Long-Term Impacts of Wastewater Irrigation on Cuban Soils

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The disposal of wastewater, known as vinasse, from the sugarcane (*Saccharum officinarum* L.) industry creates environmental problems. Agriculture can offer a potential solution to these problems by using organic residues as substitutes for chemical fertilizers. This study was conducted in Ultisol profiles from Cuba irrigated with vinasse for 40 yr. The effects of this application on physicochemical and mineralogical properties of soils were investigated. Soils fertilized with traditional inorganic fertilizers were used for comparison. Fertilization with the wastewater caused a decrease of soil pH to a depth of 100 cm. There was an increase, however, in electrical conductivity because of the large concentration of K in the wastewater. The amendment also increased the organic matter content throughout the profile. Vinasse application yielded the intercalation of some compounds in the clay mineral smectite. The formation of organo-mineral complexes produced little change in the particle size distribution, but an increase in the poorly crystalline Fe oxyhydroxides in the upper horizon up to 22%, and the crystallinity of Fe oxyhydroxide in the soil decreased substantially. This was probably due to dissolution and reprecipitation of these oxides by the acid pH of the wastewater. Total and poorly crystalline Mn contents also decreased. The amendment material increased the mobility of metals because of the formation of water-soluble complexes with organic ligands. The results showed that long-term wastewater irrigation could be of agricultural interest due mainly to its organic matter concentration, but micronutrient concentrations in the upper horizons were negatively affected because complexing of metals favored their transport throughout the soil profile, which may eventually lead to deterioration of groundwater quality and micronutrient deficiency.

Abbreviations: DCB, dithionite–citrate–bicarbonate; EC, electrical conductivity; Fe_d, iron oxides extracted by dithionite–citrate–bicarbonate; Fe_o, iron oxides extracted by oxalate–oxalic acid in the dark; Mn_d, manganese oxides extracted by dithionite–citrate–bicarbonate; Mn_o, manganese oxides extracted by oxalate–oxalic acid in the dark; OM, organic matter; XRD, x-ray diffraction.

In areas with extensive production of sugarcane, disposal of the residues from manufacturing plants of this agricultural product represent a major concern (Cruz et al., 1991; Gloeden et al., 1991). Production of sugar and its derivatives is the primary industry of Cuba. These factories yield great quantities of effluents that are discharged untreated into the sea and can cause environmental problems. This agroindustrial material can be used as a substitute for chemical fertilizers, as it contains significant amounts of organic matter and plant nutrients. Application of byproducts from the sugarcane industry could be one of the most economical and suitable methods to solve two problems: wastewater disposal and soil fertilization. Cuba has adopted its utilization, to a large extent, in the irrigation of sugarcane plantations.

Solid organic components in wastes added to soils provide new exchange sites for cations as well as other adsorption sites. Diaz-Barrientos et al. (2003) and Rodriguez-Rubio et al.

(2003) observed that organic matter and carbonate in soils are the most important components regarding metal retention. Organic molecules with the capability to complex metals can potentially increase concentrations of these metals in the soil solution by dissolution reactions at mineral surfaces. Therefore, organic amendments can increase the solubility of metals by producing ligands that chelate the metals, thereby blocking their adsorption and promoting leaching through formation of soluble metal complexes (Madrid and Diaz-Barrientos, 1998). Organic matter can modify the pH, influencing the nature and extent of metal retention. Strobel et al. (2005) showed that dissolved organic carbon (DOC) enhanced the release of Cu from <8% to >20% of extractable Cu. Del Castillo et al. (1993) found a significant increase in Cd and Zn in the soil solution of an organically amended soil. The availability of Fe was also affected by the formation of complexes of Fe with DOC (Raulund-Rasmussen et al., 1998).

The effect of vinasse application on soil was studied by Casarini et al. (1987). They observed an initial decrease in pH after its application, though later the pH increased again. Vinasse also caused an increase in Na and Mn contents to levels that were not toxic to crops, and also observed an increase in K that was beneficial to the crops. Mattiazzo and Dagloria (1987) found that vinasse application caused an initial pH reduction that increased with time because of microbial activity causing oxidation of the organic matter. Stepkowska et al. (2001) found that cyclic fertilization with vinasse improved the agrotechnical properties of soils, depending on the soil type.

