. However, a major consequence is also that any sample taken inevitably would produce a mixed signal on a high resolution temporal scale.

Recommendations

The modelling exercise presented in this chapter served its purpose of testing our hypothesis. Nevertheless, the model of organic carbon dynamics may be improved by e.g. accounting for labile organic carbon, by further adjusting the initial paleosol settings and possibly by using more parsimonious and asymmetrically shaped functions to even better describe the soil faunal distribution and mixing. Model calibration should also be done in an automated procedure to gain insight in the model structure, the parameter space, correlation between parameters and sensitivity of parameters. Extrapolation of short term field data/experiments to long term modelling periods is uncertain. Nonetheless, measurement of several parameters such as leaf and root litter production and SOM decay rates at various soil depths in this and other Andean páramo ecosystems would enhance the parameter ranges used in model calibration. A study of the vertical migrations of soil fauna currently present in the soil studied would further underpin the conclusions of this research. In addition to modelling organic carbon-depth profiles, modelling of radiocarbon depth-profiles may be useful to further constrain the model. Our model should be applied to other areas and other (SOM-rich) soil types as well to contribute to a greater understanding organic carbon dynamics. Furthermore, when applied backwards, our model may be used in combination with the VERHIB model (Jansen et al. 2008b) that was made to reconstruct the past vegetation by unravelling the ‘bulk’ biomarker signal contained in the soil using biomarker signals of individual plant species.
Conclusions

Our results show that soil volume change is a major soil forming process in the volcanic ash soil studied. SOM accumulation resulted in more than a tripling of initial soil thickness within 4800 years, from ~20 to 77 cm. Furthermore, our modelling exercise confirmed that our hypothesis of an upward shifting bioturbation zone in response to soil thickening is indeed plausible. Because of its effect on depth- dependent processes, e.g. decomposition, bioturbation and rooting, soil volume change cannot be ignored when investigating soil organic carbon dynamics at the millennia time scale, particularly in the case of SOM-rich soils that are of major importance to the global carbon cycle.

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