Organic carbon balance in Chilean volcanic soils after human intrusion and under different management practices

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Abstract
It is well known that humified soil organic matter (SOM) plays a central role in soil fertility due to its chemical and physical properties, especially by sustaining soil biological and related ecological equilibrium. Soil organic matter quantity and quality needs to be preserved in order to maintain soil productivity. In this study total organic carbon contents and their distribution were determined in several volcanic ash derived soils of Chile. Carbon balances are expressed in terms of a labile fraction (alkali-extractable less than 10.000 Dalton and polysaccharide compounds) and a stable fraction (fulvic, humic and humine compounds). The effects of different agronomic management on soil organic matter (SOM) quality and quantity are estimated and compared between agricultural and virgin forest soil sites. The results indicate that soils under native forest show a C level higher than agricultural soils. After human intrusion the stable C (m.w. >10,000 Daltons), viewed as a measurement of the humification grade, shows a mean value of 70% over the total C and follows the order: ultisols ('Rojo arcillosos') >andisols-placandepts ('Ñadis') >andisols-distrandepts ('Trumaos'). C balance demonstrates that in agricultural soils the soluble C, or 'labile C' is increased and accounts for 12–30% of the total C; these organic compounds contribute largely to the solubilization, mobility and availability of plant nutrients but also enhance losses of organic carbon by lixiviation. By using the carbon balance methodology discussed in this work, changes of quality and quantity of SOM can be followed up. The SOM of Chilean volcanic soils is being degraded after human intrusion; this needs to be considered in cultivation of these soils in order to preserve their fundamental properties.

Keywords: *C-distribution, humic polymers, soil organic matter (SOM).*

Introduction

It has been well established that soil organic matter (SOM) supports the biotic fraction of soil, composed of living microorganism. These soil components, e.g., humic and non-humic compounds, interact with them and also with plant roots, at the rhizosphere level and with the inorganic soil fraction, forming a system in ecological equilibrium under natural conditions.

Polysaccharides (PS) correspond to low and medium molecular weight molecules, which are easily available as a C source for microorganisms. Generally about 5–25% of SOM is composed of polysaccharides, mainly originating from the decomposition of animal and plant organic debris.

Humus constitutes 50 to 85% of total SOM in the earth's crust, and as such is one of the major organic C sources regulating atmospheric CO_2; humus presents a high total acidity (600–1500 meq H/100 g) and a very high cation exchange capacity (Schnitzer, 1978; Stevenson 1986; Aguilera et al.,1996). Humus is composed of humic and fulvic acids and of humine molecules which, in spite of their similar structure and functional grouping, are quite different with regard to their m.w., aromatic grade and solubility in acidic or alkaline solutions. These differences in chemical

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properties allow the fractionation of extractable soil humus; also they affect the availability of C to soil microorganisms.

The positive effects of SOM on soil properties and their fertility are based on their chemical, physical and biological behavioir, especially in those soils with high C content such as volcanic soils. Thus, knowledge of the quality and quantity of SOM is extremely important in volcanic soils to assess both their fertility and preservation state, closely associated with soil microbial ecology (Preston et al., 1994; Aguilera et al., 1995; Aguilera et al., 1996). This paper focuses on the effect of different agronomic management over SOM level and its characteristics in Chilean volcanic soils (andisols and ultisols) by determining the 'C balance' and 'C distribution' as performed by Aguilera et al. (1996).

Several soil series were selected for this study (Trumaos, Ñadis and Rojo arcillosos) located in southern Chile, where it is still possible to obtain soil samples from sites of a same soil series, both in a native state under virgin forest or subjected to human intrusion with different agricultural uses and management. Recently the SOM-metal interactions of some of these soils have been reported (Heredia et al., 2002).

Trumao andisols are young soils formed under drainage conditions fluctuating between excellent to good (Besoaín, 1985). These soils are very permeable to water intake with a low apparent density, optimal biological activity, high C content (8–14%) and high allophane content and aggregation (Tosso, 1985; Aguilera et al., 1996). Ñadis are young soils developed over poor drainage conditions. They are almost permanently flooded and are lighter than Trumao soils; C content is high (over 17%) and clay fraction is also composed of allophane. These soils present at some 80 cm depth a stone-like or cemented layer several millimetres thick, composed of iron and manganese oxides and silica. This layer is known as 'fierrillo' and it is responsible for the poor drainage conditions of Ñadis soils (Besoaín, 1985). Rojo arcilloso soils are ancient ultisols formed from mature volcanic-origin crystals highly eroded and with a lower C content (2–6%); their clay fractions, representing a final step in the degradation of the parent material, are composed mainly of halloysite-like minerals (Besoaín, 1985).