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Benke et al. (1998) studied the composition of vinasse from different sugarcane distilleries and found that the DOC from these samples was generally similar to the spectra of the fulvic acids of soils and sewage sludge. The spectra of the DOC differed from that of the fulvic acids, having a smaller amount of aromatic C and an absence of amine groups. It has been found that this functional group may be responsible for the dissolution of metals. Other researchers also indicated that DOC in soils plays an important role in the transport of nutrients (Qualls and Haines, 1991) and trace elements through surface transport and leaching. The byproduct from sugarcane contains high amounts of DOC, varying from 10.973 to 14.801 g L⁻¹ (Benke et al., 1999), which could have a noticeable effect on the status of soil metals after a few consecutive years of irrigation. While the effect of sewage sludge on the soil system has been extensively studied, investigations regarding the relationships between metals and wastewater from the sugarcane industry are scarce. In addition, it is very important to study the long-term effect on the soil residual system, because many of these studies were performed after 1 to 3 yr of application.

The objective of the present study was to determine the effect of sugarcane wastewater irrigation for 40 yr on ferralitic soils from the La Habana province in Cuba—more specifically, the effect on: (i) some physicochemical properties of the soil, (ii) the clay minerals, (iii) the Fe and Mn oxide content, (iv) the mobility of Cu, Zn, and Co in the profile, and (v) crop yield. Results were compared with those obtained under traditional mineral fertilization.

MATERIALS AND METHODS

The study area is located in the province of La Habana, in Cuba. Soils were classified as Ultisols according to Soil Survey Staff (1999). They are Ferralitic Yellow soils, with parent materials of calcareous rock. The extent of these Yellow Ferralitic soils in this province is about 76 200 ha. The soils used were classified as fine, smectitic, isohyperthermic Aquic Dystric Eutrudepts. They have two horizons and aquic conditions during certain periods in regular years and do not have free carbonates throughout any horizon in the first 100 cm of the soil profile. The water regime of these soils is udic and the temperature isohyperthermic because the average temperature of the soils is 22°C or higher and the differences between winter and summer is <6°C.

La Habana Province has 50-yr mean temperature values of 25.1°C, a maximum of 27.2°C in July and August, and a minimum in January of 22.1°C (Ministerio de Agricultura de Cuba, 1985). With respect to rain, there is a wet period in the summer and a dry period in winter. The mean pluviometric value is 1454 mm, with June and September being the wettest months.

The study was performed in profiles from a field after irrigation with wastewater from sugarcane production for 40 yr (referred to as treated soils). In a parallel study, plots that were not irrigated with sugarcane wastewater (control plots) were used for comparison (referred to as untreated soils). Four replicates per system were established (eight profiles). The sizes of the fields were about 13 and 15 ha for untreated and treated soils, respectively. The distance between the fields was 500 m.

Soil samples were collected at three depths for each horizon: 0 to 10, 10 to 20, and 20 to 30 cm for the Ap horizon, and 30 to 50, 50 to 70, and 70 to 100 cm for the Bwg horizon. The samples were initially air dried and sieved (<2-mm mesh size), and stored for analyses. Soil pH and electric conductivity (EC) were determined in the 1:5 soil/water extract, and organic

matter (OM) by potassium dichromate oxidation. Particle-size distribution was measured by the Bouyoucos densimeter (Gee and Bauder, 1979).

The clay fraction was separated by suspension. Because of the relatively large amount of Fe oxides of these soils, they were removed before the determination of the type of clay minerals. The clay minerals (<2 µm) were characterized by x-ray diffraction (XRD) before and after extraction with oxalate–oxalic acid solution in the dark and dithionite–citrate–bicarbonate (DCB) solution, using Cu Kα radiation and using oriented samples sedimented on glass slides and treated with Mg²⁺, Mg²⁺–ethylene glycol, or K⁺ saturated solutions followed by heating at 550°C. A semiquantitative estimate of non-Fe minerals was determined using the reflection powers given by Schultz (1964).

