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Original article

Biological properties, humic acids and heavy metals availability in Ferralitic soil under differents agricultural uses

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ABSTRACT

The biological properties and the organic matter of the soil can reflect the imbalance of a certain atmosphere, the sustainability of the agricultural practices and to predict processes of contamination. The objective of this work was to evaluate the effect of three different agricultural uses (fruit-bearing, cane of sugar and potato) in soil moisturized Red Ferralitic, on the properties biological basal breathing, microbial mass and the metabolic quotient. The organic carbon was also evaluated, as well as the optic coefficient E_4/E_6, the threshold of clotting and the content of groups functional acids in the sour extracted humic of those soils. Also, the contained pseudototal of cations of heavy metals was determined Cd^{2+}+, Cu^{2+}+, Ni^{2+}+, $Pb^{2+}$and Zn^{2+}. The results demonstrated that the uses of cane of sugar and of potato, they showed the lowest values in basal breathing and microbial mass, with high metabolic quotient, what indicates an unfavorable effect of the intensity of the practices agricultural employees on the microbiota edaphic. The organic carbon showed significant differences among the management. In the humic acids structural modifications were detected, reflected in the threshold of clotting and in the optic coefficient E4 /E6, as well as in the content of groups functional acids. The contained pseudototal of heavy metals was superior in the uses of bigger quantity of cultural activities, especially in the corresponding to the cultivation of the potato, where the $Cd^{2+}$is in relatively high concentrations, that which constitutes a given risk its low limit of tolerance in foods.

Key words: agronomic practices, microorganisms, organic matter, degradation

INTRODUCTION

The soil is a non-renewable natural resource and its regeneration is very slow, being constantly subjected to the processes of destruction and degradation. It is a fundamental element for agriculture by supplying water and nutrients to crops, in addition to having the ability to provide various ecosystem services: social and ecological sustainability, water and nutrient cycling, food security, adaptation and mitigation of climate change (1).

The study of the biological properties of the soil and its relationship with the content of organic matter have become good indicators of the alterations that occur as a result of its agricultural use. Both aspects are sensitive to changes in soil conditions and their involvement can be an indicator of contamination, offering timely information on the alterations of the quality of the same and allows the impact of the management system to be evaluated (2,3).

The degradation and contamination of soils, as well as the decrease in the efficiency of production systems are some of the most important aspects in agricultural sustainability. The management of organic inputs and the quality of soil organic matter represent critical components of the productivity of agroecosystems in tropical regions, in which their uses play an important role (4,5).

In Cuba, the knowledge that has been obtained about the effect of agricultural uses on the biological activity of the soil, the process of carbon humification and the concentrations of heavy metal cations is not yet sufficient. Having this information can be a valuable tool for decision making when defining an efficient use of agroecosystems in our country.

The objective of this work was to evaluate the effect of three different agricultural uses (fruit, sugarcane and potatoes) of a hydrated Ferralitic Red soil on its biological properties, the contents and properties of humic substances and the availability of heavy metals.

MATERIALS AND METHODS

Three sites were selected with hydrated Red Ferralitic soil (FRRh) from the Mayabeque province, Cuba [6], with uneven crop intensity management. A first coordinate site was chosen (N 23 0 00´21,3´´ and WO 820 09´2,3´´), located on the land of the Agrarian University of Havana "El Mangal" (San José de Las Lajas municipality), cultivated with mango plants (*Mangífera índica*), for more than 40 years, without disturbance of the soil by agricultural work (symbolized by FRR (M)). A second coordinate site (N 22º 45´50.08´´ and WO 81º 55´30,2´´), located in block # 0603, former No. 71 of the Agricultural Production Cooperative (CPA) “Amistad Cuba- Nicaragua ”(San Nicolás de Bari municipality), planted with sugarcane (*Saccharum officinarum* L), for more than 40 years (FRR (C)) and a third experimental coordinate site (N 22º 46´04,7´´ and WO 81º 55´57,4´´), located in Farm # 1 of the Basic Production Unit (UBP) "Manuel Enrique Hernández Pena" (San Nicolás de Bari municipality), grown with potatoes (*Solanum tuberasum* L), in the last five years (FRR (P)). In each site samples were collected at 15 points, randomly, on a surface of half a hectare, at a depth of 0-30 cm, to form composite samples that were subdivided into five identical portions, to evaluate in them the basal respiration by the respirometric method [7] and the microbial mass by the Fumigation-Extraction method [8]. The ratio of metabolic activity (q CO_2) was determined by the relationship between basal respiration and the amount of microbial biomass per unit of time (hour).

