Organic Matter in Volcanic Soils in Chile: Chemical and Biochemical Characterization

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ABSTRACT

Determinations were made of total soil organic matter (SOM), stable and labile organic fractions, biomass carbon (C), and chemical composition of several humus-soil-fractions in chilean volcanic soils; Andosols and Ultisols. Their physico-chemical properties and humification degree at different stages in edaphic evolution were also assessed. In addition, organic matter models were obtained by chemical and biological syntheses and the structures and properties of natural and synthetic humic materials were compared with SOM. Results indicate that Andosols have higher SOM levels than Ultisols, but the fraction distribution in the latter suggests a shift of the more stable fractions to the more labile ones. Moreover, contents of humines, and humic and fulvic acids suggest that Chilean volcanic soil SOM is highly humified. On the other hand, among the SOM labile fractions, carbohydrate and biomass are about 15% of the SOM which are one of the most important fractions in soil fertility.

INTRODUCTION

Soils of volcanic origin are widespread in Chile and account for about 60% of the actual agricultural land. They are mainly made up of allophanic clay strongly interacting with humus, forming a clay-organic matter complex where the exact nature of their physico-chemical interacting mechanisms is not well known (Zunino and Borie, 1985).

Volcanic-ash soils in Chile belong to a scarce Dystrandept edaphic system that developed from erupted volcanic ash in a mild and very humid climate with mean annual temperature below 12°C and an annual rainfall exceeding 2,000 mm.

Various researchers have described the characteristics of these soils. They have excellent physical properties, such as good permeation, adequate aggregation, and high water-holding capacity. However, the failure of these soils to serve as plant nutrition supporting systems that derives mainly from their high phosphate (P)-fixing capacity, low nitrogen (N) availability, poor base content, and aluminum (Al) phytotoxicity (Tosso, 1985), represents a serious limitation to obtain good agricultural yields and high fertilization rates have to be worked out by farmers.

Soil organic matter (SOM) constitutes a very important fraction of volcanic-ash soils. It ranges from 5 to 15% of total carbon (C), representing between 10 to 30% of the total soil bulk mass. Such accumulation is the result of a number of very complex soil formation processes in which micro flora activity is an essential factor (Haider et al., 1975). In addition to soil physical properties, plant nutrition mechanisms are undoubtedly mediated by SOM, and by N and P availability. Micronutrient translocation also depends strongly on the SOM (Zunino and Martin, 1977; Zunino and Borie, 1985).

Microbial and chemical syntheses of SOM in Chilean volcanic-ash soils must be playing a very important role in their humus accumulation (Martin et al., 1982). Enzymatic activities, e.g., dehydrogenase, phosphatase, polyphenoloxidase, are quite high as has recently been demonstrated (Aguilera et al., 1988; Borie, 1985; Peirano et al., 1987; Borie et al., 1992). The rate of organic matter decay is quite low in allophanic soils as compared to non-allophanic soils (Zunino et al., 1982a; Martin et al., 1982), whereas allophanic humus complexes seem to be a final step that regulates soil formation (Zunino and Borie, 1985). In an undisturbed soil, this complex seems to be the actual sink for P accumulation regulating plant P nutrition (Borie and Zunino, 1983).

The SOM chemical composition and properties in Chilean Andepts are not well known. Therefore, gathering information will permit a better understanding of the mechanisms in which the SOM is involved, particularly those related to plant nutrition and soil conservation. Thus, a better knowledge of such mechanisms will improve fertilization and management practices.

This work is very likely the first report on a whole view of SOM including the complete pool of SOM. Thus, the aim of this work was to determine the total soil organic matter, stable and labile organic fractions, biomass C, and chemical composition of several humus-soil-fractions present in some volcanic soils from southern Chile. Their physico-chemical properties and degree of humification at different stages in edaphic evolution were also studied. In addition, organic matter models were obtained by chemical and biological syntheses and compared with SOM.