The content of amorphous oxides and organically bound Fe (Fe_o) and Mn (Mn_o) were determined according to McKeague et al. (1971). The samples were treated with ammonium oxalate–oxalic acid in the dark. Free Fe and Mn oxides (Fe_d and Mn_d) were determined by the method of Mehra and Jackson (1960) with DCB. Iron and Mn contents were analyzed in the DCB extract and in the oxalate–oxalic acid solution. Iron and Mn contents were measured using an inductively coupled plasma–atomic emission spectrometer (ICP–OES) and given as Fe₂O₃ and MnO.

The total metal contents of the soils were determined by dissolving the samples using a three-acid method (Perez-Rodríguez et al., 1990), and the elements measured using ICP–OES.

The wastewater used was from the cooperative Pedrín Troya located in the Complejo Agroindustrial Hector Molina Riaño (La Habana Province, Cuba). The wastewater used came from the raw fabrication of sugar and alcohol. Water from the sugarcane industry and from alcohol distillation are mixed 100 m away from the factories into a channel that discharges into the sea. Part of this wastewater, however, was used for soil irrigation at a flow of 4 L s⁻¹ for several days until total flooding. This type of irrigation by flooding on the treated plots was performed once per year. Some characteristics of the wastewater are shown in Table 1. The treated soils were irrigated for 40 yr and this study presents the results after this period of treatment.

The fields of the untreated (control) and treated soils were planted for 40 yr with sugarcane of the cultivar Cuba-8751. The control fields received conventional fertilization (N, P, and K). The fields irrigated with wastewater received organic fertilization from the wastewater and inorganic N amounting to one-third of that supplied to the unirrigated sites.

Statistical Analysis

Statistical analyses were performed using ANOVA. The means were separated by Tukey's test at a significance level of *P* < 0.05 throughout the study.

RESULTS AND DISCUSSION

Influence of Irrigation on pH, Organic Matter Content, and Electrical Conductivity

The application of the wastewater had noticeable effects on certain soil chemical properties. The reaction pH of the untreated soils was 7 or near neutrality. The mean pH values of the treated soils showed a decrease of about 0.5 pH units for all depths (Table

Table 1. Some characteristics of the wastewater used in this study.

pH	DOM†	P	Na	K	Ca	Mg
	g L ⁻¹		mg L ⁻¹			
5.02	50	205.6	146	382	325	76.8

† Dissolved organic matter.

Table 2. Mean values of pH, electrical conductivity (EC), and organic matter (OM) of untreated and treated samples.

Depth	pH		EC		OM	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
cm						
0–10	7.1 a†	6.7 b	0.12 a	0.25 b	20.4 a	28.6 a
10–20	7.5 a	7.0 ab	0.11 a	0.27 b	15.7 b	26.6 a
20–30	7.4 a	6.9 ab	0.11 a	0.33 b	8.7 b	22.7 a
30–50	7.4 a	6.8 ab	0.09 a	0.21 b	5.2 b	12.3 b
50–70	7.5 a	6.9 ab	0.08 a	0.11 a	2.0 c	4.0 c
70–100	6.2 b	5.9 c	0.08 a	0.08 a	0.3 d	2.0 c

† Values followed by the same letter in the analyzed properties for untreated and treated soils are not significantly different ($P < 0.05$).

2). Long-term changes in soil pH occur largely as a result of displacing cations or adding weak organic acids (Tisdale et al., 1993). The pH value of the wastewater was much lower (about 2 pH units) than that of the soils studied, but the pH decrease of the treated soil was small because of the buffering capacity of the soil.

The EC increased greatly after the long-term irrigation (Table 2). This was attributed to the large concentration of K in this wastewater (382 mg L⁻¹). The values were always less than for normal agricultural soils, <2 dS m⁻¹, the limit used in the salt tolerance of crops (Bresler et al., 1982). Madejon et al. (2001) found that when vinasse was applied on two different occasions, there was no effect on the mean pH value. These researchers found high EC values, however, which indicated that caution should be used for soils with restricted drainage.