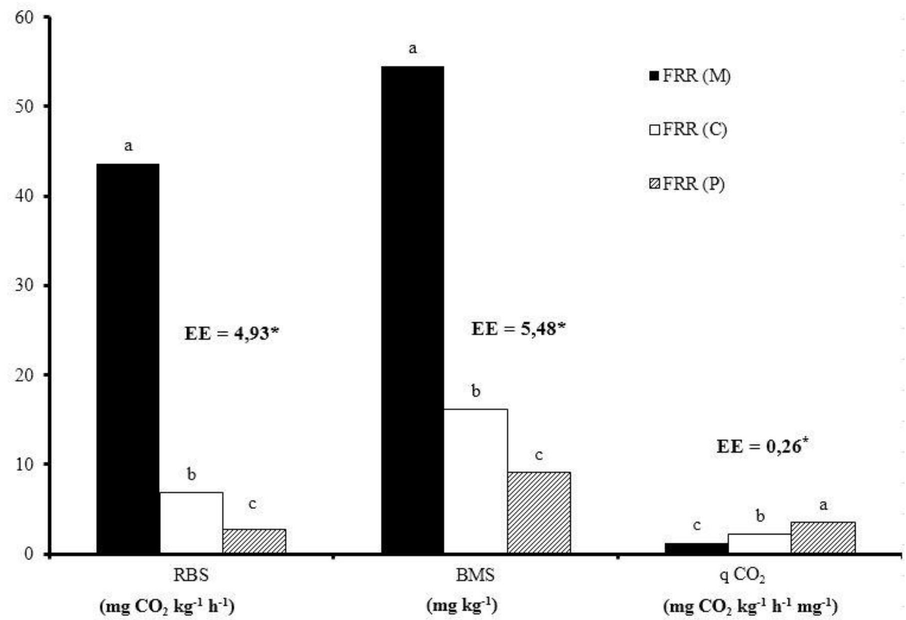
The total organic carbon (TOC) content in the soil samples was determined spectrophotometrically, after oxidation with potassium dichromate (P.A. quality) of concentration 0.2 mol L^{-1} in sulfuric acid medium 5 mol L^{-1}. The amount of Cr^{3+} produced in the reaction is proportional to the amount of organic carbon. The relationship between the absorbance reading due to Cr^{3+} and the carbon mass was previously obtained with a calibration curve, using different amounts of glucose (P.A.). The extraction of soluble organic carbon (COS), humic acids (HA) and fulvic acids (FA), as well as the purification of HA, was carried out following the methodology of the International Society of Humic Substances [9]. Some of the fundamental steps of this procedure consist in obtaining the mixture of HA and FA, treating the sample with an alkaline aqueous medium. The HA are subsequently separated by coagulation by acidifying the mixture to pH<2, using a 6 mol L^{-1} solution of hydrochloric acid. The isolated HAs are washed, redissolved and coagulated again. The determination of the optical coefficient E_4/E_6 of the HA in a solution of these in sodium hydrogen carbonate of c ($NaHCO_3$) = 0.05 mol L^{-1}, the absorbances being read at 465 and 665 nm in a Spectrophotometer (RayLeigh UV- 1601) (10). The coagulation threshold value was determined from a solution of the HA of 150 mg L^{-1} in c ($NaHCO_3$) = 0.05 mol L^{-1} at pH=8, from which equal volumes were taken and placed in contact with increasing concentrations of calcium chloride (CaC_{l2}, PA quality) from 1.25 mmol L^{-1} to 18.75 mmol L^{-1}. After 24 hours the lowest concentration of CaC_{l2} was detected visually, which caused the coagulation of humic acids (10). The total acidity and acidic functional groups (carboxylic and phenolic) of humic acids, previously dissolved in 0.1 mol L^{-1} sodium hydroxide, were determined by potentiometric titration, using a standard hydrochloric acid solution.

