

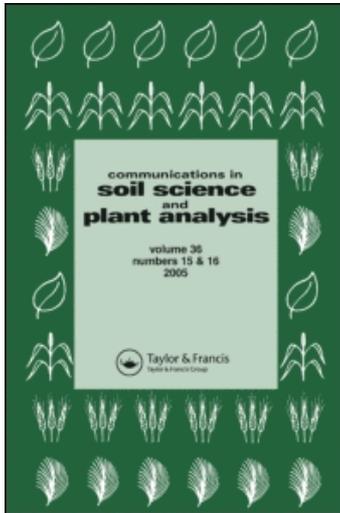
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Speciation of Aluminum in Solution of an Acidic Sandy Soil Amended with Organic Composts

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Abstract: The effects of organic amendments (10 and 50 g/kg soil of yard waste, yard + municipal waste, GreenEdge, and synthetic humic acid) on soil chemical properties related to aluminum (Al) phytotoxicity and nutrient availability were evaluated. Compost amendment increased Mehlich 3–extractable calcium (Ca), magnesium (Mg), phosphorus (P), and potassium (K) in the soil by 3.5–260 times. No significant effect of composts on total Al in solution was observed. Organic amendments increased solution pH and decreased the activities of phytotoxic Al species to less than the critical levels, as a result of the formation of aluminate and humic acid–Al complexes. Low-molecular-weight organic acids were not effective in forming complexes with Al. Application of composts increased the concentrations of most nutrients in soil solution, suggesting a potential for ameliorating subsoil, but care must be taken to avoid nitrogen (N) and P leaching. Amending composts to acidic soils appears a useful strategy for diminishing Al phytotoxicity potential and improving soil fertility.

Keywords: Aluminum speciation, leaching, organic amendment, soil solution

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INTRODUCTION

Soil solution speciation can provide information on species distribution of nutrients and contaminants and therefore can facilitate a greater understanding of their availability and toxicity to plants (Wolt 1994). Specifically for aluminum (Al), the solution speciation is closely related to its potential of risk because each chemical species of Al has different biotoxicity and bioavailability (Kinraide 1991, 1997; Sposito 1995).

Aluminum phytotoxicity is one of the important soil constraints that limit crop yields in acidic soil regions. Its toxicity can be alleviated by use of lime or organic amendments though the mechanisms of Al alleviation by organic amendments are not well understood (Kinraide 1997; Franchini et al. 1999; Haynes and Mokolobate 2001). Composts, an important source of organic amendments, have been widely used to improve physical, chemical, and biological properties of soils (He et al. 2000; Zhang et al. 2006; Weindorf, Zartman, and Allen 2006) and may be useful for alleviating Al toxicity in acidic soils because of the increase in soil pH, nutrient availability, and formation of Al–organic complexes (Haynes and Mokolobate 2001; Murhizal et al. 2003).

Composts contain humic substances and low-molecular-weight organic acids (LMWOA) that can form stable complexes with Al and other elements (Hue, Craddock, and Adams 1986; Gerke 1994; Hiradate and Yamaguchi 2003). The LMWOA in composts can be derived from cell lysis and microbial activity excretion during decomposition (Jones et al. 2003), and usually their concentrations decrease with the compost age (Ozores-Hampton et al. 2002). The LMWOA compounds can play an important role in the improvement of soil surface and subsurface concerning the alleviation of Al phytotoxicity, but it can also promote vertical movement of cations and heavy metals. The vertical movement of calcium (Ca)– and magnesium (Mg)–LMWOA complexes is important to improve the conditions of the soil subsurface after a surface liming without incorporation (Franchini et al. 1999), and the vertical movement of Al and heavy metals can be dangerous as they may contaminate groundwater (Cielinski et al. 1998).

The main purposes of this study were to evaluate the effects of organic amendments on soil chemical properties related to Al phytotoxicity and nutrient availability and to verify their effects on Al speciation in soil solution.

MATERIALS AND METHODS

The soil used for this study was an acidic sandy soil (ortestein Arenic Ultic Alaquods; Soil Survey Staff 2006) collected at 0–20 cm deep on the

experimental farm of the Indian River Research and Education Center (IRREC-IFAS-UF), Fort Pierce, FL. The soil was air dried, homogenized, and sieved (<2 mm) prior to the analyses. The soil was composed of 968, 25, and 7 g kg⁻¹ of sand, silt, and clay, respectively.