Actual conditions and agricultural management of these soils include: native forests, natural pasture, fertilized natural pasture and artificial pasture both under a normal fertilization programme and with waste purine application.

Materials and methods

Soil samples were collected, corresponding to the A_1 horizon (0–20 cm depth). They were refrigerated at 4°C before laboratory processing.

Soil samples were ground, sieved (2 mm) and homogenized to obtain representative samples of the corresponding soil site; six volcanic soil sites under different management practices were sampled which resulted in 14 final soil samples as follows: four corresponding to the Trumao series (andisols, typic dystrandeps), seven to Ñadis series (andisols, placandepts) and three to Rojo arcillosos series (ultisols) (Table I).

The laboratory methodologies used have been described and validated in previous studies. Very recently a report was published discussing the metal-binding properties of these same soils (Heredia et al., 2002). Analyses were made in duplicate and the results are the mean values, with a dispersion lower than ±5%.

SOM is extracted using a sequential extraction procedure based upon the solubility of each SOM fraction. The method implies the isolation and purification by dialysis of humic, fulvic and humine fractions; it has been tested and validated in a previous study (Aguilera et al., 1996).

The sum of these three fractions is considered the stable-C form. Furthermore, the similarity of the organic polymer structures between microbial-models polymers and the soil-extracted organic polymers

Table I. Some soil properties.

Soils	pH	Total C (%)	PS-C (%)
Andisols (Trumaos)			
Osorno P	5.04	9.40	1.52
Osorno Pf	4.69	8.69	1.22
Puerto Octay F	4.95	10.48	1.70
Puerto Octay P	4.43	10.32	2.14
Andisols-placandepts (Ñadis)			
Frutillar F	4.54	19.28	4.00
Frutillar P	4.66	14.16	3.78
Frutillar Pf	5.16	14.92	2.43
Frutillar P/B	5.35	16.44	2.64
Piedras Negras F	4.60	16.50	2.54
Piedras Negras P	4.93	14.28	2.16
Piedras Negras Pf	4.20	13.51	2.07
Ultisols (Rojo arcillosos)			
Cudico F	5.53	10.67	2.42
Cudico P	5.40	4.96	1.66
Collipulli O	5.47	3.08	0.38

PS: polysaccharides; F: wild forest; P: natural prairie; Pf: fertilized prairie; O: untreated deforested soil; B: barnyard manure
(purine).

had been checked before, working with pure microbial-model polymers obtained by growing indigenous soil microorganisms in artificial media (Aguilera et al., 1996).

Soluble C, less than 10,000 Daltons, is calculated by difference between the total C and the sum of stable-C fractions.

Total PS analyses were performed according to Aguilera et al. (1987) comprising three steps: extraction, purification and determination. Extraction is performed by applying an acidic hydrolysis to the soil sample; purification is accomplished by neutralizing the acidic extract with NaOH, and total PS are then determined by using the antrone method, applying visual spectrophotometry to calculate total sugars. To calculate the C balance it is considered that PS molecules liberated during humus extraction are easily broken up and liberated as lighter saccharide molecules when the extract is subjected to further purification by dialysis.

Total C, in soils and in each organic fraction, is determined using an elemental analyser, 'Vario EL', where the sample is subjected to an oxidative combustion at 1150°C in an atmosphere composed of He and O_2; quantitative combustion is obtained by selecting the O_2 flow rate and the combustion time.

The following equation depicts the relationship among all the C fractions discussed in this paper:

Total C = stable C + soluble C
Stable C = C-Hum + C-HA + C-FA
Hum = humine
HA = humic acid
FA = fulvic acid

Results and discussion

As shown in Table I, all the andisols studied present high SOM contents, ranging from 8.7 to 19.3% C. Ñadis soils are characterized in nature mainly by remaining under almost permanent anaerobic conditions, which of course delays the decomposition of original organic debris; consequently their total C is very high. Rojo arcillosos (Cudico and Collipulli) are ancient soils with a clay structure more crystalline than the younger ones. This diminishes organic matter stabilization processes due to the weaker physico-chemical surface activity of crystalline clay compared to allophane. Accordingly, the non-disturbed Collipulli soil presents the lowest C content of all the soils studied. Soil pH values for all the samples remain in the range 5.5–4.2, which after deforestation tend to decrease.

Table II shows the yield extraction and mass balance of total stabilized SOM in all the soils studied. The humic acid fraction varies from 3.6 to 26.0 and humine plus inorganic residue (Res-H) from 61.4 to 81.6 (g 100 g^{-1} dried soil). By adding

Table II. Extractive yield of soil organic matter fractions.