MATERIALS AND METHODS

According to age or increasing evolution, the Chilean volcanic-ash soils under study were: Andosols (Andepts), Ralún<Arrayán<Osorno<Temuco<Corte Alto; a Placandept soil, Frutillar; and Ultisols (Humults), Crucero<Cudico<Collipulli <Metrenco. All soil samples correspond to superficial horizon of undisturbed soils without vegetal cover. They were collected with their original moisture and sifted through a 2-mm sieve. Table 1 exhibits some of their main characteristics. The SOM study was done with extracted SOM fractions and compared with "model fractions" obtained by microbiological or chemical syntheses.

Organic Fractions from Soils

The traditional alkaline extraction technique (Schnitzer, 1982) was adapted to separate pure humic acids (HA) and fulvic acids (FA) present in these volcanic soils. This is particularly difficult in Chilean volcanic soils because of the strong interactions between organic matter and clays, particularly allophane.

In order to obtain the HA and FA fractions, three successive extractions were done with 250 mL 0.1N sodium hydroxide (NaOH) at 95°C for 30 min on 25 g of each soil. The alkaline extract was separated by centrifugation at 3,000 rpm. Humic acid were precipitated at pH 2.0 with 0.2N sulfuric acid (H_2SO_4) and were separated and washed three times with water. Then, they were exhaustively purified by three treatments with 50 mL of a 25% solution hydrochloric acid:hydrofluoric acid (HCl:HF)=1:1 extraction. The last purification was done by means of a dialysis treatment that removed all inorganic ions. Finally, HA were dried at 50°C under vacuum.

The FA remaining in the acid solution were purified by an ionic exchange treatment in a column with Dowex X8 resin. The solution free of inorganic ions was concentrated using a rotary evaporator and dried at 50°C and under vacuum. In order to reach the best purity, FA was dialyzed using a molecular sieve (Mw: 6,000 to 12,000). The residual soil without HA and FA was water washed three times and dried to obtain the C humine using an elementary analysis.

Humic Substance Models

Synthetical Models

Models obtained and used by Martin et al. (1975), Zunino et al. (1982a), and Zunino et al. (1982c) were compared with soil humic substance models. These

TABLE I. Main characteristics of soils.

SERIES	CLASIFICATION	PARENT MATERIAL	pH	% C
Raldn	Mesic, Umbric Vitrandept	Recent volcanic ashes and sands	5.7	8.2
Pto. Octay	Typic Dystrandept	Modern volcanic ashes	5.4	7.1
Arrayán	Typic Dystrandept	Modern volcanic ashes	6.5	6.1
Osorno	Typic Dystrandept	Modern volcanic ashes	5.6	10.2
Temuco	Entic Dystrandept	Modern volcanic ashes	5.3	8.6
Corte Alto	Typic Dystrandept	Modern and intermediate volcanic ashes	5.7	13.2
Frutillar	Typic Placandept	Volcanic ashes	5.4	11.7
Crucero	Andeptic Haplohumult	Old volcanic ashes	4.9	6.4
Cudico	Typic Palehumult	Old volcanic ashes	5.3	5.0
Collipulli	Xeric Palehumult	Old volcanic ashes	5.3	1.5
Metrenco	Palehumult	Old volcanic ashes	5.7	6.1

models were obtained by auto-oxidation or enzymatic oxidation of phenolic or carboxilic-phenolic precursors.

Microbiological Models

Microbiological models obtained with *Stachybotris Atra, Azotomicro, Aspergillus Niger*, and *Hendersorula Toruloidea*, and used by Martin et al. (1975)

and others synthesized for this work by the authors with fungal Chilean soils, were used. To this purpose, the fungal "HA-type" model from each volcanic-ash soil was obtained from dark-colored substances generator microorganisms that were isolated in a Chopex culture medium. The isolated and purified HA-type generator microorganisms were incubated in a liquid Chopex culture medium for 30-60 days. The HA-type polymers were separated by filtration, purified by dialysis, and washed from the dark solution obtained. Finally, they were dried at 50°C under vacuum.

Carbon determinations were done by a dry-combustion method and the elementary analysis using a C-H-N analyzer. The inorganic elements [Al, Fe, calcium (Ca), and magnesium (Mg)] were determined by atomic absorption spectrophotometry, and P by colorimetry.