The pseudototal content of heavy metal cations (all those present in the soil except those that are part of the primary minerals), was evaluated with an Atomic Absorption Spectrophotometer (Rayleigh WFX-210) from the Physiology Laboratory of the Institute of Animal Science (ICA), after digestion of soils with royal water (11). The values obtained were compared with what was reported for soils and plants (12).

A randomized design was used in the three agricultural uses studied and all the data obtained were analyzed in the statistical program STATGRAPHICS Plus for Windows 5.1 (13). The comparison of means was performed using the Tukey multiple comparison test for $p < 0.05$.

RESULTS AND DISCUSSION

The values of basal respiration (RBS), microbial biomass (BMS) and the metabolic activity ratio (q CO_2) showed significant differences for the three uses studied (Figure 1).



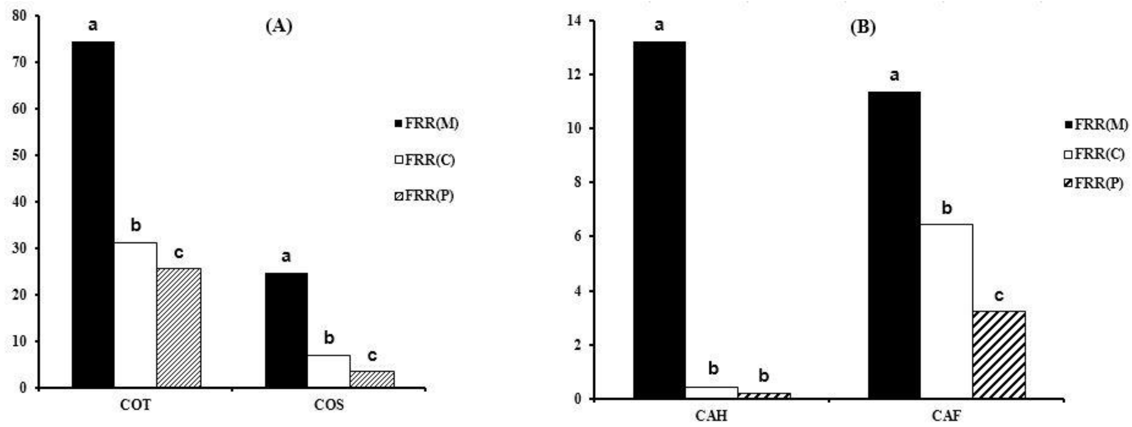
Different letters indicate significant statistical differences according to Tukey for p <0.05, n = 5

Figure 1. Basal respiration (RBS), microbial biomass (BMS) and metabolic activity coefficient (q CO_2) in sites with different agricultural uses

With regard to microbial biomass and basal soil respiration, the use of FRR (M), which is of low anthropic activity, presented higher values, which is associated with a higher carbon content, a life-enhancing aspect Edaphic in this management, contributing more to the sustainability and biological conservation of the soil.

The low values of respiration and microbial mass of the FRR (C) and FRR (P), can be associated with frequent disturbance of the edaphic environment, produced by a high degree of anthropization and a greater intensity in the agricultural management of these agroecosystems (14-15). The above should have an impact on higher contents of metal cations in these operations, which would imply conditions of metallic stress, an aspect that seems to be ratified by the higher values of the CO_2 obtained for these uses. Everything described constitutes an alert to keep in mind, since the preservation of the edaphic biota is essential in maintaining the fertility of agroecosystems (16).

With respect to the contents of total organic carbon (COT), soluble organic carbon (COS), in the form of HA (CAH) and in the form of FA (CAF) in the sites studied with different agricultural uses, there was a considerable decrease in FRR (C) and FRR (P) with respect to FRR (M) (Figure 2).