The soil was incubated with four sources of organic matter: (1) yard waste compost (Y), (2) cocompost of yard + municipal waste (YM), (3) pelletized biosolids (GreenEdge, Green Technologies, Inc., Vancouver, Canada), and (4) synthetic humic acid (HA). The Y and YM were collected from a composting facility in West Palm Beach, FL, in September 2005, air-dried, and ground (<2-mm sieved). GreenEdge was a pelletized compost derived from municipal biosolids and enriched with fertilizers to obtain 6% N (1.5% water-soluble N), 3% P₂O₅, 3% Ca, and 1% Fe. Synthetic HA was obtained from ICN Biomedicals, Inc, Costa Mesa, Calif.

Each amendment was incubated with the soil at two rates: 10 and 50 g kg⁻¹ soil (1% and 5%, respectively). The mixtures of soil plus organic amendments (1.5 kg) were incubated in closed plastic bags, where gravimetric humidity was adjusted and maintained in 100 g kg⁻¹, equivalent to 70% of the field capacity, at room temperature (22 °C), during the incubation period of 30 days. The bags were opened for about 2 h once every 4 days to oxygenate. There were three replicates of each treatment, arranged in a complete randomized design.

At the end of incubation, subsamples of the soils were taken and analyzed for pH (H₂O, 2:1 water–solid ratio) and electrical conductivity (EC) using an Orion pH-conductivity meter and for total organic carbon (TOC) and total nitrogen (TN) using a CN Analyzer (Vario Max, Elementar, Edison, N.J.). Concomitantly, soil samples were submitted to Mehlich 3 extraction and analyzed for Al, Ca, Mg, potassium (K), phosphorus (P), and sodium (Na) concentrations using inductively coupled plasma atomic emission spectrometry (ICP-AES; Ultima JY Horiba, Edison, N.J.). Some characteristics of the soil and pure composts are published elsewhere (Vieira et al. 2006).

After incubation, the mixtures were used for a column leaching study. Columns of polyethylene measuring 30 cm high and 7 cm in diameter were filled with 1.1 kg of the mixture (about 1 kg of dry weight). Whatman no. 42 filter paper was placed at the bottom of each column to prevent soil particle loss. Columns were saturated with deionized water by capillarity and maintained at this humidity for 24 h. After this period, 150 mL of deionized water were added to each column using a peristaltic pump at a rate of 100 mL h⁻¹. The leachate was collected by free drainage into a plastic bottle, and the leachate samples were immediately analyzed for pH and electric conductivity (EC). Subsamples of the leachate were filtered through a 0.2- μ m membrane and immediately analyzed for LMWOA using a high-pressure liquid chromatograph (HPLC; Waters

2695, Milford, Mass.), equipped with two Waters C18 columns (25 cm long) in series and a Waters 996 photodiode array detector, with the following chromatographic conditions: phosphoric acid 0.2% (v/v) at pH 2.3 as mobile phase; column temperature of 30 °C; diode array detector quantification in $\lambda = 210$ nm, with identification wavelength scans from 200 to 300 nm; injection volume of 50 μ L; and flow rate of 0.6 mL min⁻¹. The evaluated LMWOA included oxalate, malate, tartrate, acetate, citrate, fumarate, succinate, and propionate. Organic acids were identified by comparing retention times of standard organic acid samples, and the comparison of peak areas with an external standard curve was used to quantify them.

The leachate samples were also determined for the concentration of Al, Ca, Mg, K, P, Na, and silica (Si) using the ICP-AES and fluoride (F), chloride (Cl), bromide (Br), nitrate (NO₃)-N, phosphate (PO₄)-P, and sulfate (SO₄)-S using an ionic chromatograph (DX 500; Dionex Corporation Sunnyvale, Calif.). Ammonium was determined using an N/P discrete autoanalyzer (EasyChem, Syntex Scientific, Italy), and dissolved organic carbon (DOC) was determined using a TOC/TN analyzer (Dohrmann model DC 190, Rosemont Analytical Inc., Santa Clara, Calif.). The results obtained from the solution were used to estimate chemical speciation using the chemical equilibrium model Visual MINTEQ, version 2.40 (Gustafsson 2006). The difference between the DOC concentration in solution of HA-amended soil and the DOC in solution from nonamended soil was considered to be the carbon (C) present as HA in solution, which was used for speciation of solution from HA-amended soil. Therefore, in solution of HA-amended soils, the data of C for speciation was the same DOC concentration of the solution from control soil plus the estimated concentration of HA.