For each soil, carbohydrate (CH) and biomass carbon (C-Biom) contents were determined, the Cheshire (1979) technique for carbohydrate determination and the Jenkinson technique (1976) for biomass C, methods adapted to volcanic soils by Aguilera et al. (1987) and Borie et al. (1992). The E4/E6 corresponds to HA and FA spectrophotometric absorption ratio at 465 and 665 nm. The reagents were of analytical grade and the experiments were carried out in duplicate and only the mean values reported.

TABLE 2. Elementary analysis of humic substances in volcanic-ash soil.

SUELO	%C		%H		%N		%O		C/N	
	HA	FA	HA	FA	HA	FA	HA	FA	HA	FA
Ralún	51.1	39.9	5.5	4.4	4.2	2.0	38.5	53.0	12.1	20.5
Pto.Octay	52.6	21.5	4.4	-	4.2	-	37.2	-	12.6	-
Arrayán	49.8	7.2	5.6	4.1	2.4	0.4	41.3	-	20.8	20.5
Osorno	50.3	39.5	5.4	5.7	3.5	1.7	39.9	52.2	14.4	23.2
Temuco	48.3	11.1	6.6	-	3.7	-	40.9	-	13.0	14.6
Corte Alto	48.1	36.3	6.2	5.1	3.2	1.9	41.5	52.5	15.5	19.2
Frutillar	51.5	39.4	5.6	5.7	2.5	0.8	40.0	53.3	20.6	49.2
Crucero	50.1	27.0	5.3	1.9	4.3	1.0	37.0	69.6	11.7	27.5
Cudico	50.3	33.7	4.6	1.5	4.1	0.6	36.8	63.4	12.4	61.3
Collipulli	32.4	1.7	2.7	-	2.5	0.3	60.4	-	13.1	8.1
Metrenco	50.9	18.0	5.9	4.7	3.5	1.3	38.7	75.7	14.7	15.0

RESULTS AND DISCUSSION

Table 1 shows series, classification and main characteristics of parental material of the volcanic ash soil under study according to the compendium "Suelos Volcanicos de Chile" (Tosso, 1985). Carbon content and soil pH are also provided.

Carbon contents for these soils are usually high (5-13%) and vary according to their structure and age. Carbon content tends to increase with age except in Ralún, a young Andosol. The Frutillar soil has developed under restrictive drainage conditions which affects SOM quantity and quality, and like the other Placandepts (Aguilera et al., 1989; Aguilera et al., 1993), the SOM content is higher than 10% C. But the Ultisols, the oldest soils, have a lower C content. This is closely related to their low allophane content based on their mineralogy (Besoaín, 1985), and thus their ability to interact with SOM, stabilizing decreasing it (Zunino et al., 1982a; Zunino et al., 1982b). The C content of these soils decreases markedly with their age, being 1.5% in the Collipulli soil. The Metrenco soil could be even an older soil, its origin being different from the rest (Besoain, 1985) which might affect its organic contents. According to a recent soil report (Miller and Donahue, 1990), the acidity of Chilean volcanic-ash soils varies from medium or strong for Andosols to strong or very strong to Ultisols.

TABLE 3. Elementary analysis of "model" humic substances.

MODELS		%C	%H	%N	%O	C/N
SYNTHETICAL						
Self-oxidation	HA	56.0	3.2	0.04	40.8	-
Self-oxidation	FA	53.6	3.0	0.03	43.4	-
Phenolic	HA	51.7	-	-	-	-
Hydroxibenzoic	HA	63.5	-	-	-	-
Cystein	HA	39.7	3.3	5.52	51.6	7.2
Commercial Peat	HA	40.3	3.3	0.57	55.8	70.7
Leonardite		48.1	-	-	-	-
MICROBIOLOGICAL						
Temuco fungi		41.3	6.5	4.55	47.7	9.1
Frutillar fungi	I	39.5	6.3	6.92	47.3	5.7
Frutillar fungi	II	34.1	5.3	4.55	56.1	7.1
Azotomicro		52.1	-	-	-	-
S. Atra		51.2	-	-	-	-
Aspergillus		50.6	-	-	-	-
Hendersonula T.		52.8	-	-	-	-

This is a study of natural and synthetical humic materials and intends to compare their structures and properties. Humic acid and FA extracted from soils implied trying various techniques and then finally staying with the traditional alkaline extraction method, but with an emphasis on the purifying process necessary to remove the strong interaction of allophanes.

