# Evaluating forms of phosphorus found in soils planted to plantain

# Evaluación de formas de fósforo en suelos cultivados con plátano

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#### Abstract

The extractable phosphorus represent a small fraction of the soil and it is found in a dynamic balance between organic and inorganic forms. The behavior of phosphorus forms was studied in two zones dedicated to the plantains plantations in the municipality of Moñitos (Cordoba, Colombia). A random stratified sampling design was applied to take samples of both soil and foliar tissue (plantain leaves). The different forms of the phosphorus were determined: Easily-replaceable P; Non-apatite P-Ca; P-Al; P-Fe; and Apatite P-Ca, using the fractionation method (Chang and Jackson, 1957) modified by Petersen and Corey, (1966) and Williams et al., (1967). In both soil units, CM-CA (Inceptisols from high and medium hills) and PM (Inceptisols from marine terraces), the major contribution to inorganic phosphorus in the soil was from P-Fe, apatite P-Ca, and the non-apatite P-Ca, while the easily replaceable P and the P-Al had low percentages for these kinds of soil types. With the process of fractionation of the inorganic phosphorus, part of the organic soil phosphorus was also extracted, which is evidenced with the obtained levels of total soil phosphorus, and total inorganic phosphorus. This latter is exceeded by the content of inorganic phosphorus produced as a result of the fractionation.

Key words: Phosphorus, organic phosphorus, inorganic phosphorus, assimilation, musa AAB.

#### Resumen

El fósforo (P) extractable representa una pequeña fracción del presente en el suelo y se encuentra en un equilibrio dinámico con las formas orgánicas e inorgánicas. Se estudió el comportamiento de las formas de fósforo en dos zonas dedicadas a plantaciones de plátano (Musa AAB Simmonds) en el municipio de Moñitos, Córdoba, Colombia. Para el efecto se tomaron muestras de suelo y de tejido foliar (hojas de plantas de plátano) mediante un muestreo al azar estratificado. Se determinaron las diferentes formas de fósforo: P-fácilmente reemplazable, P-Ca no-apatítico, P-Al, P-Fe, P-Ca apatítico, por el método de fraccionamiento propuesto por (Chang y Jackson, 1957) modificado por Petersen y Corey (1966), y Williams et al. (1967). En ambas unidades de suelo CM-CA (Inceptisole de colinas altas y medias) y PM (Inceptisoles de terrazas marinas) el mayor aporte al fósforo inorgánico se obtuvo por parte del P-Fe, el P-Ca apatítico y el P-Ca no-apatítico, mientras que el P-fácilmente reemplazable y el P-Al presentaron porcentajes muy bajos para estos tipos de suelo. Con el proceso de fraccionamiento del P inorgánico también se logró extraer parte del fósforo orgánico del suelo, lo cual se evidencia con los niveles obtenidos por el P total del suelo y el P total inorgánico, este

último se ve superado por los contenidos de fósforo inorgánico producto de la suma del fraccionamiento.

**Palabras clave:** Fósforo, compuesto orgánico del fósforo, compuesto inorgánico del fósforo, asimilación, *musa* AAB.

#### Introduction

Phosphorus (P) is the least mobile and least bioavailable of all the plant macronutrients. This characteristic gives it a high resistance to leaching in the majority of soils. However, at the same time it frequently causes nutritional deficiencies in agricultural production (Holford, 1997). Phosphorus availability is affected by physical and chemical processes in the soil, such as mineral dilution, precipitation, absorption, retention by ferric (Fe) and aluminum (Al) oxides and hydroxides, and retention in clays (Martínez, 1988). The use of bioavailable forms of P by plants is dependent on the pH (Potash and Phosphate Institute -PPI, 1996). The ionic forms of P present in the soil are H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>2</sup>- y PO<sub>4</sub><sup>3</sup>-. When the pH is low, the monovalent form,  $H_2PO_4$ , tends to dominate. The divalent form  $HPO_4^{2-}$  begins to appear at pH = 4, and reaches a maximum at pH = 9. The two ions are in equilibrium at pH = 7. The ions  $PO_4^{3-}$  appear in small quantities between pH = 9 - 0 (Garavito, 1979). Thus, considering only the pH, P assimilation by plants would be normal at low pHs, given that the form HPO<sub>4</sub><sup>2-</sup> is the most easily assimilated. This condition also contributes to the solubility of the free hydroxides of Fe and Al, liberating the ions Fe<sup>3+</sup> and Al<sup>3+</sup>, precipitating the ions H<sub>2</sub>PO<sub>4</sub>-, which in turn form insoluble compounds, unavailable for the plant (Jackson, 1964). The H<sub>2</sub>PO<sub>4</sub>- could also react with the hydrated oxides of these same elements under conditions of low acidity (Garavito, 1979). In alkaline soils, the P is immobilized under in the form of calcium phosphates. Additionally, the anion HPO<sub>4</sub><sup>2</sup>-, whose formation is favored in alkaline ranges of pH, is precipitated by the action of calcium yielding HPO<sub>4</sub>Ca, which is insoluble (Ortega, 1978). The chemical fractionation is an important technique for the interpretation of the dynamics of P in soil, in relation to the mineral nutrition of this element in plants. The application of extract reagents in an adequate sequence provides information on the form of the different phosphates, and the solubility of each ionic H<sub>2</sub>PO<sub>4</sub>- form bioavailable to plants.

