Chemical Characterization of Sewage Sludges in Chile and Their Potential Utilization as Amendment to Reclaim Soils for Forestation Purposes

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ABSTRACT

Soils open for forestation in Chile are characterized by their very low organic carbon content; therefore, new forest plantations, needed to restore soil ecological equilibria, are scarcely developed. Stabilized sewage sludge contain organic compounds which have been demonstrated can serve as good soil amendments. To evaluate their actual uses in Chile it is necessary to characterize the carbon (C)-distribution pattern of such sludges in order to foresee their potential contribution for soil reclamation and plant growth, acting both as a source of stable C-reservoir and as readily available C-source.

The molecular weight (m.w.) distribution and carbon balance in Chilean sewage sludges are quite similar to soil humus and some woody by-products, as sawdust and bark dust. Total C varies from 30 to 35%, N from 5 to 9%, and P from 10,000 to 12,000 ppm. No significant content was found for heavy metals.

The C-balance indicates that around 70% of total-C is under stabilized forms as humine and humic macromolecule structures. The sewage sludge can be considered as good amendments for forest soils, especially in areas heavily eroded and depleted of natural humus. Their soluble-C fractions (13% of total-C) will serve as good energy starter source to strengthen indigenous soil microbial ecology, while their high m.w. fractions (humic acid-like and humine-like macromolecules) will serve both as good humus reservoir and as microelement frame in soils treated with such sewage sludges.

Keywords: sewage-sludge; soil amendment; stable organic matter; labile-C; heavy metals

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INTRODUCTION

The environmentally safe disposal and utilization of sewage sludge as a soil amendment, specially oriented towards the reclamation of eroded soils is a very important area of study (Mujeriego and Carbó, 1994; Costa et al., 1995; Glynn, 1999).

As a developing country, Chile recently began installing and operating modern waste water treatment plants, under high technological standards. Agricultural disposal of their stabilized sewage sludge products appears as one of the major procedures to achieve their practical and beneficial utilization (Mujeriego and Carbó, 1994; Costa et al., 1995). Chilean territory runs from North to South in the Southern Hemisphere, involving a wide variety of soils and agriculture; the Northern part of the country has primarily dried deserts (Aridisols), the soils of the Central zone belong to ordinary sandy and montmorillonite series (Entisols, Alfisols, Inceptisols) while Southern soils are classified under the order of volcanic ash-derived soils, mainly Andisols and Ultisols (Besoain, 1985). A very important fraction of these extensive lands is oriented toward forest plantations, where pine and eucalyptus trees are the most frequent species cultivated; moreover there are some very interesting studies claiming for the reintroduction of several indigenous species (Redford et al.,1990; Simonetti, 1997). All these soils show very poor fertility as the result of hundreds of years of exploitation over their early natural forest and vegetation, followed by non-rational agricultural management. Soil organic matter fraction appears as one of the most affected components, subjected to serious chemical and physical degradation (Aguilera et al., 1998) leading very often to heavy soil erosion processes.

Disposal policy of stabilized sewage sludge, onto these types of land shortly described above, appears as a very interesting opportunity to accomplish the two main objectives clearly discussed and demonstrated elsewhere. First, it does represents an environmentally acceptable route to get rid of huge amounts of sewage sludge, and secondary it should constitute a good tool to help soil bioremediation by improving soil properties and their associated fertility (Mujeriego and Carbó, 1994; Costa et al., 1995). These soil amendments increase soil fertility, favoring the establishment and development of forest plantations, especially on the new and younger ones. It is a fact that stabilized sewage sludge do provide valuable source of plant and microflora nutrients, among them mainly C, nitrogen (N), phosphorus (P), and sulfur (S). Of course, toxic effects from the eventual presence of heavy metals must be overcome (Mujeriego and Carbó, 1994; Costa et al., 1995; Hernández, 2001). It is expected that stabilized sewage sludge disposal helps to improve soil organic matter content impacting on the chemical, physical and microbiological properties of the soils under treatment. The national policy and its experimental approach briefly described needs to begin with a deep study of the chemical composition and molecular structure characterization of the target stabilized sewage sludge (Hernández et al., 1990; García et al., 1991, 1992; Aguilera et al., 1995; Costa et al., 1995; Borie et al., 2000).