Results of soil and solution were statistically analyzed by one-way analysis of variance (ANOVA) with three replicates, using SAS version 8.02 (Statistical Analysis System Institute, Cary, N.C.). Difference between means was evaluated by Duncan multiple range test ($P < 0.05$). ANOVA for LMWOA concentrations was not performed because of the high number of samples below the detection limit. Relation between soil and solution pH was evaluated by means of determination coefficient (r^2).

RESULTS AND DISCUSSION

Soil Incubation Study

The application of composts promoted a significant increase in values of soil pH, EC, and TOC, with the greatest rate of amendment (5%)

resulting in the greatest values (Table 1). The increase in pH was mainly due to the low buffering capacity of the soil and the high pH of the composts, in addition to the high buffering capacity of the composts. The greatest values of pH and EC occurred in soils amended with HA and G, whereas Y and YM promoted a moderate effect. However, amendment with only 1% of Y and YM was enough to increase soil pH to 5.22 and 5.74, respectively. To a lesser extent, the amendments increased also the TN in the soil. The greatest increase in TN occurred in G-amended soil, which is a result of its enrichment with fertilizers in the manufacturing process, whereas the other composts had smaller increases in TN concentrations in soil.

The amendment with organic composts to the soil significantly affected the content of Mehlich 3-extractable Al and nutrients (Table 2). Aluminum concentration ranged from 7.2 mg kg^{-1} in Y-amended soil at 5% to 109.1 mg kg^{-1} in G-amended soil at 5%. Apart from G, the greater level of amendments (5%) contributed to the decrease in Mehlich 3-extractable Al as compared with the lesser rate (1%) of amendment, suggesting the formation of stable organo-Al complexes, which were not extractable by the Mehlich 3 solution.

The soil amended with G at 5% had the greatest concentrations of Ca, Mg, and P, as expected, because this compost is enriched with lime and nutrients in its manufacturing process. Although the other composts are not enriched with fertilizers, each contributed greatly to the increase in nutrients (Ca, Mg, K, and P) extractable by Mehlich 3, highlighting the potential benefits of the amendments in improving nutrient availability to the crops. Calcium contents increased, at average, about 3.5 times for soils amended with 1% of composts and 8 times for soils that received

Table 1. Soil chemical properties as affected by soil amendments

Treatments ^a	pH-H ₂ O	EC ^b ($\mu\text{S cm}^{-1}$)	TOC (g kg^{-1})	TN (g kg^{-1})
1. Soil (control)	4.42 h ³	17.02 d	5.95 d	0.24 c
2. Soil + Y 1%	5.22 g	113.47 d	9.76 c	0.35 c
3. Soil + Y 5%	6.69 e	492.23 c	25.01 a	0.82 bc
4. Soil + YM 1%	5.74 f	138.67 d	9.28 c	0.43 c
5. Soil + YM 5%	6.63 e	487.87 c	22.61 a	1.19 b
6. Soil + G 1%	7.03 d	934.73 b	8.19 cd	0.89 bc
7. Soil + G 5%	8.23 b	2631.33 a	17.13 b	3.51 a
8. Soil + HA 1%	7.62 c	778.33 bc	9.49 c	0.34 c
9. Soil + HA 5%	9.13 a	2497.00 a	23.66 a	0.75 bc

^aY, yard waste; YM, cocompost of yard waste and municipal waste; G, GreenEdge pelletized biosolids; and HA, humic acids.

^bEC, electrical conductivity; TOC, total organic carbon; TN, total nitrogen.

Note. Means followed by the same letter in the column do not differ by the Duncan multiple range test at the 5% significance level.

Table 2. Mehlich 3–extractable aluminum and nutrients in a sandy soil amended with organic composts

Treatments ^a	Al (mg kg ⁻¹)	Ca (mg kg ⁻¹)	Mg (mg kg ⁻¹)	K (mg kg ⁻¹)	P (mg kg ⁻¹)	Na (mg kg ⁻¹)
1. Soil (control)	73.7 bc ²	161.3 h	18.4 g	9.7 f	5.88 g	90.9 e
2. Soil + Y 1%	84.5 ab	606.4 e	52.4 f	136.0 e	46.42 f	138.5 cd
3. Soil + Y 5%	7.2 e	930.7 c	168.9 d	601.6 d	172.95 d	244.0 a
4. Soil + YM 1%	80.6 ab	776.8 d	67.9 f	141.1 e	121.38 e	86.1 e
5. Soil + YM 5%	18.1 de	1776.6 b	237.1 c	633.6 d	481.20 b	194.5 b
6. Soil + G 1%	59.3 bc	612.5 e	123.4 e	156.9 e	234.61 c	15.5 f
7. Soil + G 5%	109.1 a	2043.0 a	474.9 a	733.7 c	938.63 a	253.8 a
8. Soil + HA 1%	84.7 ab	327.7 g	120.9 e	2071.3 b	8.58 g	105.9 de
9. Soil + HA 5%	45.2 cd	481.7 f	363.5 b	8049.3 a	5.59 g	169.1 bc