ES_x en COT= 5,58*, ES_x en COS = 2,47*, ES_x en CAH = 1,62* y ES_x en CAF=0,89*. Different letters indicate significant statistical difference according to Tukey for $p < 0.05$, n = 5

Figure 2. (A) Total organic carbon content (COT) and soluble organic carbon (COS). (B) Carbon as HA (CAH) and as FA (CAF) in soils with different handles

In the case of COT and COS, a reduction of more than 50 % was detected in the uses of greater anthropic activity (sugarcane and potato crops), with respect to FRR (M).

The results obtained in the uses FRR (C) and FRR (P) confirm the appreciable decrease caused by the intensive application of agricultural work, in terms of carbon conservation, an issue that continues to be reported in recent scientific literature (17,18) on agricultural soils in other geographical regions.

A different behavior was also recorded in the proportion that the COS represented with respect to the COT, obtaining values of 64.29 % in FRR (M), 23.14 % in FRR (C) and 21.8 % for FRR use (P). This suggests that intensive management, in addition to inducing a net loss of organic carbon in the soil, affects the normal humification process. Under tropical conditions, the sustainability of agricultural productivity and food security are affected by the agricultural practices that are carried out, in which the conservation of soil organic matter is a transcendental aspect (19).

The affectation caused to the normal process of humification of the organic carbon of the soil was evidenced in the differences found in the carbon, forming part of humic acids (CAH) and fulvic acids (CAF), when comparing the agricultural uses studied. In addition, the CAH/CAF ratio, both in FRR (C) and FRR (P), has a much lower value than unity, suggesting that the formation of HA is disadvantaged compared to FRR (M).

What was found with respect to carbon is related to what was obtained in terms of microbiota activity.

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These results reaffirm what has been reported regarding carbon losses and agricultural productivity in surface horizons in Cuban Red Ferralitic soils, used in low-root crops [(20)].

In the HA isolated from the soils of the sites under study, differences in the values of the optical coefficient E_4/E_6 and the coagulation threshold were found (Table 1).

Table 1. E_4/E_6 optical coefficient and coagulation threshold of humic acids from soils with different handles

Humic Acid-Use	E_4/E_6 coefficient	Coagulation threshold (mmol Ca^{2+} kg^{-1} AH)
AH FRR(M)	4,43 c	20,36 a
AH FRR(C)	6,52 b	13,82 b
AH FRR(P)	7.66 a	9,34 c
ES_x	0,36	0,76

Different letters indicate significant differences between different uses according to Tukey for $p < 0.05$

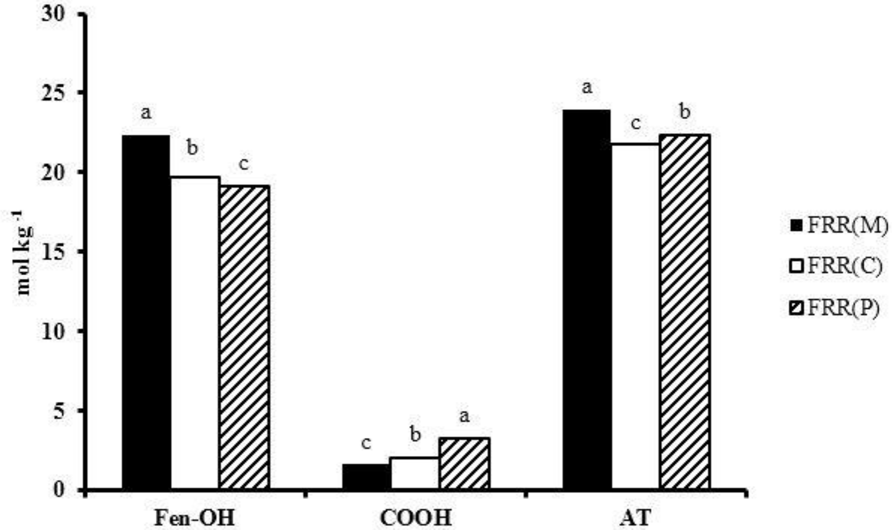
The optical coefficient values found correspond to the range reported for this type of substance [(10)]. Since the numerical value of this indicator is in inverse proportion to the degree of aromatic condensation of the structure of humic acid [(10)], it was found that the HA belonging to the FRR (M) use has a structure with a higher level of aromatic condensation. This evidence may be supported by the permanent contribution of fresh organic matter, contributed by this type of agricultural use and its less disturbed edaphic environment, which favors the activity of biota and greater structural stability.

