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THE SOIL MANAGEMENT MODIFIES THEIR HUMIC ACIDS AND THE AVAILABILITY OF HEAVY METALS

El manejo del suelo modifica a sus ácidos húmicos y la disponibilidad de metales pesados

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ABSTRACT. The agronomic management not efficient and with not very sustainable conditions induces unfavorable effects in the agro ecosystem, constituting source of entrance of pollutants and modifications of soil properties. In Cuba this information is not modernized, representing a danger for the agricultural production and the alimentary security. The objective of this work was to evaluate the effect of the management practices on properties of the acids humic and the availability of heavy metals two different management of a Nitisol soil of Mayabeque province, one with low antropic activity (natural grasses) and another of high antropic activity, dedicated to several cultivations. In the extracted humic acids they were evaluated optic coefficient E4/E6, threshold of clotting, the carboxylic, fenolic acidity and total acidity. It was also evaluated the pseudototal content of cations of metals heavy availability. The results demonstrated the effect of the management system, evidencing differences in the evaluated properties. The hydrophobicity, the level of structural condensation, the quantity of carboxylic groups and the total acidity of the humic acids diminished as consequence of the intensive cultivation, what could imply that they are affected the functions that the humic acids should exercise in the soil plant system. In that management they also registered affectations in the remaining evaluated properties, registering the biggest values for Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}, as well as that was a superior content to the one referred as permissible maximum in several countries in the case of the Cd^{2+} and for the Nitisol soils of Cuba.

Key words: contamination, agricultural practical, humic substances

RESUMEN. El manejo agronómico no eficiente y con condiciones poco sustentables, induce efectos desfavorables en los agroecosistemas, constituyendo fuente de entrada de contaminantes y modificaciones de las propiedades del suelo. En Cuba no está actualizada esta información, lo que representa un peligro para la producción agrícola y la seguridad alimentaria. El objetivo de este trabajo fue evaluar el efecto de las prácticas de manejo sobre propiedades de los ácidos húmicos y la disponibilidad de metales pesados en dos manejos diferentes sobre un suelo Ferralítico Rojo de la provincia Mayabeque; uno con baja actividad antrópica (pastizal) y otro de alta actividad antrópica, dedicado a cultivos varios. En los ácidos húmicos extraídos se evaluaron el coeficiente óptico E4/E6, el umbral de coagulación, la acidez carboxílica, fenólica y total. En el suelo se evaluó el contenido seudototal de cationes de metales pesados. Los resultados demostraron el efecto del sistema de manejo, evidenciándose diferencias en las propiedades evaluadas. La hidrofilicidad, el nivel de condensación estructural, la cantidad de grupos carboxílicos y la acidez total de los ácidos húmicos disminuyeron como consecuencia del cultivo intensivo, lo que pudiera implicar que se vean afectadas las funciones que ellos deben ejercer en el sistema suelo-planta. En ese manejo de alta actividad antrópica también se detectaron afectaciones en las restantes propiedades evaluadas, registrándose las mayores concentraciones de Cu^{2+}, Ni^{2+}, Pb^{2+} y Zn^{2+}, siendo en el caso del Cd^{2+} un contenido superior al referido como máximo permisible en varios países y para los suelos Ferralíticos Rojos de Cuba.

Palabras clave: contaminación, prácticas agrícolas, sustancias húmicas

INTRODUCTION

Currently with the development of the global economy, there is great global concern for the degradation and contamination of soils. Several

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authors state that contamination by toxic heavy metals in the soil, caused by human activities, has caused a gradual detriment of the environment, which constitutes a risk to health and the deterioration of soils for agricultural purposes (1, 2).

This has led to the need to carry out studies on the current state of soils under different management practices in terms of their physical, chemical and biological properties, as well as humic substances, as the main component of soil organic matter. The quality of the soils and the management carried out with them are determining factors in the sustainability of agricultural production and environmental quality (3,4).

In Cuba, soil degradation is also one of the main environmental problems, a situation that is accentuated by the synergy among multiple factors: loss of biological diversity, erosion, salinization, reduction of nutrients, climate change, among others. The Red Ferralitic soils (FRR) of Mayabeque province, for being the most productive in the country, have been subjected for years to an intensive agricultural exploitation, with high inputs management that involve the use of mineral fertilization, phytosanitary products and machinery employment, which can constitute sources of heavy metal cations (5,6).