^aY, yard waste; YM, cocompost of yard waste and municipal waste; G, GreenEdge pelletized biosolids; and HA, humic acids.

^bMeans followed by the same letter in the column do not differ by the Duncan multiple range test at 5% significance level.

5%. For the other elements, the increase was even larger. For 1% and 5% of amendment, respectively, concentrations increased about 5 and 17 times for Mg, 17 and 68 times for P, and 65 and 260 times for K. The concentrations obtained for these nutrients in amended soils were greater than the minimum levels indicated for supplying the general crop requirements (Miranda et al. 2002; Sawyer et al. 2002).

Column Leaching Study

Similar to the results from the incubation study, results showed that the organic amendments significantly increased pH values of the soil solution, which ranged from 4.14 in control soil to 8.41 in HA-amended soil (Table 3). The amendment with compost at the 5% level promoted a larger increase in pH than 1%. However, the presence of 1% compost was sufficient to raise the solution pH to 5.95 or more, a value that is supposed to eliminate the toxicity of Al^{+3} to roots (Wolt 1994; Sposito 1995). The pH in solution had a close relationship with the pH of soil solid phase ($r^2 = 0.83$, $P < 0.001$, Figure 1).

The addition of Y, YM, and G to the soils did not significantly affect Al in solution. However, the content of Al in solution is not a reliable and adequate indicator of Al availability and toxicity to plants, as this metal can be present in solution as free species, hydroxy monomers and polymers, ionic pair, and complexes, and each species has its own potential phytotoxicity (Kinraide 1991, 1997; Sposito 1995). Organic or inorganic ligands can form complexes with Al, releasing it from the solid phase and elevating its concentration in solution, which makes the Al chemistry in soil solution–solid phase very complex (Wolt 1994; Li et al. 2006). Among the complexes between Al and ligands, some are soluble and raise the total Al concentration in solution, whereas others diminish the concentration, depending on the tendency of the complex to precipitate or to stay in solution. According to McBride (1994), ligands such as fluoride, oxalate, citrate, fulvate, and monomeric silicate tend to increase Al solubility, whereas phosphate, sulfate, polymeric silicate, and hydroxyl usually decrease Al solubility. It is probable that the greatest Al concentration in solutions of HA-amended soil was due to the presence of dissolved HA-Al complexes, as HA has great solubility in alkaline pH. It is worth noting that solution samples were filtered to 0.45 μm , which may have held most particulates in suspension. Nevertheless, according to Bloom and Erich (1996), the Al as polymers and colloid-adsorbed forms can have diameters ranging from 1 to 100 nm, which includes the Al complexed to HA, whereas most of the complexes between Al and inorganic ligands or low-molecular-weight organic ligands have diameters smaller than 1 nm. In the present study, Al in leachate did not have any relation with Al extractable by Mehlich 3.

Table 3. Chemical properties of leachate from soils amended with different organic materials