On the other hand, the coagulation threshold values also reflect differences in the hydrophilicity of HA, since the greater the interaction with water, higher concentrations of the coagulating electrolyte are required. The HA of the FRR (M) use have the highest hydrophilicity, while those corresponding to FRR (P) have a significantly lower coagulation threshold. This constitutes a risk in the event of any salinization process, since the HA would lose their functionality in the soil-plant system when coagulating.

The higher values found in FRR (C) and FRR (P) for this indicator, together with the decrease in the organic carbon content and a lower biota activity as it has been proven, reflect affectation in the normal humification process, which implies that productive capacity and its sustainability in these soils are compromised [(21).]

Several authors in recent studies [(22)], found a similar situation for handling various crops and natural pastures in Ferralitic soils of Mayabeque.

Regarding the content of the acid functional groups present in humic acids extracted from soils with different management, significant differences were found between the sites under study (Figure 3).



ES_x para Fen-OH=0,38*; ES_x para COOH=0,25* y ES_x para AT=0,25*. Different letters indicate significant statistical differences according to Tukey for $p < 0.05$, $n = 5$

Figure 3. Content of carboxylic functional groups (COOH), phenolics (Fen-OH) and total acidity (TA) in soils with different management

The evidenced decrease in the content of phenolic groups of HA in the most intense anthropic activity management confirms what was obtained before in terms of aromaticity reflected in the E_4/E_6 coefficient. In the same way, the fact that in them the total amount of these ionizable groups is smaller is in close correspondence with that found in terms of the coagulation threshold. The latter also has an unfavorable impact on the contribution that humified carbon can make to the cation exchange capacity of the soil, an aspect closely related to its fertility. The determination of the pseudototal contents of Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} heavy metal cations also showed significant differences between the studied uses (Table 2).

Table 2. Pseudo-total contents in soils with different agricultural uses

Handling	Heavy metal cations ($mg \cdot kg^{-1}$)				
	Cd	**Cu**	**Ni**	**Pb**	**Zn**
FRR(M)	2,33 c	8,27 c	21,04 c	15,71 c	22,69 c
FRR(C)	4,1 b	15,35 b	64,41 a	18,89 a	33,05 b
FRR(P)	6,63 a	19,16 a	44,99 b	17,21 b	44,31 a
ES_x	0,47	1,2	5,03	0,35	2,38

Different letters indicate significant differences between soils by the Tukey test for $p < 0.05$, n = 5

The values obtained in the pseudototal content indicated that in the intensive uses FRR (C) and FRR (P) were found significantly higher values for the cations Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}, compared to FRR (M), which is lower anthropic activity

As for the significant increase in the content of Cu^{2+} with respect to the ground FRR (M), it is probably related to the application of pesticides, based oxides and salts of this metal. In these soils the values found outperform those obtained previously for Red Ferrallitic soils [23], employed in various farming systems, soil indicating that in recent years has continued to increase its levels.

The high contents of Pb^{2+} in the FRR (C) and FRR (P) operations could be attributed to the use of agricultural machinery with internal combustion engines, as well as to burning in the case of sugarcane cultivation.

In the case of Cd^{2+} the corresponding ground FRR (P) presented a pseudototal content that exceeds even the concentration values, considered permissible limits in other places of the world; such as 1 to 3 mg kg^{-1} in the European Union and 3 mg kg^{-1} in Great Britain [24].