Soils	Hum (g/100 g soil)	HA (g/100 g soil)	FA (g/100 g soil)	Total (g/100 g soil)
Andisols (Trumaos)				
Osorno P	62.14	4.69	14.10	80.93
Osorno Pf	61.43	3.57	14.04	79.04
Puerto Octay F	67.87	4.29	4.29	92.80
Puerto Octay P	63.25	4.07	4.07	91.47
Andisols-placandepts (Ñadis)				
Frutillar F	67.62	13.27	25.32	106.21
Frutillar P	69.43	8.47	19.91	97.81
Frutillar Pf	76.82	7.16	20.94	104.92
Frutillar P/B	73.76	8.92	21.83	104.51
Piedras Negras F	72.45	9.27	22.88	104.60
Piedras Negras P	75.83	6.19	26.03	108.05
Piedras Negras Pf	81.56	5.28	22.60	109.44
Ultisols (Rojo arcillosos)				
Cudico F	74.70	4.85	24.99	104.54
Cudico P	73.30	3.67	15.73	92.70
Collipulli O	67.30	4.14	12.15	83.59

F: wild forest; P: natural prairie; Pf: fertilized prairie; O: untreated deforested soil;
B: barnyard manure (purine). Hum: inorganic residues plus humane; HA: humic fraction; FA: fulvic fraction.

Table III. Carbon content of extracted stable soil organic matter fractions.

Soils	Hum-C (%)	HA-C (%)	FA-C (%)
Andisols (Trumaos)			
Osorno P	3.20	47.30	7.14
Osorno Pf	3.16	49.26	5.94
Puerto Octay F	3.70	47.60	7.02
Puerto Octay P	2.54	50.60	6.46
Andisols-placandepts (Ñadis)			
Frutillar F	11.19	50.31	9.97
Frutillar P	6.83	50.92	10.38
Frutillar Pf	8.49	50.73	9.76
Frutillar P/B	8.04	50.42	10.59
Piedras Negras F	8.82	48.95	9.12
Piedras Negras P	8.57	50.30	8.09
Piedras Negras Pf	7.21	40.50	9.74
Ultisols (Rojo arcillosos)			
Cudico F	5.58	47.27	5.80
Cudico P	1.96	33.21	5.20
Collipulli O	1.26	19.62	4.15

F: wild forest; P: natural prairie; Pf: fertilized prairie; O: untreated deforested soil;
B: barnyard manure (purine); Hum: inorganic residues plus humane; HA: humic fraction; FA: fulvic fraction.

all the fractions together it confirms the good recovery pattern of the extraction procedure applied.

Table III shows C contents for each organic fraction. Humic fractions show the highest C content, ranging between 19.6 and 50.9%, while fulvic fractions fluctuate between 4.2 and 11.4%. These data are in agreement with those reported for volcanic soils by Schnitzer (1982) and Aguilera (1996). When comparing the type of soil and its management, there are almost no differences in C content among stable SOM fractions.

From the data of Tables II and III it is possible to calculate the corrected values for the level of C which contributes to the SOM pool in each organic fraction. These data have been designated as 'carbon balance in soils' (Aguilera et al., 1996).

The C balance is shown in Table IV and allows examination of the soil organic matter quality composition, e.g., total C and its distribution among soluble C and stabilized forms of C (HA-C+FA-C+Hum-C). Therefore, soil organic C balance may reflect a measurement of C availability. Stable C is mainly found in the form of the humine fraction and to a lesser extent in humic and fulvic fractions. Deforestation diminishes the total C, and consequently also diminishes each organic fraction.

Table IV shows data for total C, stable C and soluble C. The measure of soluble C is related to C availability; the C contained in polysaccharides and other low m.w. organic molecules are easily available for soil microbial metabolism. The figures in Table IV indicate that for andisols the soluble C fraction accounts for almost 50% of total C, whereas in placandepts and ultisols this diminishes to a mean value of the order of 20%. This means that andisol soils constitute soil systems with a high potential to

Table IV. Carbon balance (expressed on the basis of 100 g of dried soil).