The determination of the current state of these soil properties, as well as the existing concentrations of heavy metals in agricultural soils with different management is necessary, since it increases the theoretical and practical knowledge about the influence of the management systems, which will allow taking measures to counteract or prevent degradation and pollution. The objective of this work was to evaluate the effect of two different management systems on chemical and physico-chemical properties of humic acids and the availability of heavy metals in a Red Ferralitic soil of Mayabeque province.

MATERIALS AND METHODS

Two different handlings were selected, subjected to unequal anthropic activity, corresponding to a type of Red Ferralitic soil, belonging to the Ferralitic grouping (7).

A site of low anthropic activity of coordinates N 22095 62.8 and W82020 42.7 "was chosen, which is located in the Nazareno livestock Company in San José de las Lajas, with a typical Red Ferralitic soil (FRR) , on loamy limestone rock, cultivated with natural pastures for more than 35 years. The site of high anthropic activity selected corresponds to Block # 0603 of the Agricultural Production Cooperative (CPA) "Amistad Cuba-Nicaragua" (San Nicolás de Bari), with the same soil type, coordinates N 22046 04.7 and W81055 57.4 dedicated to various crops, in the last 20 years and before sugarcane. At each site samples were collected in 15 points randomly on a surface of half a hectare, at a depth of 0-20 cm, to form three composite samples.

The total organic carbon (COT) content in soil samples from both sites was determined by oxidation with potassium dichromate in a sulfuric acid medium. The extraction of soluble organic carbon (COS), humic acids (AH) and fulvic acids (AF), as well as the purification of the AH was carried out in the Chemistry Laboratory of the Faculty of Agronomy of the Agrarian University of Havana, following the methodology of the International Society of Humic Substances (IHSS) (8). The carbon content in the extracted soluble fractions was evaluated with the same COT procedure. The Degree of Humification (GH) was made by calculating the percentage that represents the total carbon in the form of AH and AF with respect to COT, extracted from the soils under study.

For the determination of the optical coefficient E_4/E_6 of the AH, a solution of 3 mg of the AH obtained from the soils with low and high anthropic activity (AH (CV) and AH (PN) respectively) was prepared in 10 mL of hydrogen-carbonate. sodium of c ($NaHCO_3/2$) = 0,05 mol L^{-1}, the absorbances being read at 465 and 665 nm in a spectrophotometer (RayLeigh UV-1601) of the aforementioned Chemistry Laboratory (9).

The coagulation threshold value was determined from a mass of 26 mg of AH (CV) and AH (PN) respectively, and dissolved in solution of ($NaHCO_3/1$)=0.05 mol L^{-1} at pH=8, from which equal volumes were taken that were contacted with increasing concentrations (from 1.25 to 18.7 mmol L^{-1}) of $CaCl_2$ (PA quality). After 24 hours of rest, the lowest concentration of calcium chloride ($CaCl_2$) that caused the coagulation of humic acids (9) was visually detected. The total acidity and acid functional groups (carboxylic and phenolic of the humic acids) were determined by potentiometric titration.

The pseudototal content of the heavy metal cations was determined after a digestion with *aqua regia* in the soils (10). An Atomic Absorption Spectrophotometer (Rayleigh WFX-210) from the Physiology Laboratory of the Institute of Animal Science (ICA) was used and compared with the maximum permissible limits and the hazardous levels for soil (11).

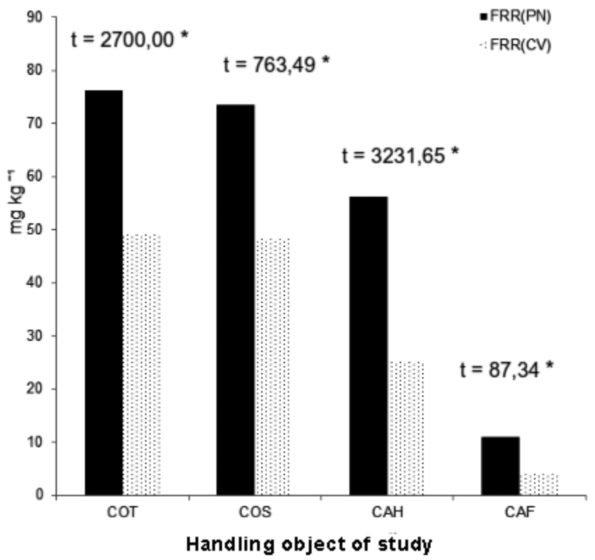
A randomized sampling was used in two different experimental procedures, subjected to unequal anthropic activity and all the data obtained were analyzed in the statistical program STATGRAPHICS Plus for Windows 5.1 (12). The comparison of means was carried out using the Student's nonparametric t test, to determine between which levels the significant difference was established.