Treatments ^a	pH	Ionic strength	Metals (mmol L ⁻¹)					DOC	NH ₄	Inorganic ligands (mmol L ⁻¹)						
			Al	Ca	Mg	K	Na			Si	Br	NO ₃ -N	PO ₄ -P	SO ₄ -S	F	Cl
		mol L ⁻¹														
1. Soil (Control)	4.14 e ²	0.0094 cd	0.020 b	1.631 d	0.737 d	0.162 d	0.296 e	0.224 cd	20.312 b	0.047 c	0.000 c	0.848 b	0.044 d	0.056 b	0.005 b	0.380 c
2. Soil + Y 1%	6.21 cd	0.0134 cd	0.008 b	0.905 de	0.404 de	2.981 cd	2.448 de	0.206 d	66.536 b	0.000 c	0.000 c	0.004 b	0.141 bc	0.208 b	0.002 b	10.563 c
3. Soil + Y 5%	7.24 b	0.0362 b	0.021 b	3.042 c	1.277 c	10.351 abc	7.871 ab	0.274 bcd	153.279 b	0.001 c	0.000 c	0.001 b	0.106 c	0.346 b	0.002 b	9.103 c
4. Soil + YM 1%	5.95 d	0.0252 bc	0.015 b	3.173 bc	1.270 c	4.090 cd	3.618 d	0.360 abc	74.843 b	0.007 c	0.001 c	1.458 b	0.238 a	0.563 b	0.002 b	4.708 c
5. Soil + YM 5%	7.31 b	0.0408 b	0.028 b	3.969 b	1.865 b	11.866 ab	10.223 a	0.405 ab	193.590 b	0.044 c	0.011 bc	0.753 b	0.197 ab	1.275 b	0.020 b	16.546 c
6. Soil + G 1%	6.99 bc	0.1034 a	0.030 b	5.584 a	3.755 a	10.083 abc	4.908 cd	0.500 a	477.101 ab	53.037 b	0.039 ab	65.753 a	0.169 b	12.397 a	0.147 ab	64.834 b
7. Soil + G 5%	7.46 b	0.1163 a	0.038 b	5.212 a	3.881 a	16.024 a	6.932 bc	0.401 ab	791.881 a	70.824 a	0.056 a	58.000 a	0.100 c	17.327 a	0.196 a	154.487 a
8. Soil + HA 1%	7.21 b	0.0086 cd	0.455 a	0.874 de	0.392 de	6.879 bcd	0.389 e	0.046 e	464.083 ab	0.085 c	0.000 c	0.161 b	0.002 d	0.209 b	0.075 ab	0.065 c
9. Soil + HA 5%	8.41 a	0.0040 d	0.173 b	0.457 e	0.234 e	3.483 cd	0.152 e	0.007 e	222.254 b	0.007 c	0.000 c	0.002 b	0.002 d	0.076 b	0.002 b	0.010 c

^aY, yard waste; YM, cocompost of yard waste and municipal waste; G, GreenEdge pelletized biosolids; and HA, humic acids.

Note. Means followed by the same letter in the column do not differ by the Duncan multiple range test at the 5% significance level.

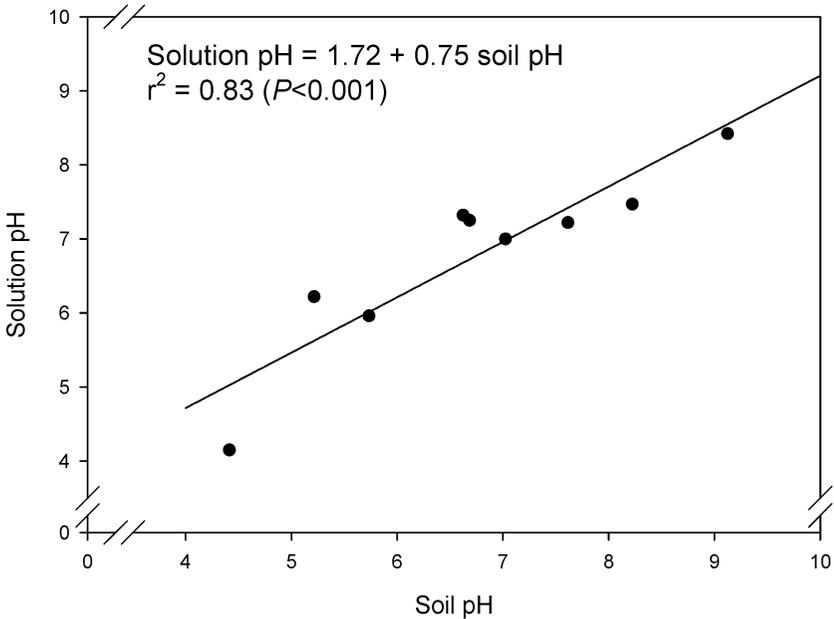


Figure 1. Relationship between soil pH and leachate pH in an acidic sandy soil amended with various organic materials.