The main purpose of this paper is to report the chemical distribution of the stabilized C-compounds, contained in sewage sludge emerging from several modern waste water treatment plants located in several cities nearby forest plantations in three geographical regions of Central Chile, correlating the results with the patterns usually found in soil humus and in other types of organic soil amendments.

The laboratory methods to determine C-balance and C-distribution in soils have been recently developed, and applied successfully to several Chilean volcanic-ash derived soils to investigate N and S cycles and distribution (Aguilera et al., 1997; Borie et al., 2002; Aguilera et al., 2002). By applying that laboratory methodology C-compounds conforming natural soil-humus have been classified according to the following fractions: C-humine (m.w. compounds >100,000) C-humic acid (m.w.10,000–100,000) C-fulvic acid (m.w. 2,000-10,000) and finally C-soluble compounds (m.w. < 2,000).

The same methods have been also applied to determine C-distribution in several natural organic residues susceptible to be used as soil amendment like sawdust, barkdust, and animal farm manures (Aguilera et al., 1995; Borie et al., 2000).Through the measurements of these types of compounds, carbon balance can be appropriately established and projected in relation to the microbial C-availability required by plants roots at the rhizosphere level and also to the state of stabilized C-pool.

The study is applied to stabilized sewage sludge produced in modern sewage sludge treatment plants (Glynn, 1999; Hernández, 2001)

Organic matter composition and its C-distribution in stabilized sewage sludge are compared with similar data obtained previously for naturally occurred humus of several Chilean soils and for some wood residues. The possibility of using sewage sludge as soil forest amendments oriented toward the reclamation of soil humus status, and its associated metal-binding ability impacting microelement availabilities, is discussed.

MATERIALS AND METHODS

The stabilized sewage sludge included in this work were obtained in modern waste water treatment plants, built and working under validated and regulated techniques including all their physical, chemical and biological processes. All sewage sludge samples were representatively collected with their original moisture.

The isolation of several organic fraction from the sewage sludge was performed by using the method adapted for soil by Aguilera et al. (1997), that includes the traditional alkaline soil extraction technique reported by Schnitzer (1982) to separate pure humic acids (HA) and fulvic acids (FA) and humine (Hum) present in Chilean volcanic soils. This is particularly difficult in Chilean volcanic soils because of the strong physico-chemical interactions naturally occurring between organic matter and allophanic clays.

Carbon, nitrogen, and sulfur determinations, in sewage sludge samples and organic fractions, were performed by elemental analysis using a Vario-El Elemental Analyzer calibrated accurately for these types of samples.

Data reported in tables correspond to the mean value of two independent samples whose variability between each other was less than 1%.

For discussion the C-content of each fraction, referred to 100 g of dried sewage sludge, represents the carbon balance figures in this work (Aguilera et al., 1997).

The soluble-Carbon corresponds to all organic C-compounds not included in any of the humified fraction. It is obtained by calculating:

$$\text{soluble} - \text{C} = \text{total} - \text{C} - (\text{Hum} - \text{C} + \text{HA} - \text{C} + \text{FA} - \text{C})$$

Carbon distribution is defined as the percentage of C in each fraction as compared to total-C (100%). It helps to evaluate the contribution of each form of C to the total C-pool in that fraction.

Carbohydrates (CH) contents were determined by the Cheshire method adapted to volcanic soils, according to Aguilera et al. (1987).

Total phosphorus was spectrophotometrically determined by the Dick and Tabatabai Method (1977).

All chemical analyses were made in duplicate and the results were expressed over an oven dry weight basis. Values are mean of two replicates +/- standard deviation.

Metal ions in sewage sludge and in organic raw materials were determined by Atomic Absorption Spectrometry and by inductively coupled plasma- mass spectroscopy (ICP-MS) in a Fisons VG-PlasmaQuad.