RESULTS AND DISCUSSION

Figure 1 shows the contents of total organic carbon (COT), soluble organic carbon (COS), in the form of AH (CAH) and in the form of AF (CAF) in the sites studied with different management.

It was evidenced that all the indicators shown in Figure 1 for the management of Miscellaneous Crops (high anthropic activity) were lower than those recorded for the management of low anthropic activity (Natural Pastures).

The marked difference in the values of COT between both managements can be attributed to that in the intensive organic amendments were not used or any other similar alternative that they assured the recovery or contribution of a certain level of carbon.



(FRR (PN) = Management of Natural Pastures and FRR (CV) = Management of Various Crops)

Figure 1. Content of total organic carbon (COT in mg kg^{-1}), soluble organic carbon (COS in mg kg^{-1}), carbon as AH (CAH in mg kg^{-1}) and carbon as AF (CAF in mg kg^{-1}) in Red Ferralitic soils (FRR) with different management

No such behavior was registered in terms of the proportion represented by the COS with respect to COT (9.62 % in the management of low anthropic activity and 9.77 % in the case of miscellaneous crops). However, when calculating the degree of humification (GH), that is to say the total of CAH and CAF in relation to the COT, values of 88.2 and 59.3 % were found in the management of natural pastures and miscellaneous crops, respectively. On the other hand, in the CAH/CAF ratio, values of 5.12 were recorded for the management of low anthropic activity and 5.89 for the management of miscellaneous crops.

From the above it is inferred that the intensive management has not only induced an organic carbon loss in the soil, but also has affected the normal process of humification, possibly due to a lower contribution of fresh organic matter and as a consequence of the soil preparation work, which affect the microbiota responsible for decomposing the original deposited material (13).

The preservation of the quantity and quality of soil organic matter is an important aspect for the sustainability of agricultural productivity and food security, especially in tropical conditions. Inadequate agricultural practices can cause serious damage to the ecosystems dedicated to food production (14,15).

In the case of Red Ferralitic soils, the progressive degradation of organic carbon in its superficial layer has already been verified in an area with intensive cultivation of shallow rooted plants, with a marked loss of fertility (4).

The determination of the E_4/E_6 optical coefficient and the coagulation threshold in the humic acids obtained from soils with different management are shown in Table 1.

Table 1. Optical coefficient and coagulation threshold (mmol Ca^{2+} kg^{-1} AH) of humic acids from soils with different management

Humic acids	Coefficient E_4/E_6	Coagulation threshold (mmol $Ca^{2+}kg^{-1}$ AH)
AH(CV)	6,67a	55,02b
AH(PN)	4,78b	63,23a
t	274,29	254,59
p	0,0000	0,0000

Averages with unequal letters differ significantly by the t-Student test

The values of the optical coefficient obtained for both AH are within the recognized range for this type of substance and for the type of soil from which they were extracted (16). It was proved that the AH (PN) belonging to the management of natural pastures, have the lowest value, which is related to a higher level of structural aromatic condensation.

This is completely understandable considering the diversity of fresh organic matter contributed by this type of management, its edaphic environment more conducive to the activity of biota and greater structural stability, which favor an appropriate evolution of humification (17).

The value found in AH (CV) reflects the impact of high anthropic activity management, which disfavors the normal development of humus formation. This translates into a lower stability of these substances and consequently their functions in soil-plant system are affected (18).

In summary, it can be stated that the management system used in Ferralitic soils studied can modify the structure of humic acids and that the E_4/E_6 ratio is an indicator that reflects it.

The values found for the coagulation threshold reveal that the AH (CV) show a lower hydrophilicity, compared with the AH (PN), which could be associated with a lower presence of ionizable functional groups in its structure, which are decisive in the affinity for a polar solvent such as water.

This leads to the fact that AH (CV) will have greater susceptibility to coagulation when in the soil the content of dissolved salts is increased, as occurs due to excess fertilizers, salinization or other agricultural work within this management.

Other authors have found differences in the threshold of coagulation of humic acids, derived from changes in composition and structure (19).

The evaluation of acid functional groups present in humic acids extracted from soils with different management is shown in Figure 2.