The OM contents of these soils was between 20.4 and 0.3 g kg⁻¹ for the top- and subsoils. The increase in soil OM was one of the effects of wastewater application to the soil. The OM of the treated profiles increased (Table 2) with the addition of organics in the wastewater. This increase ranged between 40 and 500%, with the higher increase at a depth of 70 to 100 cm. This is due, in part, to the very small OM concentration at the bottom of the profiles, and consequently, any increase in OM resulted in high values when expressed as a percentage of the initial amount. Using sugarbeet (*Beta vulgaris* L. subsp. *vulgaris*) vinasse, Madejon et al. (2001) found that soil oxidizable C significantly increased in soil treated with the organic amendment, and the differences were statistically significant in most cases.

Influence on Particle Size Distribution

The clay content of the untreated soils increased with depth (Table 3), while the mean silt content decreased. The sand content also decreased with depth, but the difference was not statistically significant.

Irrigation with wastewater caused a decrease in the clay fraction at all depths in comparison with the untreated soils, although these differences were not significant in the top 20 cm; as a consequence, an accumulation of the silt fraction occurred along the pro-

file. This behavior could be related with an association of the added organic matter with the clay fraction (formation of organo-mineral complexes), giving an increase in the particle size of this fraction. In addition, the dissolution and precipitation of Fe oxides may coat the particles, acting as cement, and bind the particles together. The dispersant used for the determination of the textural fractions of the soils (sodium hexametaphosphate) did not readily dispersed the soil and may have altered the particle size distribution.

The amount of silt-sized particles in the subsoil of the treated soils increased more than that in the topsoil (Table 3)—about 200 and 2%, respectively. This was due, in part, to the fact that the silt contents in the subsoil at the bottom of the profiles were less than in the untreated soils and the increases were significant. Others have also found that vinasse application to soil caused a difference in the textural fractions and this distribution was dependent on soil type (Stepkowska et al., 2001).

Influence of Irrigation on the Clay Minerals of Soil

The XRD patterns for the clay fraction of two representative profiles (untreated and treated soils) are shown in Fig. 1. The XRD diagram of the clay fraction of the untreated soil shows a peak at about 14 Å that expanded to 18 Å with ethylene glycol (data not shown). The treatment with K and subsequent heating at 550°C for 30 min decreased the 14 Å peak to 10 Å (data not shown). These data confirmed that the predominant clay mineral was of smectite type. The peaks at 7.14, 4.43, and 3.55 Å that remain after treatment with ethylene glycol confirmed the presence of kaolinite in a large proportion. The semiquantitative estimation of the phyllosilicate minerals, using the reflection powers given by Schultz (1964), is 65% smectite, 35% kaolinite. Removal of the Fe oxides in this soil was necessary for the characterization of the clay minerals by XRD.

The XRD data for the soil after 40 yr of treatment showed a decrease in intensity and broadening and asymmetry of the diffraction peak at 14 Å that expanded to 18 Å with ethylene glycol, corresponding to smectite. The Mg²⁺ saturation was performed to obtain homoionic clay in the interlayer space. In the treated soil, however, the peak was broad and not well defined, which may be

Table 3. Mean values of particle size distribution of untreated and treated soil samples.

Depth	Sand		Silt		Clay	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
cm						
0–10	306a†	328a	148a	151a	547a	521a
10–20	300a	336a	125a	134a	574a	529a
20–30	305a	323a	84ab	114a	610ab	562a
30–50	282a	318a	97ab	124a	620ab	558a
50–70	266a	286a	78b	112a	660b	602a
70–100	277a	280a	40c	121a	683b	598a

† Values followed by the same letter in each textural fraction for untreated and treated soils are not significantly different ($P < 0.05$).

attributed to modification of the clay mineral to an organo-clay with the interlayer spaces occupied by mainly organic substances. This effect decreased with depth along the profile, being almost negligible in the lowest horizon (Fig. 1c). It was observed that in the treated soil, there was a greater difficulty in decreasing the 14 Å peak to 10 Å after treatment with K⁺, in comparison with the untreated soil, confirming the presence of organic substances in the interlayer space. The crystalline Fe oxide present in all the samples was goethite, with diffractions at 2.45, 2.69, and 4.18 Å.