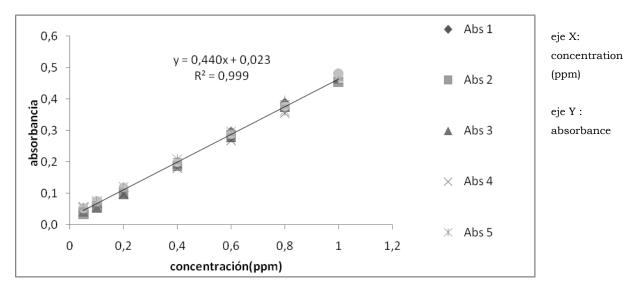
Various extraction methods have been used to understand the distribution of P in the soil. Some measure the quantity of organic P in relation to total content, such as the method of Saunders and Williams (1955). Other fractionation methods separate the distinct forms using sequentially applied extraction solutions. Amongst these techniques, one of the best known is that of Chang and Jackson (1957), which separates the distinct fractions of inorganic P, and estimates the organic P as the difference between the sum of all the inorganic fractions extracted and the total P quantified (Boschetty, 2003).

Plants absorb the majority of P as  $H_2PO_4$ , and to a lesser extent as  $HPO_4$ . The absorption of the former is ten times more rapid than the latter, although this depends to a large extent on the pH of the soil. Other forms of P that may be absorbed by plants are  $P_2O_7$  and  $PO_3$ , as well as certain soluble organic phosphates (Salinas & García, 1985). The objective of the present study was to evaluate the different forms of P that exist in soils cultivated with plantain in the municipality of Moñitos, Department of Córdoba, Colombia, and to evaluate the P quantification method using Molecular Absorption Spectrophotometry (MAS).

#### Materials and methods

The study was carried out in two stages; the first being conducted in the field in plantain crops (*Musa* AAB Simmonds) in the municipality of Moñitos, department of Córdoba, (9° 06' 04.4" N 76° 04' 19,4" WO and 9° 18' 39,7" N and 76° 10,42' WO). Two units of soil were studied, differentiated by their geological and morphological characteristics: 1. Soil from medium or high hills (CM-CA) with a predominance of clay particles, and classified principally as Inceptisols; and to a lesser extent as Vertisols; and 2. Marine terraces (PM), soils with granulometric variation, classified as Inceptisols (POT-Alcaldía Municipal de Moñitos y Costa Atlántica Ltda., 2001).

Each unit constituted a stratum and each sample consisted of four subsamples taken in 10 m², at a soil depth of 0-20 cm, in both the wet and the dry season. The analyses included the physical-chemical characterization according to methodologies recommended by the Geographic Institute Agustín Codazzi (IGAC, 1990). P fractionation was carried out following the method of Chang and Jackson (1957), modified by Petersen and Corey, (1966) and Williams et al., (1967). The modifications varied the extraction order of some forms, increased the pH of the ammonium fluoride solution to extract Al phosphates, separated the apatite and non-apatite phosphate, determined the easily replaceable P, and introduced new nomenclatures for some fractions (Benavides, 1978). To quantify the P a molecular absorption spectrophotometer Perkin - Elmer Lambda 11, 660 nm, lineal calibration mode, was used. The parameters validation-precision, precision, work range, detection limit and quantification were evaluated using eight curves with different patterns of P concentrations from 0.05 ppm to 3.00 ppm. The statistical analysis was carried out in Microsoft Excel coupled with Addinsoft XIstat (2006) with a confidence interval of 95%.