RESULTS AND DISCUSSION

Chemical compositions, expressed on dry-weight basis, for sewage sludge collected from different sources are presented in Table 1; it shows the composition of sewage sludge produced by three modern waste water treatments.

These sludges were obtaining by working under the methodology briefly informed in the preceding chapter, following strictly the quality assurance regulation to render adequate low heavy metal compositions. These plants correspond to “Los Maitenes” (V Region), “Chancón” (VI Region), and “Curicó” (VII Region). It can be seen that their compositions are quite similar and their pH is identical (6.0).Their contents for organic matter varies from 51 to 61%, or total-C from 30–35%, Nitrogen 5 to 5.9%, and phosphorus from 10,000 to 12,000 mg/Kg. The exception for this chemical composition regularity is given for carbohydrates : total contents vary from 20 mg/g for “Chancón” plant to 64 mg/g for “Los Maitenes” plant. This pattern is also followed for free carbohydrate which varies from 8 to 18 mg/g.

Table 1
Characteristics of modern plant-sewage sludge

Sewage sludge	pH	O.M. %	C %	N %	P mg/Kg	Total-CH mg/g	Sol-CH mg/g
“Los Maitenes” V region	6	60.9 ± 0.2	35.5 ± 0.2	5.85 ± 0.05	12113 ± 206	63.7 ± 5.4	18.2 ± 0.3
“Chancon” VI region	6	56.8 ± 3.4	33.5 ± 2.5	5.3 ± 0.6	10420 ± 670	19.5 ± 2.2	3.5 ± 0.7
“Curico” VII region	6	51.3	29.8	5.0	12044	49.6	7.7

O.M. = organic matter; CH = carbohydrates; sol. = water soluble.

Table 2
Carbon balance for modern plant-sewage sludge (g C/100 g dried biosolid)

Sewage sludge	Total-C	Hum-C	HA-C	FA-C	Sol-C
“Los Maitenes” V region	35.5 ± 0.2	16.4 ± 0.1	2.9 ± 0.2	3.5 ± 0.3	12.6 ± 0.7
“Chancon” VI region	33.5 ± 2.5	14.3 ± 0.6	4.4 ± 0.7	1.9 ± 0.2	12.6 ± 1.7
“Curico” VII region	29.8	12.8	0.09	3.5	13.4

Hum = inorganic residues plus humine; HA = humic fraction; FA = fulvic fraction; Sol-C. = calculated by difference total-C – (Hum-C + HA-C + FA-C)

The results obtained for sewage sludges produced in the modern plants indicate that these products have been chemically well stabilized, after the completion of the water purification processes. This agrees with previous report (Costa et al., 1995). Also, the chemical composition for C, N, P and pH found in these sewage sludge produced in Chile are quite similar to data given elsewhere for other sewage sludge (Costa et al.,1995; Borie et al., 2000).

Table 2 depicts the C-balance and Figure 1 depicts the C-distribution pattern of total-C contained in the stabilized sewage sludges. The two major fractions are Hum-C and soluble-C. “Chancon” and “Curico” sewage sludge show around 50% of their total-C as soluble-C, while Hum-C accounts for a similar level on “Los Maitenes” plant. The sum of HA-C and FA-C account for 25% of total C.

Carbon-distribution pattern is an expression of the humification grade for a given macromolecular compound produced in nature, i.e., humus, plant residues, stabilized animal manure. As the level of the higher m.w. fraction increases (humine and humic type polymers) so does the humification or stabilization grade. Therefore, given the C-distribution patterns found in this work for sewage sludge as compared to soil humus, sawdust and barkdust (Figure 2),