With the exception of HA, the amendments significantly raised the ionic strength (I) in solution (Table 3). Amendment with G promoted the highest I values, imparted by the dissolution of lime and NPK fertilizers from this compost. The decrease of I in solution of HA-amended soils may be due to the adsorption of elements in the exchangeable sites of the HA, diminishing the concentration of “free” salts in solution. Indeed, for most of the analyzed nutrients, HA-amended soils had the weakest concentrations. Oppositely, amendments with Y, YM, and G significantly increased the concentration of most of the nutrients in soil solution, which means a great benefit to plant growth from this practice of amending soils with composts. In addition to the improvement in nutrient availability to plants, the greater nutrient concentrations in solution indicate a large potential for ameliorating chemical conditions also in the subsoil level, even without incorporating the composts in the soil after their application, as a result of the leaching of basic cations and nutrients in general through the soil profile. According to the results, the leachate from the amended soils with Y, YM, and G would increase Ca, Mg, K, P, S, and DOC contents in subsoil, accompanying the vertical movement of the leachate, whereas it would not significantly increase Al content, improving subsoil chemical conditions in general and aiding its exploitation by roots.

Although the composts promoted significant increase in the concentrations of most nutrients in solution (Table 3), these increases were smaller than those for Mehlich 3-extractable nutrients (Table 2). This indicates that the amendments provide an important reserve for buffering the nutrients in solution, avoiding their depletion and improving nutrient uptake by roots. However, special attention to N is needed when composts with high C-N ratio are applied to the soil. Amendment with Y clearly promoted depletion of mineral N in solution because of the microbial immobilization, requiring a greater quantity of N fertilizer to supply a possible crop demand. On the other hand, soil amended with G had concentrations of NO_3 and PO_4 in the leaching solution greater than the thresholds advised for avoiding environmental problems. Although threshold values for $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ are, respectively, 10 mg L^{-1} (L'Hirondel and L'Hirondel 2002) and 0.1 mg L^{-1} (Sharpley et al. 1996) to avoid eutrophication and allow the water to be potable, the lowest rate of amendment with G (1%) was enough to raise the concentrations to $812 \text{ mg NO}_3\text{-N L}^{-1}$ and $5.24 \text{ mg PO}_4\text{-P L}^{-1}$. Amendment with YM also promoted strong concentrations of P in solution. This stresses the importance in adjusting the rates and frequency of application of such compost, especially in sandy soils with low cation and anion exchange capacity as the soil used in the present study to decrease the risks to the environment.

The organic amendments increased the content of DOC, although statistically the soils amended with Y and YM did not differ from the control. The greatest values occurred in solution from soils amended with G and HA. In the columns containing soil + HA 5%, however, the flow of leachate through the column was hampered by the strong concentration of HA, reducing the volume of leachate obtained (about 50% of the average collected volume), which could explain the greater DOC content in solutions from HA 1%-amended soil than from HA 5%-amended soil. Apart from the soil + HA 5% treatment, a very similar volume of leachate was collected in all other treatments.

The amendments promoted different kinds and concentrations of LMWOA (Table 4). Concentrations ranged from less than the detection limit to about $264 \mu\text{mol L}^{-1}$. The LMWOA were not detected in HA-amended and in nonamended soil. The found organic acids possibly came with the composts or originated from bacterial activity during the 30 days of incubation. The soil amended with G had the strongest concentrations of LMWOA, and the same species of organic acids detected in the rate of amendment of 1% were found in higher concentration in the 5% amended. Malic and acetic acid were detected in Y and YM in the 5%-amended soils, but their concentrations were less than the detection limit in the lowest rate of amendment. It is probable that concentrations in general were a lot stronger in the beginning of the incubation, as

Table 4. Concentration of low-molecular-weight organic acids in leachate of a sandy soil amended with various organic materials

Treatments ^a	Tartaric ($\mu\text{mol L}^{-1}$)	Malic ($\mu\text{mol L}^{-1}$)	Acetic ($\mu\text{mol L}^{-1}$)	Citric ($\mu\text{mol L}^{-1}$)	Fumaric ($\mu\text{mol L}^{-1}$)	Propionic ($\mu\text{mol L}^{-1}$)
1. Soil (control)	bdl ^b	bdl	bdl	bdl	bdl	bdl
2. Soil + Y 1%	1.5	bdl	bdl	bdl	bdl	bdl
3. Soil + Y 5%	12.8	9.5	12.7	bdl	bdl	4.0
4. Soil + YM 1%	2.6	bdl	bdl	bdl	bdl	bdl
5. Soil + YM 5%	bdl	25.4	25.2	bdl	bdl	bdl
6. Soil + G 1%	bdl	bdl	138.9	33.0	6.0	29.2
7. Soil + G 5%	bdl	bdl	198.5	56.7	11.4	264.4
8. Soil + HA 1%	bdl	bdl	bdl	bdl	bdl	bdl
9. Soil + HA 5%	bdl	bdl	bdl	bdl	bdl	bdl
Detection limit (μM)	0.50	1.15	3.50	0.60	0.01	3.00

^aY, yard waste; YM, cocompost of yard waste and municipal waste; G, GreenEdge pelletized biosolids; and HA, humic acids.