**Figure 1**. Values obtained by molecular absorption spectrophotometry for phosphorus quantification in the range 0.05-1.0 ppm.

### Results and discussion

The soils in the plantain cultivation zone of the municipality of Moñitos (Córdoba) present moderately acid to neutral pHs, average organic material content, with values between 1% and 3%, low sulphur content in the hillside soils, with a notable leaching of minerals towards the coastal plains (Box 1). The soil content of interchangeable calcium was approximately 20 ppm, and soluble calcium 3 ppm. Iron concentration was normal (20 ppm), except in the site corresponding to sample PM7, which presented levels of around 60 ppm in both seasons. These results coincide with data for the zone from the Colombian Agricultural Institute (ICA, 1992).

The evaluation of the phosphorus quantification method using molecular absorption spectrophotometry showed a linear behavior between absorption and concentration of P up to 1 ppm ( $r = 0.9999 \text{ y } r^2 = 0.9998$ ) (Figure 1). The precision study showed no significant differences in the variability of measures due to random error, in concordance with the test of significance applied to the assays of repeatability and reproducibility (Box 2). All the means of the measures were inside the confidence interval found for each point on the calibration curve, with coefficients of variation lower than those stipulated for acceptance n = 4 (repetitions). The Student T test showed no significant differences between the value calculated and the real value, along the calibration curve for n = 4 (repetitions) (Box 3). The limit of detection and the method quantification yielded values of 0.007 ppm P and of 0.048 ppm P respectively, using 3 and 10 times the standard deviation of the signal of the negative.

The model of P distribution for the wet and dry seasons presented the following decreasing order: P-Fe, P-Ca, easily replaceable P, P-Al (Boxes 4 & 5), revealing that available P

is a minimal proportion of the total, being less than 3% and 1% in the CM-CA and PM soils respectively. The different characteristics of the soils influence the solubility and the absorption-desertion of this nutrient, affecting the quantity available to plants (Havlin, et al., 1999). The principal forms of P that contribute to the total content of this element in units of CM-CA and PM soils are P-Fe, P-Ca, which are not available for plant absorption but that constitute a medium term reserve through solubilization processes.

Box 1. Physical-chemical characterization of soil samples in the municipality of Monitos, in the plantain-cultivating region of Córdoba (Colombia).

Sample	pН	MO (%)	S (ppm)	Ca	CICe	Fe ppm	Ca	CE μS/c
	(meq/100 g soil)		_	meq/lt	μο, σ			
Wet season:								
CM-CA 1	6.7	1.89	5.14	13.5	24.7	10.0	1.71	357
CM-CA 3	6.3	1.75	7.72	19.0	31.9	7.2	1.63	337
CM-CA 7	7.1	3.96	5.14	25.0	38.8	2.0	2.57	290
CM-CA 10	6.4	2.24	7.72	16.0	37.8	23.2	4.09	289
PM 1	7.6	2.41	62.0	21.0	30.2	18.0	5.0	1047
PM 2	6.8	2.75	28.4	13.5	28.6	24.8	1.35	408
PM 7	7.3	2.75	28.4	12.0	23.9	62.0	2.5	577
PM 9	6.5	1.89	48.9	16.0	23.3	17.2	1.2	262
mean	6.8	2.46	24.18	17.0	29.9	20.6	2.51	445.8
S.D.	0.5	0.72	21.86	4.4	6.0	18.5	1.37	262.6
Dry season:								
CM-CA 1	6.4	2.75	10.6	15.5	26.0	10.0	1.67	316
CM-CA 3	6.6	3.44	10.6	20.5	25.6	5.2	4.06	257
CM-CA 7	6.7	3.44	5.8	23.0	29.6	1.6	1.59	294
CM-CA 10	6.3	1.89	2.5	17.0	33.6	13.6	1.88	213
PM 1	7.5	1.72	5.8	22.0	24.0	17.6	3.08	526
PM 2	6.3	1.72	30.3	15.5	24.8	28.4	4.78	1864
PM 7	6.8	1.55	2.2	14.5	18.8	50.0	1.25	28.0
PM 9	6.4	2.58	7.1	15.5	25.2	17.2	1.68	185
mean	6.6	2.39	9.4	17.9	26.0	18.0	2.5	460
S.D.	0.4	0.78	9.0	3.4	4.3	15.3	1.32	584