Influence on Iron and Manganese Oxides

The mean Fe content of the samples from the different depths of the untreated profiles was between 93.3 and 108.8 g kg⁻¹, with the highest content at a depth of 30 to 50 cm. The mean values of total Fe for the treated soils were less than untreated soils (89.8–102.0 g kg⁻¹; Table 4).

The Fe_o and Fe_d contents are also shown in Table 4. The values of the short-range-ordered Fe oxide (Fe_o, amorphous oxides) were in the range of 6.3 to 20.5 and 5.7 to 25.1 g kg⁻¹ for untreated and treated soils, respectively, and the values decreased with depth with the exception of the sample from the 30- to 50-cm depth. Increased amounts of poorly crystalline Fe oxides in the upper layer of the treated soils were probably due to the organic matter accumulation, which may have retarded the effect of the crystallization of Fe oxides (Schwertmann, 1966). The content of crystalline oxides (Fe_d – Fe_o) decreased in the same proportion, possibly because of the amorphisation of these oxides due to the acid pH of the wastewater; also, with regular water flooding, it is highly probable that reducing conditions occur that would bring about solubilization of Fe and Mn oxides and their subsequent precipitation as amorphous phases once the system becomes oxidizing again.

The Fe_d value was used as a measure of the free Fe oxide content. The Fe_d values had a uniform distribution through the profile and those values were, in general, less than for untreated soils. The Fe_d values were logically larger than Fe_o in all samples studied because DCB extracts both crystalline and amorphous oxides. The amount of Fe present in crystalline Fe oxides (Fe_d – Fe_o) increased along the profile (except for the 30- to 50-cm depth), with values from 45.8 to 58.8 and 40.5 to 62.8 g kg⁻¹ for untreated and treated soils, respectively. The difference between the total Fe content (Fe_t) and Fe_d corresponds to Fe in the silicate structure, by exchange of other cations or filling octahedral positions. These values were about one-third of the total Fe content and, in general, very constant along the profiles.

The Fe_o/Fe_d ratio is an indication of the degree of crystallinity of free Fe oxides or aging of soils. Ratios <0.12 indicate that crystalline

Fig. 1. X-ray diffraction pattern of the clay fraction of untreated and treated soils at three depths (S: smectite; K: kaolinite; G: goethite).

Fe oxides are dominant in the soils (Fitzpatrick and Schwertmann, 1982). High values of the Fe_o/Fe_d ratio were found at the top of the profile where the organic matter content was the highest, which may have retarded the crystallization of Fe oxides. This can be also the consequence of a change in redox conditions.

Table 4. Average of total Fe oxides (Fe_t), Fe oxides extractable by dithionite–citrate–bicarbonate (Fe_d), Fe oxides extractable by oxalate–oxalic acid in the dark (Fe_o), and indices in untreated (Untr) and treated (Tr) soils.

Depth cm	Fe _t		Fe _d		Fe _o		Fe _t – Fe _d		Fe _d – Fe _o		Fe _o /Fe _d		Fe _d /Fe _t	
	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr
	g kg ⁻¹													
0–10	97.7 a†	94.3 a	66.3 a	65.6 a	20.5 b	25.1 ab	31.4	28.7	45.8	40.5	0.31	0.38	0.68	0.69
10–20	93.3 a	91.0 a	62.9 a	61.9 a	9.4 c	12.0 c	30.4	29.1	53.5	49.9	0.15	0.19	0.67	0.68
20–30	93.5 a	89.8 a	61.8 a	62.8 a	7.6 c	9.8 c	31.7	29.0	54.2	53.0	0.12	0.16	0.66	0.70
30–50	108.8 b	95.4 a	64.4 a	66.1 a	18.1 b	24.4 ab	44.4	29.3	46.3	41.7	0.28	0.37	0.59	0.69
50–70	103.0 b	98.5 a	67.2 a	68.2 a	9.0 c	8.8 c	35.8	30.3	58.2	59.4	0.13	0.13	0.65	0.69
70–100	104.0 b	102.0 b	65.1 a	68.5 a	6.3 d	5.7 d	38.9	33.5	58.8	62.8	0.10	0.08	0.63	0.67

† Values followed by the same letter in the analyzed Fe oxides for untreated and treated soils are not significantly different ($P < 0.05$).