^bbdl, below detection limit.

LMWOA can have a very rapid decomposition (Jones et al. 2003). The room temperature of 22 °C in which the incubation was performed is suitable to a myriad of microorganisms and probably facilitated the LMWOA decomposition in this study, making the detection of LMWOA difficult in solution from nonamended soil in this study. Typical concentrations of LMWOA in soil solution are usually in the range 0–50 μM, with the greatest concentrations usually occurring in soil solutions from temperate forested areas and pastures (Strobel, 2001).

Aluminum Speciation in Solution

The soil solution speciation was performed using the data from Tables 3 and 4, and the results for Al are depicted in Table 5. In comparison to the control, which had Al^{+3} activity $\{\text{Al}^{+3}\}$ of 2.98×10^{-6} , all the amendments decreased the $\{\text{Al}^{+3}\}$ in rates from 125 times (2.39×10^{-8} in soil amended with YM 1%) to more than one billion times (2.70×10^{-15} in soil amended with HA 5%) smaller than the $\{\text{Al}^{+3}\}$ in control. The decrease was mostly due to the raised pH and, to a lesser extent, to the formation of Al–organic complexes. Some threshold values of $\{\text{Al}^{+3}\}$ found in literature, linked to a decrease of 10% in root elongation, are 1.5×10^{-6} for cotton (Adams and Lund 1966), 9×10^{-6} for some gramineous species (Brenes and Pearson 1973), 4×10^{-6} for coffee seedlings (Pavan, Bingham, and Pratt 1982), 4×10^{-6} for soybean (Bruce et al. 1988), and 3.5×10^{-7} for mungbean (Murhizal et al. 2003). Taking into account these values, all the amendments were effective in reducing Al^{+3} activity far below the critical levels, while the control soil had active $\{\text{Al}^{+3}\}$ of 2.98×10^{-6} , which indicates that the $\{\text{Al}^{+3}\}$ might be toxic to the Al-sensitive species. Murhizal et al. (2003) also reported a decrease in the activities of Al^{+3} and monomeric Al due to amendment of five different composts, in addition to an increase in pH of the solution. However, the authors verified a decrease in total Al in solution after amending the soil, whereas in the present study this was not found.

For most of the amended treatments of the present study, the predominant Al species was the $\text{Al}(\text{OH})_4^-$ (aluminate ion), which accounted for approximately 90% of the total Al in solution for treatments where pH was great than 7.0, suggesting that in these alkaline solutions the Al preferred to form aluminate ion instead of Al–organic complexes. One exception is the soil amended with HA where, in spite of the high pH, a big portion of the Al was bounded to DOC. As mentioned in the material and methods section, the only treatment that had HA concentration in the input data for speciation was the solution from HA-amended soil, as HA contents were not determined analytically. The presence of aluminate ions in solutions with high pH has been shown in

Table 5. Activity of Al⁺³ and percentage distribution among Al species in leachate of a sandy soil amended with various organic materials

Treatments ^a	Concent. Al (mM)	Ativ. Al ⁺³ (%)	Al ⁺³ (%)	Al-DOC (%)	Al(OH) ₄ ⁻ (%)	Al-F (%)	Al-hydroxides (%)	Al-HPO ₄ (%)	AlSO ₄ ⁺ (%)	Al-Si (%)	Al-acet (%)	Al-cit (%)
1. Soil (control)	0.0201	2.98×10^{-06}	36.63	33.44	<0.01	22.22	0.52	3.81	3.32	<0.01	<0.01	<0.01
2. Soil + Y 1%	0.0081	8.58×10^{-09}	0.30	6.47	8.21	3.16	2.76	53.77	0.10	0.24	<0.01	<0.01
3. Soil + Y 5%	0.0213	1.76×10^{-11}	<0.01	<0.01	89.59	<0.01	10.28	0.10	<0.01	<0.01	0.01	<0.01
4. Soil + YM 1%	0.0148	2.39×10^{-08}	0.64	4.09	1.19	4.84	12.57	75.96	0.31	0.40	<0.01	<0.01
5. Soil + YM 5%	0.0283	1.24×10^{-11}	<0.01	<0.01	91.16	0.07	8.64	0.10	<0.01	<0.01	0.02	<0.01
6. Soil + G 1%	0.0300	1.36×10^{-10}	<0.01	0.07	52.41	34.45	11.27	0.69	0.01	0.03	0.42	0.65
7. Soil + G 5%	0.0379	3.97×10^{-12}	<0.01	<0.01	91.84	2.58	5.48	0.01	<0.01	<0.01	0.04	0.03
8. Soil + HA 1%	0.4552	1.80×10^{-11}	<0.01	96.45	3.01	0.14	0.40	<0.01	<0.01	<0.01	<0.01	<0.01
9. Soil + HA 5%	0.1733	2.70×10^{-15}	<0.01	26.68	72.78	<0.01	0.54	<0.01	<0.01	<0.01	<0.01	<0.01