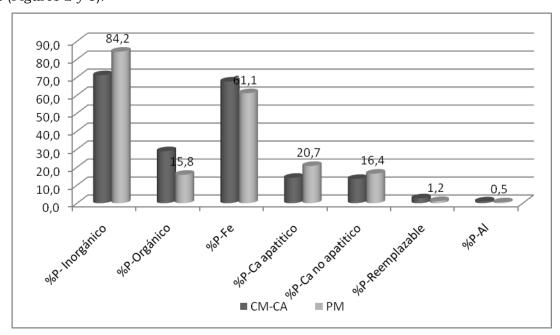
CM-CA = Inceptisol, medium and high hillsides.

PM = Inceptisol, marine terraces.

Box 2. Signific	cance values for r	epeatability for	the work range.
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Parametric				
pattern (ppm)	0.06	0.3	0.5	0.9
mean (patrón)	0.065	0.31	0.52	0.89
S.D.	0.001	0.005	0.003	0.003
CV (%)	0.033	0.029	0.012	0.007
Variance	4.53E-06	8.15E-05	3.73E-05	3.73E-05
I.C. (+/-)	0.007	0.03	0.02	0.02
I.C. (+/-) mean	0.019			

The soils from the zones CM-CA and PM can be classified as neutral to lightly acidic, a condition that favors the formation of insoluble phosphates with calcium. The influence of the soil pH was observed, which was on average 6.8 for the soils PM and 6.5 for the soils CM-CA (Ortega, 1978), favoring a higher proportion of insoluble P in PM soils: 40% vs 30% in the CM-CA soils (Figures 2 y 3).



**Figure 2.** Distribution of phosphorus as proportions with respect to total P. Wet season. Municipality of Moñitos, plantain-cultivating zone of Córdoba (Colombia). CM-CA = Inceptisol, medium and high hillsides. PM = Inceptisol, marine terraces.

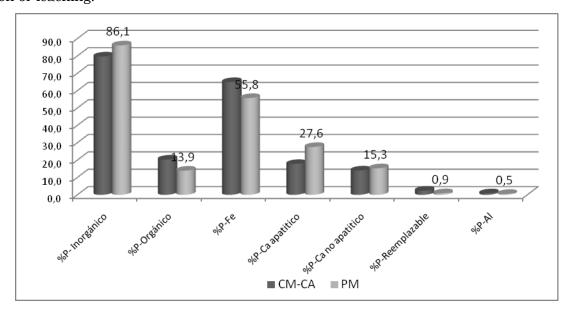
The level of P bound to Fe was high in both zones (PM = 57% and CM-CA = 66%) (Figure 2a, b). Once again, the pH plays an important role for this form, as the soils with a high clay content (2:1), a pH between 5 and 7 fix P with oxides and hydroxides of iron and aluminum (Navarro & Navarro, 2000).

To this, it must be added that in these soils, the organic material, specifically humic and fulvic acid, may affect the extraction with bases such as sodium hydroxide, that also extract organic P (Hedley et al., 1982; Tiessen & Moir, 1993).

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Pattern	Mean	Standard	't' –Table	't' -
(ppm)	(pattern)	Deviation	(0.05;3)	calculated
0.06	0.062	0.004	3.182	0.543
0.3	0.298	0.004	3.182	0.4
0.5	0.528	0.01	3.182	2.91
0.9	0.906	0.007	3.182	0.895

Box 3. Significance values of precision for the work range.

Taking into account the level of P bound to both iron and calcium in both the dry and the wet seasons are in both soil units it appears that, despite the low mobility of this nutrient in the soil, there is a flow from the CM-CA soil area to the PM soils, due to the steep slopes present in the relief of the Moñitos municipality. This situation indicates the necessity to implement a program of fertilization with sources of rapidly soluble P, eliminating losses, fixation or leaching.