Apart from the "HA-type" models reported earlier (Zunino et al., 1982a; Martin et al., 1982), three microbial polymers synthesized by dark-colored-substances, the generator fungi from the Frutillar and Temuco soils were prepared in order to have standards of soil microorganisms polymers without the alterations caused by the extraction methods (Martin et al., 1975; Haider et al., 1975). Tables 2 and 3 show the elementary analysis of the soil humic substances and of the "HA-type" synthetic and microbial models. The C content in HA is about 50% for most soils independent of age or classification even for the Arrayan, Temuco, and Corte Alto soils that have slightly low values which could account for a lower condensation of the humic material.

As very low C contents for FA result from problems derived on purifying, the values of most impure FA were adjusted according to extraction yield and ash content. Carbon contents in the humic models permit us to determine the synthesis rate of microorganisms in the Temuco and Frutillar soils since they can condense

TABLE 4. Ranges of elementary analysis of HA and FA extracted from Chilean. volcanic-ash soils and "models".

	HA				FA			
	%C	%H	%N	%O	%C	%H	%N	%O
SOILS								
Dystrandept	48.1 52.6	4.4 6.6	2.4 4.2	37.2 41.5	36.3 39.9	4.1 5.7	1.4 2.0	52.2 53.0
Palehumults	50.1 50.9	4.6 5.9	3.5 4.3	36.8 38.7	27.0 33.7	1.9 4.7	0.6 1.2	63.4 75.7
Placandept	51.5	5.6	2.5	40.0	39.4	5.7	0.8	53.3
Acid soils *	53.8 58.7	3.2 5.8	0.8 2.4	35.4 38.3	47.6 49.9	4.1 4.7	0.9 1.3	43.6 47.0
MODELS								
Synthetical	39.7 63.5	3.2 3.3	0.04 5.5	40.8 51.6	53.6	3.0	0.03	43.4
Microbiological	34.1 52.8	5.3 6.5	4.6 6.9	47.3 56.1				
Commercial Peat	40.3	3.3	0.6	55.8				
Leonardita	48.1							

*Described by Schnitzer (1978).

in one or two months humic matter with a 34-41% C content from simple sugars (glucose, sucrose, etc.) present in growth culture. The other models exhibit C contents according to the substrate used, thus the higher C contents correspond to phenolic or hydrobenzoic models from already condensed or cyclic substrates. The model containing N exhibits a lower level of condensation. Other microbial models have higher polymerization levels than those obtained in the Chilean volcanic-ash soils (Table 3). This brief analysis could be an important approach to the humification process that can be obtained in the synthesis of SOM according to the quality and quantity of substrates available in the edaphic system.

TABLE 5. Humic substances condensation degree's E4/E6 ratio.

SOILS	E4/E6	
	HA	FA
Ralún	5.5	8.8
Pto.Octay	4.7	9.8
Arrayán	3.5	6.0
Osorno	4.5	20.0
Temuco	4.1	10.0
Corté Alto	4.4	10.8
Frutillar	4.3	15.3
Cudico	4.3	2.0-7.0
Crucero	3.9	6.0
Collipulli	2.6	6.2
Metrenco	4.1	10.3

MODELS	E4/E6
SYNTHETICAL	
Phenolic	7.1
Hydroxibenzoic	7.7
Cystein	9.3
Selfoxidation	9.0
Leonardite	6.2
Commercial Peat	7.2
MICROBIOLOGICAL	
Azotobacter	4.0
S. Atra	5.6
Frutillar fungus	4.0
Frutillar fungus I	4.9
Frutillar fungus II	5.2
Temuco fungus	4.9
Aspergillus	4.4

Table 4 summarizes the elementary content ranges for all Chilean soils and the values for the acid soils reported by Schnitzer (1978). A comparison of both types of soils may be a valuable approach even though their origin and characteristics may be quite different.