All of the above is related to agricultural management with intense anthropic activity, which entails the application of a large number of agrochemicals and phytosanitary actions in both management, with recognized agro-environmental risk [25]. These results reaffirm published studies, which suggest that agricultural soils are receiving high amounts of heavy metal contaminants due to reckless and inappropriate agricultural practices, causing disorders in the functions of the soil-plant system [26]. This situation must be taken into account when using these soils for the production of food for human consumption, given the toxicity levels recognized in the literature [27].

In general, the results obtained in this work demonstrate that microbial biomass, soil respiration, organic carbon, soluble humic substances and the content of heavy metal cations are sensitive indicators that can be used to monitor changes derived from agricultural management.

CONCLUSIONS

- The unfavorable effect of the intensity of agricultural practices employed on the preservation of edaphic biota was verified, reflected in the low content of total organic carbon and soluble organic carbon in those uses of high anthropic activity.
- The optical coefficient E_4/E_6, the coagulation threshold and the contents of acid functional groups in humic acids, confirm the unfavorable structural modifications that occur in agricultural uses with intensive exploitation, which compromise the direct and indirect functions of humidified fraction of organic matter.
- The heavy metal contents available in the soils of the FRR (C) and FRR (P) uses, registered the highest values for Cu^{2+}, Pb^{2+}, Ni^{2+} and Zn^{2+}. In the case of Cd^{2+}, a high content was found with risk for food safety.

BIBLIOGRAPHY

1. Espinoza IDN, Zenteno MDC, Chávez JC, Moreiral VN, Solarte KEA, Intriago FLM. Propiedades físicas del suelo en diferentes sistemas agrícolas en la provincia de Los Ríos, Ecuador. Temas agrarios. 2018;23(2):177-87.

2. Rivero Herrada M, Remigio Gaibor Fernández R, Mozena Leandro W, Petrônio de Brito Ferreira E, Maris Ferraresi T, Reyes Pérez JJ. Evaluación de atributos biológicos de un suelo latosol bajo producción agroecológica. Centro Agrícola. 2016;43(4):14-20.

3. Paolini Gómez JE. Actividad microbiológica y biomasa microbiana en suelos cafetaleros de los Andes venezolanos. Terra Latinoamericana. 2018;36(1):13-22. doi:10.28940/terra.v36i1.257

4. Vásquez JR, Schellekens J, Kaal J. Composición de la materia orgánica en los suelos de seis zonas edafoclimáticas del Magdalena (Colombia). Spanish Journal of Soil Science. 2015;5(3):243-58.

5. Moreno C, González MI, Egido JA. Influencia del manejo sobre la calidad del suelo. ECUADOR ES CALIDAD: Revista Científica Ecuatoriana. 2015;2(1):33-40. doi:10.36331/revista.v2i1.8

6. Hernández Jiménez A, Pérez Jiménez JM, Bosch Infante D, Castro Speck N. Clasificación de los suelos de Cuba 2015. Instituto Nacional de Ciencias Agrícolas (INCA)/Instituto de Suelos; 2015. 93 p.

7. Durango W, Uribe L, Henríquez C, Mata R. Respiración, biomasa microbiana y actividad fosfatasa del suelo en dos agroecosistemas y un bosque en Turrialba, Costa Rica. Agronomía costarricense. 2015;39(1):37-46.

8. Vance ED, Brookes PC, Jenkinson DS. Microbial biomass measurements in forest soils: the use of the chloroform fumigation-incubation method in strongly acid soils. Soil Biology and Biochemistry. 1987;19(6):697-702.

9. Perminova IV, Kulikova NA. From Molecular Understanding to Innovative Applications of Humic Sustances Society. En: 14 th International Meeting September. 2008. p. 59-63.