The results obtained confirm structural differences between both humic acids, especially as regards the content of carboxylic functional groups and, consequently, in the total acidity.

The fact that in AH (CV) a smaller quantity of these ionizable functional groups is present is in correspondence with the result shown in relation to the coagulation threshold. These groups have a high hydrophilicity and the fact that they are in a lower quantity means that the HA molecule can coagulate at lower concentrations of electrolytes in the medium.

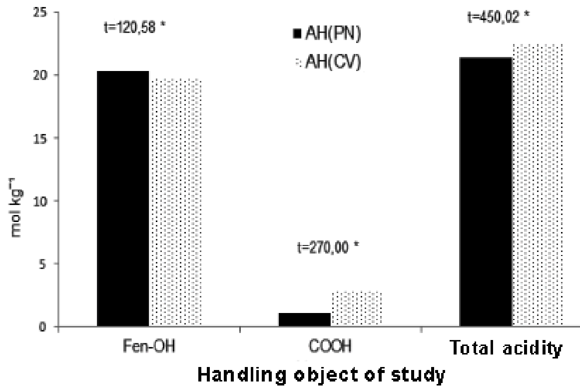


Figure 2. Content of carboxylic functional groups (COOH), phenolic (fen-OH) and total acidity (AT) in mol kg^{-1} of AH, in soils with different management

Regarding the content of the phenolic groups there are also differences although less marked than the carboxylic ones, since the latter can be associated with the aliphatic chain, which are more susceptible to chemical transformations than the aromatic rings, which corresponds to the results obtained at Evaluate the optical coefficient E_4/E_6 for both operations.

This difference in total acidity must also have an impact on the cation exchange capacity of these humic acids, since the interaction with the metal cations is fundamentally established with these groups.

The determination of the pseudo-total contents of heavy metal cations is presented in Table 2.

Table 2. Pseudototal contents (mg kg^{-1}) in soils with different management

Handling	Heavy metal cations (mg·kg^{-1})				
	Cd	Cu	Ni	Pb	Zn
FRR(PN)	19,64b	39,57b	226,22b	16,10b	127,87b
FRR(CV)	40,25a	77,59a	290,44a	16,26a	144,07a
t	33,12	42,11	13,47	14,98	7,96
p	0,0000	0,0000	0,0000	0,0001	0,0000

FRR (CV) = Miscellaneous Crops and FRR (PN) = Natural Pastures
Different letters indicate significant differences between soils by the t-Student test

The results showed that in the soil of high anthropic activity, FRR (CV) always detected higher contents of the heavy metal cations evaluated Cd, Cu, Ni, Pb and Zn, which differ statistically from those found in the FRR (PN). In this sense, the case of cadmium stands out, since in the FRR (CV) it is more than double that in FRR (PN) and the reference levels or the limits of intervention for this cation are extremely low (between 3 and 5 mg kg^{-1}) as reported by other countries (20) and even for the recently obtained natural values for Ferralitic soils of Cuba (21).

Regarding this last information, the pseudo-total contents found for copper and for zinc are also relatively high.

These results require special attention, since the increase in the concentrations of these heavy metals in the soil, evidently is a consequence of the agricultural practices implemented in the management of high anthropic activity, probably due to an excessive use of mainly phytosanitary products. This fact becomes more important if we take into account that many of the plant species that are included within the systems of various crops are recognized as accumulators or hyperaccumulators of these pollutants, which would put food security at risk due to their possible inclusion in the food chain.

In this sense, it is also necessary to consider that the sensible decrease detected in terms of organic matter in FRR (CV) management is another factor that affects the regulatory action that humic substances could effect on the bioavailability of the heavy metal cations evaluated, fundamentally because of their possibility of forming stable coordination compounds with them.

CONCLUSIONS

- The determination of the different forms of organic carbon evaluated in selected soils with different management showed that a high anthropic activity appreciably decreases the COT and the degree of humification. The latter derives in that the humic acids present have a structure of less aromatic condensation, as well as greater susceptibility to coagulation due to a decrease in the total amount of acid ionizable functional groups, which affects the functionality of these substances in the soil system -plant.
- The pseudototal contents of the determined heavy metal cations showed significant differences between the two studied treatments, showing that in the soil of high anthropic activity FRR (CV), the highest values were recorded for Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+}. For the latter, the value found exceeds the maximum permissible values of several countries and even the content reported as reference for this type of soil in Cuba. This result constitutes an alert regarding the agro-food risk that it represents.

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