Soil organic matter composition shows that C contents are lower than those indicated by Schnitzer (1978) and by Kuwatsuka et al. (1978) with values fluctuating between 40 and 53% C in HA Andosols (andepts) and 51% in Ultisoles (humults). The HA elementary percentages ranged as follows: H from 4.4 to 6.6%; H from 2.4 to 4.6%; and O from 37 to 42%. The same trend was observed for FA, C about 40%, N 2%, and O near 50%. These percentages are in accordance with the evolutionary state of the soils used, since their structure, though very stable, is not so polymerized as in other soils. This was confirmed by the E4/E6 ratio that ranged between 3.5 to 5.5 for the Andosols and 2.6 to 4 for the Ultisols (Table 5).

Table 5 shows E4/E6, humification, and condensation values, for all organic polymers under study which agrees with those reported by Schnitzer (1978), Stevenson (1982), and Ruggiero and Interesse (1980) for HA and FA humification. The lower E4/E6 value for the most condensed and polymeric products would account for the HA results for the old Collipulli soil and the young Ralun soil which exhibits the higher value.

TABLE 6. Inorganic element contents of humic substances (ppm).

		Dystrandept	Palehumult	Placandept	Model B *
P	HA	950- 1400	1700- 2400	1000	60-6000
	FA	400- 6500	400- 3000	850	
Al	HA	300- 6000	4000-13000	1000	1500
	FA	5000-47000	1100- 5000	7000	
Fe	HA	1500- 4500	2350-13000	2060	
	FA	350- 950	230- 1200	620	
Ca	HA	150- 5000	360-21000	230	
	FA	55- 1000	5- 75	75	
Mg	HA	70- 700	700- 3800	185	
	FA	30- 700	5- 75	60	

*Microbiological.

After exhaustive purification, the content of inorganic elements bound to the organic fractions is lower than 1% for HA and FA and they correspond essentially to Al, Fe, Mg, Ca, and P (Table 6). The highest content of Al was found in FA, whereas Ca and Mg content was higher in HA. The highest P concentration occurred in HA of the older soils. The strong interaction between inorganic elements and organic fractions should be stressed, since the polymers were subjected to drastic treatments, including hydrolysis with HCl-HF.

Percentual Distribution of Organic Matter Fractions in Chilean Volcanic Soils

Apart from stable and polymeric HA and FA fractions, determinations were made of the most condensed or strongly retained C in the humus-allophane complex, namely C-humines, and of the labile pool of SOM, namely carbohydrates (CH). Carbon biomass, the missing important fraction of the organic pool, was also determined and together with the rest of the fractions permitted to evaluate quality and reactivity of SOM of various soils.

Table 7 summarizes the results of the experiments with values expressed as soil total C and their fractions are expressed as total C percentages. The SOM

TABLE 7. Carbon fraction distribution in Chilean volcanic-ash soils (%).

SOIL	Total C	Humine	HA	FA	CH*	Biomass
Ralún	8.2	30.5	31.7	12.2	14.9	3.7
Pto.Octay	7.1	54.9	8.5	16.9	7.0	4.2
Arrayán	6.1	60.7	18.0	13.1	6.6	5.6
Osorno	10.2	48.0	20.6	12.7	9.8	4.9
Temuco	6.6	66.6	16.6	7.6	4.8	0.6
Corte Alto	13.2	50.8	9.0	17.4	8.3	2.3
Frutillar	11.7	69.2	16.2	13.7	11.1	2.6
Crucero	6.4	28.1	21.9	29.7	10.3	3.6
Cudico	5.0	36.0	26.0	6.0	10.4	3.4
Collipulli	1.5	33.3	20.0	26.7	6.7	1.3
Metrenco	6.1	41.0	34.4	11.5	-	-

*CH=carbohydrates

high stability and humification was evident based on its fraction sizes. Humines are one-third of the younger soil, HA another third, and FA, CH, and 4% of the biomass C correspond to the remaining third.