10. Canellas LP, Santos G. Humosfera: Tratado Premilinar Sobre a Química das Substâncias Húmicas/Luciano Pasqualoto Canellas e Gabriel Araújo Santos. Campos dos Goytacazes: Santos. 2005;

11. Standardization IO for. Soil quality-Extraction of trace elements soluble in aqua regia. ISO; 1995.

12. Kabata A. Trace elements in soils and plants. 4th ed. Boca Raton: CRC press; 2011. 534 p.

13. StatPoint. Statgraphics Plus 5.1. StatPoint Rockville, MD; 2000.

14. WingChing-Jones R, Lorío LU. Biomasa y actividad microbiana en suelos de uso ganadero y en regeneración de bosque. Research Journal of the Costa Rican Distance Education University (ISSN: 1659-4266). 2016;8(1):107-13.

15. Cabrera-Dávila G de la C, Socarrás-Rivero AA, Hernández-Vigoa G, Ponce de León-Lima D, Menéndez-Rivero YI, Sánchez-Rendón JA. Evaluación de la macrofauna como indicador del estado de salud en siete sistemas de uso de la tierra, en Cuba. Pastos y Forrajes. 2017;40(2):118-26.

16. Mesa-Pérez MA, Echemendía-Pérez M, Valdés-Carmenate R, Sánchez-Elías S, Guridi-Izquierdo F. La macrofauna edáfica, indicadora de contaminación por metales pesados en suelos ganaderos de Mayabeque, Cuba. Pastos y Forrajes. 2016;39(3):116-24.

17. Mehraj I, Mir A, Bhat G. Comparative evaluation of physic-chemical properties of rural and urban soil, along river Jhelum, Kashmir, India. International Journal of Recent Scientific Research. 2014;5(2):500-4.

18. Rossi CQ, Pereira MG, García AC, Berbara RLL, Gazolla PR, Perin A, et al. Effects on the composition and structural properties of the humified organic matter of soil in sugarcane strawburning: A chronosequence study in the Brazilian Cerrado of Goiás State. Agriculture, ecosystems & environment. 2016;216:34-43.

19. de MP do N, Robervone S, Ramos ML, de Figueiredo CC, Silva AM, Silva SB, et al. Soil organic matter pools under management systems in Quilombola Territory in Brazilian

Cerrado. Revista Brasileira de Engenharia Agricola e Ambiental-Agriambi. 2017;21(4):254-60.

20. Silva JR, Silva DJ, Gava CAT, Oliveira TCT de, Freitas M do SC de, Silva JR, et al. Carbon in Humic Fractions of Organic Matter in Soil Treated with Organic Composts under Mango Cultivation. Revista Brasileira de Ciência do Solo [Internet]. 2016 [citado 21 de noviembre de 2019];40. doi:10.1590/18069657rbcs20150095

21. Páez LEC, Realpe I del SB, Peinado FJM, Flores JCM. Extracción secuencial de metales pesados en dos suelos contaminados (Andisol y Vertisol) enmendados con ácidos húmicos. Acta Agronómica. 2016;65(3):232-8.

22. Trinidad SA, Velasco-Velasco J. Importancia de la materia orgánica en el suelo. Revista Agroproductividad. 2016;9(8):52-8.

23. Reyes-Rodríguez R, Guridi-Izquierdo F, Valdés-Carmenate R. El manejo del suelo modifica a sus ácidos húmicos y la disponibilidad de metales pesados. Cultivos Tropicales. 2018;39(2):15-20.

24. Ballesta R, Bueno P, Rubi J, Giménez R. Pedo-geochemical baseline content levels and soil quality reference values of trace elements in soils from the Mediterranean (Castilla La Mancha, Spain). Open Geosciences. 2010;2(4):441-54.

25. Delince W, Valdés Carmenate R, López Morgado O, Guridi Izquierdo F, Balbín Arias MI. Riesgo agroambiental por metales pesados en suelos con Cultivares de *Oryza sativa* L. y *Solanum tuberosum* L. Revista Ciencias Técnicas Agropecuarias. 2015;24(1):44-50.

26. Sidhu GPS. Heavy metal toxicity in soils: Sources, remediation technologies and challenges. Adv. Plants Agric. Res. 2016;5:00166.

27. Edao HG. Heavy metals pollution of soil; toxicity and phytoremediation techniques. Indian J. Adv. Eng. Res. 2017;1(1):2456-9992.