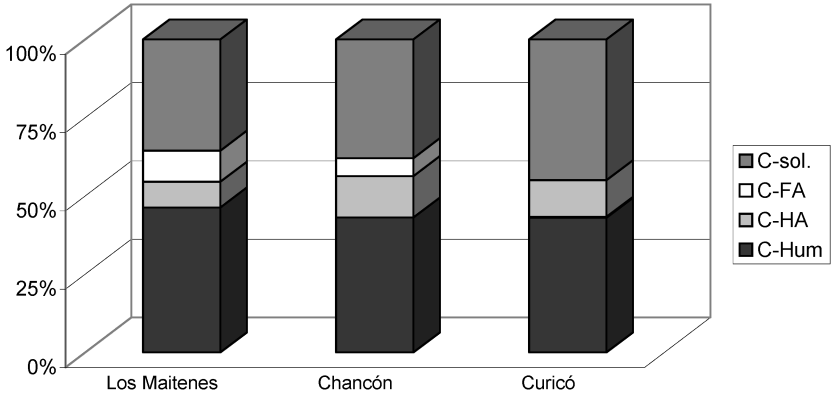

Figure 1. Carbon distribution for modern plant sewage sludge.

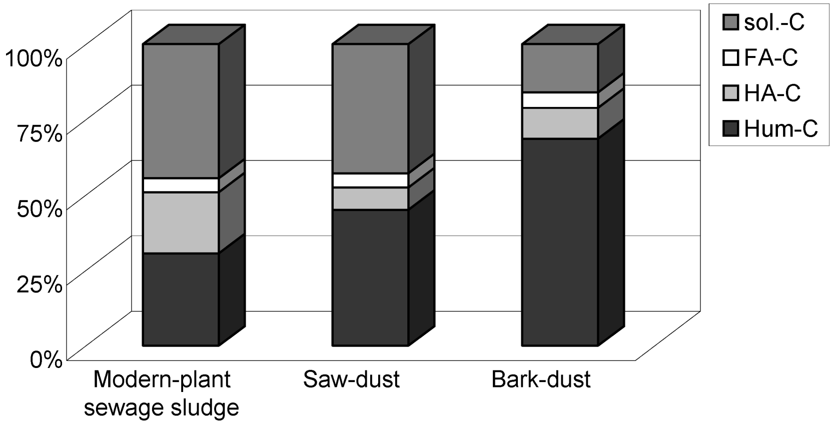

Figure 2. Carbon distribution pattern of forest residues and sewage sludge.

it can be concluded that sewage sludge are in a primary stage with high levels of soluble-C; however it is expected that after its application to soil the soluble-C fraction in the soil will diminish rapidly; thus after a certain period of time the C-distribution of the remaining sewage sludge macromolecules will follow a pattern similar to humus and other stabilized residues.

Considering the concept of soil biological availability, we can advance that these sewage sludge will enhance notably soil microbial growth, due to the easily C-availability of their C-soluble fractions. However, it can also be predicted that this microbial-welfare will last a short period of time, but enough to behave as a good starter to improve native soil microbial activity. This strongly suggests that a convenient approach to enhance soil fertility may be based on the use of mixtures of sewage sludge with other organic residues, such as common agronomic residues (straw, green manures, etc.).

The more stabilized C-fractions such as Hum-C plus HA-C and FA-C, should contribute to improve soil structure and will also serve as a frame or chemical support to essential metal ions as calcium (Ca), potassium (K), and magnesium (Mg) and microelements as copper (Cu), zinc (Zn), iron (Fe), manganese (Mn), cobalt (Co), etc.

Altogether, the three waste plant treatments considered in this work cover a territorial land area estimated to be 650,000 to 700,000 ha, which presents good geographic conditions to be forested. The total Chilean territory includes over 2 million ha of degraded soils which can be potentiality reclaimed for agronomic and forestry uses. Since the chemical methodology applied to measure the C-distribution pattern in sewage sludge has been the same as the one specially developed to study the C-status in soils, it can be concluded that all the experimental results can be rationally compared (Aguilera et al., 1992, 1997). Thus, the fate of the organic sewage-C and their edaphic effect after application

Table 3
Macro and Micro elements contents in sewage sludge VII region (mg/Kg)