In the older andosols, humines amount to 50 to 60%; HA, 10 to 30%; FA, 13%; CH, 10%; and biomass-C, 2.6%. In the Ultisoles, the humine content is lower (23-40%), but the HA constitute 20 to 34%, the other fractions are similar to those in the other soils. Total CH contents in these soils are 0.1 and 1.3%; the lower value corresponds to Collipulli Ultisol and the higher value to the Frutillar soil which was developed under greater anaerobiosis which facilitates holding CH in the soil. These values are high when compared with those reported for soils with 1-4% C having C-CH contents of 90-247 mg C-CH kg^{-1} (Deng and Tabatabai, 1994).

Soil C-biomass content corresponds to 0.1-0.5% which is 1.3-5.6% of total C content. These values are similar to those appearing in literature (Anderson and Domsch, 1989; Kaiser et al., 1992) for high C-content soils; however, the relationship with total organic C is greater which confirms the important biological activity in Chilean volcanic soils.

Figure 1 shows, as independent values, the contribution of C fractions, i.e., humines, HA, FA, CH, and biomass-C, to the total sum of soil C as a "Balance or Profile of SOM" for each soil in order to detect the extent of SOM recovery, the stability of humic fractions, the availability of low molecular weight compounds that are a source of energy in microbiological processes, and the bioactivity based on the various C sources that make up the pool of SOM.

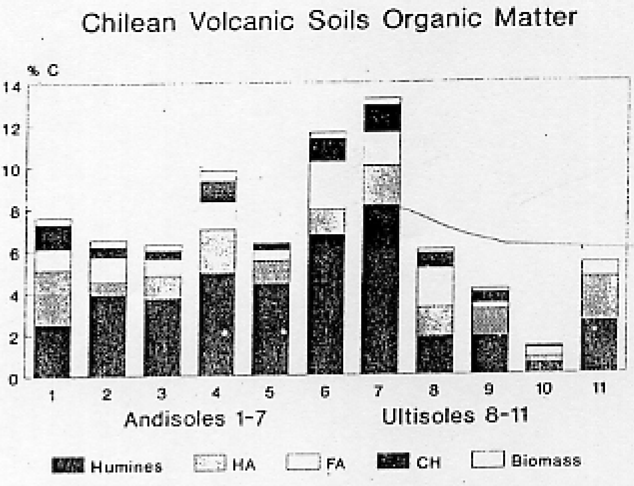

FIGURE 1. Carbon fraction distribution.

The balance of SOM permits the following conclusions: (i) the sum of th extracted or determined C for each fraction in relation to the total shows a goo yield which suggests that it is a good parameter to assess SOM, (ii) there are hig levels of SOM in andosols compared with ultisols, for in the Ultisols, SOM distribution suggests a shift of the more stable fractions to the more labile ones with a risk of SOM loss, (iii) although Chilean volcanic-ash soils have a high content of SOM, the CH content in these soils confirm that its availability is limited, and (iv) although quantitatively less important, soil biomass is undoubtedly one of the most significant fractions in relation to soil fertility as it becomes evident by the high yield of Osorno and Arrayán soils.

Finally, if humines, HA, and FA are considered the humic fraction, we can conclude that Chilean volcanic-ash soils are made up of highly humified substances, but because of their properties (Aguilera, 1990a,1990b), potentially active materials. In addition, Chilean volcanic-ash soils have a very important biomass closely related to the amount of available SOM.

We believe that the most important aspect is to evaluate thoroughly and study in greater detail all those parameters contributing to a resulting total SOM balance including the stable and labile carbohydrate fractions and active biomass, since this will permit SOM assessment in all its potential, and its close relationship with bioactivity in the edaphic systems with all the variables of use and management required in order to improve soil management practices and yield by preventing SOM exhaustion that leads to erosion and loss of fertility.

ACKNOWLEDGMENTS

The funding source was FONDECYT 1115-92, Chile.

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