Table 5. Average of total Mn oxides (Mn_t), Mn oxides extractable by dithionite–citrate–bicarbonate (Mn_d), Mn oxides extractable by oxalate–oxalic acid in the dark (Mn_o), and indices in untreated (Untr) and treated (Tr) soils.

Depth	Mn_t		Mn_d		Mn_o		$Mn_t - Mn_d$		$Mn_d - Mn_o$		Mn_o/Mn_d		Mn_d/Mn_t	
	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr
cm	g kg ⁻¹													
0–10	4.7 a†	2.1 c	4.1 a	2.1 c	2.9 a	1.2 c	0.6	0.1	1.2	0.8	0.70	0.60	0.88	0.98
10–20	5.0 a	2.4 c	4.4 a	2.2 c	3.5 a	1.3 c	0.6	0.2	0.9	0.9	0.80	0.60	0.89	0.92
20–30	4.8 a	2.6 c	4.4 a	2.4 c	3.3 a	1.3 c	0.5	0.2	1.0	1.1	0.77	0.54	0.89	0.92
30–50	7.2 b	2.9 c	5.8 b	2.6 c	5.4 b	1.8 c	1.4	0.3	0.5	7.0	0.92	0.71	0.81	0.90
50–70	5.4 a	3.8 a	4.8 a	3.4 a	3.9 a	2.4 c	0.6	0.4	0.8	1.0	0.83	0.70	0.89	0.89
70–100	6.6 b	4.0 a	5.8 b	3.7 b	4.4 ab	2.4 c	0.8	0.3	1.4	1.2	0.75	0.66	0.89	0.92

† Values followed by the same letter in the analyzed Mn oxides for untreated and treated soils are not significantly different ($P < 0.05$).

The Fe_d/Fe_t ratio was used to assess the extent of weathering of primary Fe-bearing minerals and it has also been used to estimate the relative soil age (Blume and Schwertmann, 1969; Arduino et al., 1986). The Fe_d/Fe_t ratios ranged between 0.59 and 0.70, indicating that significant amounts of Fe silicate were still present in the soil. The weatherability of the parent material and the soil age are the factors that influence this ratio the most.

The values of total Mn oxides, Mn_o , and Mn_d are shown in Table 5. The mean values for total Mn contents increased with depth, with the highest value in the 30- to 50-cm depth, similar to Fe contents. These values were similar to Mn_d (free Mn oxides), showing that practically all Mn present in the soils was extractable with DCB, that is to say, they were free Mn oxides. The effect of the amendment greatly decreased the values of total Mn and also the values of Mn_d and Mn_o . This behavior can be due to the formation of soluble complexes of Mn with the organic compounds in the wastewater. The values of total Mn content after the organic amendment presented a notable increase with depth when compared with the untreated soil—almost double at the lowest depth compared with the upper horizons. It is known that microbial decomposition of organic matter leads to reducing conditions by utilizing free O_2 in the soil atmosphere and free metal oxides (mostly Fe and Mn), which results in the production of CO_2 and organic acids, under which Fe and Mn become free in the soil solution (Mandal and Mitra, 1982). In soils, microorganisms use Fe(III) and Mn(IV) as final electron acceptors (and organic matter as the electron donor) when O_2 is depleted. The resulting reduced forms of these elements are much more soluble than their oxidized counterparts. Normally, Mn is reduced before Fe. The results seem to confirm this expectation.

The difference between the Mn_d and Mn_o contents was the crystalline Mn oxides. The wastewater addition did not significantly change the content of the crystalline Mn oxides in the topsoil.