^aY, yard waste; YM, cocompost of yard waste and municipal waste; G, GreenEdge pelletized biosolids; and HA, humic acids.

studies employing the technique of ^{27}Al NMR. Howe et al. (1997) reported the formation of aluminate in pH 9.0, accompanying the disappearance of the other peaks. Hundt and O'Melia (1988) observed a peak due to $\text{Al}(\text{OH})_4^-$ species in pH > 8.0, suggesting that $\text{Al}(\text{OH})_3$, as precipitated or insoluble complexes, had redissolved in high pH. The $\text{Al}(\text{OH})_4^-$ was formerly considered as a potentially phytotoxic Al species in an alkaline environment (Foy 1984). Later, Kinraide (1990) postulated that the toxicity was not attributable to the aluminate but to the Al_{13} formed in the acidic free space in the roots. In the experiments of Ma, Rengasamy, and Rathjen (2003), though, they demonstrated that Al present in soil solution as free anionic species in pH > 9.0 was toxic to wheat roots, even at concentrations as weak as 1 mg Al L^{-1} . The authors hypothesized that this free anionic species is probably the aluminate ion, but this has not been proved. In the present study, except for the HA-amended soils, the total Al concentration in leachate was usually near or less than 1 mg L^{-1} , with the soil amended with G 5% accounting for the greatest concentration of Al in solution as aluminate, corresponding to 0.035 mM or 0.95 mg L^{-1} .

Apart from aluminate or organically bounded, the other Al species were scarce. The mononuclear hydroxoaluminum (Al-OH_x) species had about 8.5% of presence, on average, for soil amended with Y, YM, and G. Mononuclear fluoroaluminum and Al bounded to phosphate were also representative in some cases. According to Kinraide (1997) and Stevens et al. (1997), high activity of Al-F species, mainly AlF^{2+} and AlF_2^+ , has a strong possibility of being toxic to roots.

The Al species linked to LMWOA were also rare, in spite of the elevated constants of these complexes. This result can be due to the low molar ratio of LMWOA-Al, in addition to the high pH of the solutions. These acids usually have a huge spatial and time variation in soil and can be strongly adsorbed on exchange sites (Jones et al. 2003); that summed to the possible decomposition during the incubation time can explain their relatively low concentrations in solution and their low participation in the Al speciation. According to the results of the speciation, except for citric acid, the organic acids had on average about 85% of the total concentration presented as dissociated form (data not shown), which is due to the effect of the high pH in their speciation.

To estimate what would possibly happen with the distribution and activities of the Al species if the obtained leachate reached deeper acidic subsoil layers, where the pH of solution could decrease to acidic values to equilibrate with the pH of the subsoil, we simulated the speciation using the same data of Tables 3 and 4, except the pH values, which were substituted by 4.5 for all treatments. The activity of amended soils, with exception of HA-amended soil, ranged from 1.31×10^{-7} for soil + Y 1% to 7.18×10^{-10} for soil + G 5% (data not shown), suggesting that Al

toxicity would not be a serious constraint to root growth in the subsoil. The relatively low Al activity is mainly due to the formation of complexes with DOC and fluorine, in addition to the increase in ionic strength.

CONCLUSIONS

The practice of amending composts to the soil improved the chemical characteristics related to alleviation of Al toxicity and nutrient availability after a short period of incubation. The composts increased soil pH and nutrients in both soil solution and on exchange sites of solid phase. Amended composts decreased the activity of the toxic Al species in soil solution to far less than the threshold values for plant growth found in the literature.

Future studies must deal with the dynamic of the compost mineralization and the acidification process in soils amended with these composts for a longer term to observe the possible implications of such processes in acidic soil management and its potential risk to the environment.

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