**Figure 3.** Distribution of phosphorus as proportions with respect to total P. Dry season. Municipality of Moñitos, plantain-cultivating zone of Córdoba (Colombia). CM-CA = Inceptisol, medium and high hillsides. PM = Inceptisol, marine terraces.

In both the dry and the wet seasons, when the pH came closer to alkalinity, levels of P bound to Ca (P-Ca) increased, while P bound to iron (P-Fe) remained high in all the seasons of sampling. According to the pH values (6.4 - 7.5 in the dry season and 6.7 - 7.3 in the wet season) it is possible that the disassociation of the  $HPO_4^{2-}$  and  $H_2PO_4^{-}$  ions occurs frequently

These soil reaction conditions suggest a high dynamic of the apatite and non-apatite calcium phosphates, which dissolve more easily in these pH conditions, and possibly supports more soluble P than the other fractions. The organic P that was found in the humic and fulvic acids or in the fresh organic material, and which depends on microorganism activity to undergo the mineralization process forming inorganic P, represented around 25% of the CM-CA soils and 14% of the PM soils. This agrees with the levels of organic material seen, with CM-CA soils richer in organic material than the PM soils. These latter are sandy, having a large influence of marine sediments, with low organic material content, and favoring a low content of organic P (Fassbender & Bonermisza, 1987; Harrison, 1987).

**Box 4.** Phosphorus fractionation (ppm) in soils from the municipality of Moñitos in the plantain-cultivating region of Córdoba (Colombia).

wet	season.

Samples	P	P-Ca	P-A1	P-Fe	P-Ca	P	P	P
	fac. rep.	non apat.			apat.	total	org.	inorg.
CM-CA 1	3.5	55.6	1.2	167.2	8.9	289.1	71.4	217.7
CM-CA 3	4.9	5.1	0.6	97.3	23.1	199.8	91.5	108.3
CM-CA 7	15.2	58.9	3.9	190.5	45.5	387.6	86.3	301.2
CM-CA 10	2.6	10.3	3.7	195.9	57.9	262.5	79.6	182.9
PM 12	5.8	28.2	0.0	130.5	14.8	226.6	40.2	186.4
PM 13	0.0	26.5	0.2	180.2	71.2	271.2	53.6	217.6
PM 18	3.1	38.6	0.2	125.6	63.5	257.9	38.0	219.9
PM 20	4.7	86.7	4.7	233.1	77.1	303.7	35.4	268.3
Mean	5.0	38.7	1.8	165.0	45.3	274.8	62.0	212.8

fac. rep. = easily replaceable phosphorus.

**Box 5.** Phosphorus fractionation (ppm) in soils from the municipality of Moñitos in the plantain-cultivating region of Córdoba (Colombia).

Dry season.	
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Samples	P-	P-Ca	P-Al	P-Fe	P-Ca	P	P	P
	fac. rep.	non apat.			apat.	total	org.	inorg.
CM-CA 1	9.3	78.5	2.2	189.3	46.7	313.6	65.8	247.8
CM-CA 3	3.3	13.0	0.8	126.4	45.7	219.9	91.5	128.4
CM-CA 7	10.7	52.1	2.0	227.4	41.2	387.2	20.1	367.3
CM-CA 10	3.0	10.3	4.4	170.4	61.6	265.9	63.5	202.3
PM 12	2.5	44.5	0.2	83.7	86.0	244.5	35.7	208.7
PM 13	1.2	31.0	0.4	148.1	66.5	258.4	29.6	228.8
PM 18	0.2	18.8	0.0	133.7	47.1	208.7	22.3	186.4
PM 20	4.5	53.1	4.4	172.4	66.1	283.7	50.8	232.8
Promedio	4.4	37.7	1.8	156.4	57.6	272.7	47.4	225.3

fac. rep. = easily replaceable phosphorus.

It is important to note that when a specific form of P is determined it is possible that other forms are also extracted. In this study, differences were observed between inorganic P levels obtained by the sum of the different fractionated forms, and the inorganic P obtained using the  $H_2SO_4$  method.