The content of Al oxides (210 g kg⁻¹) was greater than the usual amount in soils (median 134 g kg⁻¹; Bowen, 1979), and this was associated with the presence of Al-containing clay minerals in

this soil (such as kaolinite and smectite), as confirmed with XRD. Kaolinite is the clay mineral containing the greatest amount of Al in its structure (about 400 g kg⁻¹) and smectite also contains a relatively large proportion (about 210 g kg⁻¹) of Al (Newman, 1987). Aluminum contents remained constant after 40 yr of irrigation with the wastewater, probably attaining equilibrium.

Influence on Iron and Manganese Oxides in the Clay Fraction

Table 6 shows the Fe contents, expressed as an oxide, extracted from the clay fraction with the different extractants. The values of Fe_d and Fe_o were less for the clay fraction than for the whole soil, and this was more noticeable for the short-range-ordered metal oxides (amorphous oxides). The irrigation with the wastewater increased twofold the amounts of the amorphous oxide in the top layer. This increase was parallel to the decrease in the content of crystalline Fe oxides, possibly because of the amorphization of these oxides due to the pH of the wastewater. The crystallinity index was less for the clay fraction than the soil, and it increased in the topsoil after amendment.

The addition of organics caused a decrease in the Mn content of crystalline oxides in the soil (Table 7), even in the subsoil (70–100 cm); however, the amorphous Mn oxide content (Mn_o) increased in the topsoil of the treated soils. Similarly to the Fe oxides, for Mn the index Mn_o/Mn_d was lower in the clay fraction than in the soil, indicating that the short-range-ordered oxides were less in the clay fraction than in the whole soil (Table 4).

Influence on Metal Leaching

Movement of metals in soils requires that they should be in the soluble phase or associated with mobile particulates. It has been shown that metals such as Zn and Cu are complexed strongly by humic acids at pH levels around 4.5 to 5.0 (Waller and Pickering, 1992). Movement is essentially related to speciation of the metals in soils because, depending on the species,

Table 6. Average of Fe oxides extractable by dithionite–citrate–bicarbonate (Fe_d), Fe oxides extractable by oxalate–oxalic acid in the dark (Fe_o), and indices in the clay fraction of the untreated (Untr) and treated (Tr) soils.

Depth	Fe_d		Fe_o		$Fe_d - Fe_o$		Fe_o/Fe_d	
	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr
cm	g kg ⁻¹							
0–10	55.1 a†	49.4 a	3.6 b	7.1 a	51.5	42.3	0.07	0.14
10–20	50.8 a	50.0 a	3.6 b	5.0 ab	47.2	45.0	0.07	0.10
20–30	48.0 ab	46.0 b	4.4 ab	4.8 ab	43.6	41.2	0.09	0.10
30–50	45.1 b	49.7 a	5.6 ab	5.5 ab	39.5	44.2	0.12	0.11
50–70	45.0 b	40.0 c	4.3 ab	3.8 b	40.7	35.7	0.10	0.09
70–100	43.1 b	34.6 c	3.6 b	3.1 b	39.5	31.4	0.08	0.09

† Values followed by the same letter in the analyzed Fe oxides for untreated and treated soils are not significantly different ($P < 0.05$).

Table 7. Average of Mn oxides extractable by dithionite–citrate–bicarbonate (Mn_d), Mn oxides extractable by oxalate–oxalic acid in the dark (Mn_o), and indices in untreated (Untr) and treated (Tr) soils.

Depth	Mn_d		Mn_o		$Mn_d - Mn_o$		Mn_o/Mn_d	
	Untr	Tr	Untr	Tr	Untr	Tr	Untr	Tr
cm	g kg ⁻¹							
0–10	1.9 a †	0.8 b	0.1 b	0.3 a	1.8	0.5	0.05	0.40
10–20	1.9 a	0.9 b	0.1 b	0.2 a	1.8	0.7	0.05	0.22
20–30	1.9 a	1.0 b	0.2 a	0.2 a	1.7	0.8	0.11	0.20
30–50	2.5 a	1.1 b	0.3 a	0.3 a	2.2	0.8	0.12	0.27
50–70	1.6 a	0.9 b	0.3 a	0.3 a	1.3	0.6	0.19	0.33
70–100	1.8 a	1.1 b	0.3 a	0.3 a	1.5	0.8	0.17	0.27

† Values followed by the same letter in the analyzed Mn oxides for untreated and treated soils are not significantly different ($P < 0.05$).

they may have different potential for undergoing mobilization by organic or inorganic ligands that are present in the soil solution (McBride, 1989; Li and Shuman 1997a).