Soils	Total Soil-C (%)	Hum-C (%)	Stable-C HA-C (%)	FA-C (%)	Stable-C (%)	Sol-C (%)
Andisols (Trumaos)						
Osorno P	9.40	1.99	2.22	1.01	5.22	4.18
Osorno Pf	8.69	1.94	1.76	0.83	4.53	4.16
Puerto Octay F	10.48	2.51	2.04	1.45	6.00	4.48
Puerto Octay P	10.32	1.61	2.06	1.56	5.23	5.09
Andisols-placandepts (Ñadis)						
Frutillar F	19.28	7.57	6.68	2.52	16.77	2.51
Frutillar P	14.16	4.74	4.31	2.07	11.12	3.04
Frutillar Pf	14.92	6.52	3.63	2.04	12.19	2.73
Frutillar P/B	16.44	5.93	4.50	2.31	12.74	3.70
Piedras Negras F	16.50	6.39	4.54	2.09	13.02	3.48
Piedras Negras P	14.28	6.50	3.11	2.10	11.71	2.57
Piedras Negras Pf	13.51	5.88	2.61	2.20	10.69	2.82
Ultisols (Rojo arcillosos)						
Cudico F	10.67	4.17	2.29	1.45	7.91	2.76
Cudico P	4.96	1.44	1.22	0.82	3.48	1.48
Collipulli O	3.08	0.85	0.81	0.50	2.16	0.92

F: wild forest; P: natural prairie; Pf: fertilized prairie; O: untreated deforested soil;
B: barnyard manure (purine); Hum: inorganic residues plus humane; HA: humic fraction; FA: fulvic fraction; Sol-C: calculated by difference (Total-C- stable-C).

behave as a biological reservoir to sustain biological activity; therefore the natural C turnover mechanisms are being preserved in these soils. By applying the concept of C balance, methodologically based on the calculation of stable and soluble C, it is possible to examine the carbon distribution in a soil and to determine how the actual C status is related to the sustenance of soil biological equilibrium.

Figure 1 depicts 'carbon distribution'; in order to evaluate the grade of humification of the SOM in the corresponding soils studied, each fraction is represented as a percentage of the total C. It is shown that the stable C (equivalent to humified C-forms) corresponds to 50–87% of total C, while labile C (PS plus non-PS soluble C lost by dialysis) accounts for 12–20% of the total C. Ñadis and Rojo arcillosos soils show the higher stabilized C values (70–87%) while for Trumao soils the variation is from 51 to 57%. The humification grade for Chilean volcanic ash soils follows: Ñadis > Rojo arcilloso > Trumao or placandepts > ultisols > andisols. Stabilized C forms follow C-Hum > C-HA > C-FA. The agricultural management does not modify C-HA appreciably, but C-FA does show important changes due to their susceptibility to agricultural management.

The content of total organic C is closely related to soil management. Soil under native forests shows a high level of total C ranging from 10.5 to 19.3%, most probably due to high annual leaf deposit; soils under natural prairies present total C varying from 9.4 to 14.3% in andisols; in ultisols, around 5%. This demonstrates that organic macromolecules are not fully disturbed after forest disappearance with no further cultivation. With regard to soils under artificial or planted prairie (only Frutillar soil) it can be seen that the highest C content is found with purine application, while C content is not affected by fertilization except in Cudico soil.

Table V shows total polysaccharides, directly measured by applying the anthrone method, including also the data for soluble C obtained from the calculation of the corresponding C balance. Both types of data are expressed as soil C percentage. The pool of available C, especially in Trumao soils, is greater and well described by considering soluble C as available source of C. There is an exception in Frutillar soil, where wild forest and natural prairie samples show higher PS. This would indicate the presence of some non-extractable PS. Therefore, by applying the C balance concept developed in this work it is possible to better appraise the sense and meaning of all the C forms which comprise the SOM.

Chilean volcanic soils subjected to some agricultural management show higher polysaccharide levels than similar virgin soils as cited by Cheschire (1979),