#### **Conclusions**

- The phosphorus quantification method using molecular absorption spectrophotometry allows a high degree of confidence in the measures in the range 0.05 1ppm, which may be extended up to 3 ppm.
- The phosphorus fractionation method revealed the high levels of non-bioavailable forms that exist in the two areas of plantain cultivation, while the bioavailable forms are found at low levels.
- From the pH, these soils may be classified as neutral or lightly acidic, being optimal for the cultivation of plantain, but with problems of P solubility, especially P-Fe.
- The pH detected for these soils suggests a high dynamic in the apatite and non-apatite calcium phosphates, which dissolve most easily under these conditions.
- The largest proportion of total phosphorus in these soils comprised soil inorganic phosphorus (80%), while organic phosphorus only comprised the remaining 20%.
- In soils in the zone PM more forms of inorganic phosphate predominate than in the zone CM-CA.
- The phosphorus fractionation method proposed by Chang and Jackson extracts a part of the organic phosphorus in addition to the inorganic phosphorus.

## References

- Benavides, G. 1978. Fraccionamiento de fósforo en suelos de la Amazonia colombiana y estimación del grado de meteorización. Suelos Ecuatoriales 9(1):20-30.
- Boschetti, N.G; Quintero, C.E; Benavidez, R.A; y Giuffre, L. 2003. Cuantificación de las fracciones orgánicas e inorgánicas de fosforo en suelos de la Mesopotamia argentina, Ciencia del Suelo 21(1):8 p
- Bravo, G y Gómez, A. 1974. Capacidad de fijación de fósforo en seis unidades de suelo de la zona Cafetera Colombiana. Cenicafe 25(1):19-29.
- Chang, S y Jackson, M. 1957. Fractionation of soil phosphorus. Soil Sci. Soc. Am. J. 84:133-144.
- Fassbender, H. W. y Bornemisza, E. 1987. Química de suelos, con énfasis en suelos de América Latina. Costa Rica. Instituto Interamericano de Cooperación Agrícola (IICA). PAGINAS

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- Garavito, F. 1979. Propiedades químicas de los suelos. Instituto geográfico Agustín Codazzi (IGAC).
- Harrison, A. 1987. Soil organic phosphorus. A review of world literature. Reino Unido: CAB International. 257 p.
- Havlin, J; Beaton J; Tisdale S; y Nelson W. 1999. Phosphorus. En: Soil fertility and fertilizers. An introduction to nutrient management. 6<sup>th</sup> ed., USA: Prentice Hall. p. 154-195. .
- Hedley, M; Stewart, J y Chauhan, B. 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. Soil Sc. Soc. Am. J. 46:970-976.
- Holford, I. 1997. Soil phosphorus: Its measurement, and its uptake by plant. Aust. J. Soil Res. 35: 227 239.
- IGAC (Instituto Geográfico Agustín Codazzi). 1970. Propiedades químicas de los suelos. IGAC 10(11):323-360.
- Jackson, M. 1964. Análisis químico de los suelos. Barcelona. Omega. p. 243 244.
- Martínez, M. 1988. Algunos aspectos de la química del fósforo en suelos del Cauca. Suelos Ecuatoriales. v. 18(1).
- Miller, J y Miller, J. 1993. Estadística para química analítica. 2<sup>nd</sup> ed. E.U. Adisson Wesley Iberoamericana.
- Navarro, S y Navarro, G. 2000. Química agrícola: El suelo y los elementos químicos esenciales para la vida vegetal. Madrid. Mundi-Prensa.
- Olarte, R.; Muñoz, B.; Benavides, G.; Garavito, F.; Mejia, L.; y Rozo, E. 1979. Métodos de análisis de laboratorios de suelos. Instituto Geográfico Agustín Codazzi (IGAC). 4 ed. Bogotá.
- Ortega, T. 1978. Química de suelos. Universidad Autónoma Chapingo.
- Petersen, G; Rey, R. 1966. A modified Chang and Jackson procedure for routine fractionation of inorganic soil phosphates. Soil Sci. Soc. Am. J. 30:563-565.
- POT (Plan de Ordenamiento Territorial Alcaldía de Moñitos Costa Atlántica). 2001. Generalidades urbano – rural, componente urbano, cabecera municipal de Moñitos. Esquema de ordenamiento territorial del municipio de Moñitos. Córdoba EOT –MOÑI. Moñitos. 350 p.
- Skoog, D; Leary, J. 1994. Análisis instrumental. Madrid: McGraw-Hill. 4th.