The mean values of Cu in the upper horizons were larger in the treated soils than the untreated soils, and similar for the other depths (Fig. 2). This behavior could be due to the interaction of this element with the soil OM, whose content is the highest in the upper horizon. Temminghoff et al. (1997) reported that dissolved OM enhanced the mobility of Cu; however, Han and Thompson (2003) indicated that dissolved OM over the long term inhibited Cu mobility. The low mobility of some metals can be related to the retention of these elements in the upper layer by OM (Giusquiani et al., 1992), as observed in our experiments.

The mean values of Zn from untreated and treated soils (Fig. 2) indicated that irrigation with the wastewater mobilized this metal from the surface to subsurface horizons. Decreasing pH mobilizes most metals, and low pH favors more solubilization and hence mobility, but the decrease in treated soils was only 0.5 units. Therefore an enhanced transport of this metal by dissolved OM should be considered because of the increase in Zn concentration with depth. The low-molecular-weights hydrophilic dissolved OM components are highly mobile and could influence metal transport in the soil system. Giusquiani et al. (1992) reported an increased mobility for heavy metals added to the soil by urban waste compost. Organic molecules with the capability to complex metals can potentially increase concentrations of these metals in soil solution by dissolution reactions at mineral surfaces (Ashworth and Alloway, 2004). The application of vinasse may increase some metal's mobility, because soluble organic ligands can form water-soluble complexes with metals (Li and Shuman, 1997b). A process that affects heavy metal solubility may also influence heavy metal leaching in soils, explaining why the content of Zn was higher in the subsoil of the treated soils (Fig. 2).

The mean concentrations of Co for treated and untreated soils are also shown in Fig. 2. The complexes of the metal with the dissolved OM may contribute to the release of metals so that the values in the treated soils were less than those in the untreated profiles. Cobalt is one of the divalent cations that is strongly complexed with OM according to the sequence $Cu^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+}$ (Stevenson, 1994). Moreover, part of the metal released is dissolved by other factors, probably by

the slightly acidic nature of the supplied OM. In addition, Co is correlated with Fe and Mn oxides of soil because soil microorganisms use organic matter as an electron donor for reducing Fe(III) and Mn(IV). The resulting reduced forms of these elements are much more soluble than their oxidized counterparts and therefore they would leach through the soil profiles.

Crop Yield

In the treated soils there was a noteworthy increase in sugarcane production. The cultivar Cuba-8751 yielded mean values

Fig. 2. Mean values of total Cu, Zn, and Co for untreated (patterned bars) and treated (shaded bars) soils from 0- to 100-cm depth. Values followed by the same letter for untreated and treated soil do not differ significantly ($P < 0.05$).

from the last 5 yr of 24.88 and 76 Mg ha⁻¹ for the untreated and treated soils, respectively.

CONCLUSIONS

The results presented here show that irrigation with wastewater from the sugarcane industry may be used successfully in agriculture. It increased crop yield and the organic matter content in the lower part of the soil profile. The large concentration of K in the wastewater increased EC, but the EC values were less than the limiting values for salt tolerance of crops. Vinasse application yielded the intercalation of organic compounds in the clay mineral smectite. The formation of organo-mineral complexes and particle coating with Fe oxides produced little change in the particle-size distribution, but the increase in the poorly crystalline Fe oxyhydroxides in the upper horizon was very significant. The crystallinity of Fe oxyhydroxide in the soil decreased substantially because of dissolution and reprecipitation of these oxides by the acidic pH of the wastewater. Total and poorly crystalline Mn contents were also decreased. The applied wastewater contained soluble organic matter that complexed metals, favoring their leaching throughout the soil profile, which may eventually lead to deterioration of groundwater quality and a decrease in some micronutrient contents in the soils.

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