Micro and macro elements	mg/Kg	Micro and macro elements	mg/Kg
Ta	0.01	As	3.67
Nb	0.03	Ga	4.48
Pd	0.05	Sc	5.42
Tm	0.09	Co	6.36
Tl	0.10	Li	6.70
Sn	0.10	Nd	6.84
Sb	0.10	Ce	12.66
Tb	0.17	Rb	18.07
Ho	0.23	Ni	39.60
Eu	0.30	Ti	41.66
Yb	0.66	Pb	50.05
Er	0.71	V	55.55
Cd	0.94	B	59.58
Bi	1.14	Cr	74.33
Gd	1.17	Sr	84.72
Zr	1.20	Ba	112.77
Dy	1.22	Cu	255.01
Ag	1.25	Mn	280.93
Sm	1.29	Zn	501.98
Th	1.46	Mg	4, 624.69
Pr	1.69	Fe	7, 752.71
Mo	2.37	Ca	13, 462.34
U	3.56		

Be, Ge, Se, Ru, Rh, Te, Hf, Re, Ir, Pt, Au, and Hgelements were under the detection limit of ICP method.

to a soil can be foreseen with a high level of certainty, which will facilitate the use of sewage sludge as forest-soil amendments.

A complete study of nutrient and contaminant elements is presented in Table 3; ultra trace elements were determined by applying ICP methodology with detection limits as low as a few part per billion. The safety of the sewage sludge mineral composition is confirmed in Table 4, wherein EPA and Chilean official limits are included for comparison. Therefore sewage sludges produced in Chile are not contaminated so far with heavy metals. This important characteristic supports the agronomic uses of such biosolids, since there is no risk of heavy metal contamination upon their field application. On the contrary, the corresponding enrichment of SOM will strong the capabilities of the soil forest under treatment to absorb and/or inactivate any heavy metal pollution event, derived from some industrial process which may eventually occur in the future.

The relationships between natural soil organic matter and micronutrient availability in soils has been thoroughly studied in soil science from the very

Table 4
Comparison of stabilized sewage sludge with Chilean and EPA norms in relation to heavy metal contents (mg/kg)

	Sewage sludge	Chilean norm	EPA norm
As	4	40	—
Cd	1	40	85
Cr	74	1200	3000
Cu	255	1500	4300
Hg	n.d.	20	57
Mn	281	—	—
Mo	237	20	
Ni	40	420	420
Pb	50	400	840
Se	n.d.	40	—
Zn	502	2800	7500

beginning. As far as the knowledge of chemical composition, structure, biological origin and fate of soil humus increased, it became evident that metal complexes or chelate-like structures represent the most important source of microelements in any edaphic system. Thus, concentrated efforts were dedicated early during a long time to measure the so-called “stability constants” of such type of metal—macromolecule structures occurring in soils by applying an ion-exchange method (Schnitzer, 1982). However, some severe chemical argument practically ended up with such type or works, demonstrating that the widespread use of that method was not applicable to such high molecular weight and polyfunctional metal-organic associated compounds.

New theoretical and laboratory methodologies were developed later, allowing new focus and experimental approaches onto this subject (Aguilera et al., 1997; Zunino et al., 1979, Zunino, 1979; Heredia et al., 2002). This stimulated the development of computational methods to appraise multiple and simultaneous interactions to study speciation of metal ions in soils and waters among metal ions and polyfunctional organic macromolecules, widely used up to the present (Sposito, 1980; 1989; Chang, 1984; Ahumada, 2004).All these methods can be also advantageously applied to the study of sewage-sludge/microelements behavior and the amelioration of some eventual heavy-metal pollution which may occur in these soils as the consequence of industrial activities.

The similarity between biosolids and humus in relation to their chemical composition, C-distribution, and C-balance reported in this work, besides the well known equivalence of their IR spectra, open an interesting opportunity to investigate deeper their potential use as micronutrient-carriers to be applied agronomically for correcting several micronutrient deficiencies occurring in several soils with a number of industrial crops. The low level of harmful heavy metal found for this type of sewage sludge (Tables 3 and 4) constitutes another good characteristic, which encourages their use both as soil amendment and as essential micronutrient sources.

ACKNOWLEDGMENTS

Financial support was received from FONDEF, Project N° D01I1034.

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