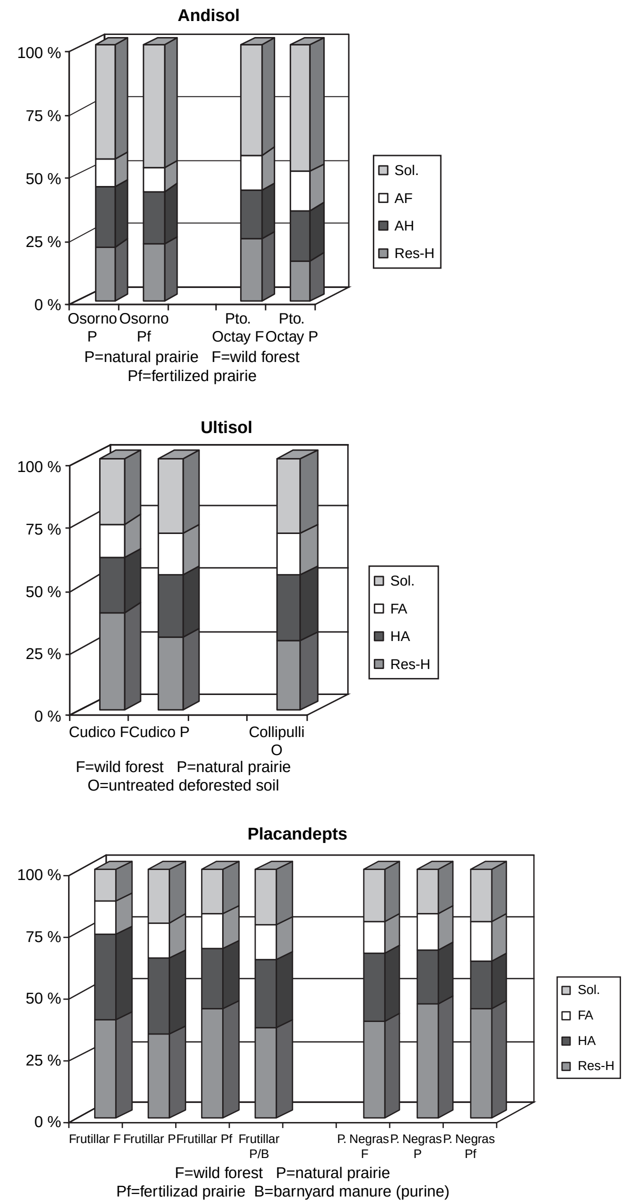

Figure 1. Soil carbon distribution.

Aguilera et al. (1987) and Peirano et al. (1992). Ñadis soils (Frutillar) show the highest level of total polysaccharides, which should be a consequence of their anaerobic conditions imposing a lower rate of organic matter decomposition. Collipulli (Rojo arcilloso) soils present the lowest level of total polysaccharides (0.38%), confirming results previously reported (Aguilera et al.,1987; Peirano et al., 1992). With regard to the effect of soil management, the results indicate that Frutillar soils under native forest, and also under naturally implanted prairie, show the highest level of total polysaccharides (4% to 3.8%). Piedras Negras soil shows similar total PS among different managements, while in Puerto Octay and Osorno a slight difference is observed between native forest and natural prairie.

Table V. Easily available carbon (expressed on the basis of 100 g of dried soil).

Soils	Sol-C (%)	PS-C (%)	Total easily available C (%)
Andisols (Trumaos)			
Osorno P	4.18	1.52	5.70
Osorno Pf	4.16	1.22	5.38
Puerto Octay F	4.48	1.70	6.18
Puerto Octay P	5.09	2.14	7.23
Placandepts (Ñadis)			
Frutillar F	2.51	4.00	6.51
Frutillar P	3.04	3.78	6.82
Frutillar Pf	2.73	2.43	5.16
Frutillar P/B	3.70	2.64	6.34
Piedras Negras F	3.48	2.54	6.02
Piedras Negras P	2.57	2.16	4.73
Piedras Negras Pf	2.82	2.07	4.89
Ultisols (Rojo arcillosos)			
Cudico F	2.76	2.42	5.18
Cudico P	1.48	1.66	3.14
Collipulli O	0.92	0.38	1.30

F: wild forest; P: natural prairie; Pf: fertilized prairie; B: barnyard manure. PS: polysaccharides; O: untreated deforested soil; Sol-C: calculated by difference (Total-C- stable-C).

In conclusion, for a given soil it is clear that total organic C content follows the sequence forest > prairie > cultivation. This demonstrates that SOM is being degraded after human intrusion, which needs to be considered to preserve volcanic soil systems. Carbon balances, within each particular total SOM fraction, indicate that agricultural management shifts the equilibrium towards more soluble and available organic compounds (such as polysaccharides), thus diminishing the pool of stable organic matter. However, although the increment of soluble C helps plant and microbial nutrition processes by enhancing C and micronutrient availabilities, there is a corresponding increment in the risk of C losses by lixiviation.

The changes in C balance described in this work can be related to the N and S influences, studied in other recent works (Borie et al., 2002; Aguilera et al., 2002), and also to mycorrhizal behaviour reported by Rubio et al. (2003). In so doing, it can be concluded that agricultural uses of land sites composed of volcanic soils after human intrusion need to be carefully controlled and planned. This must include soil management practices, such as no-tillage methods and appropriate fertilization programmes, focusing towards the preservation of the natural and delicate equilibrium state among SOM microorganisms characterizing these soils. Only by considering this management principle can volcanic soils be simultaneously cultivated and preserved for future generations.

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