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Soil fertility in calcareous tropical soils from Yucatan, Mexico, and Villa Clara, Cuba, affected by land use and soil moisture effects.

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Cuvillier Verlag Göttingen

Soil Fertility in Calcareous Tropical Soils from Yucatan, Mexico, and Villa Clara, Cuba, affected by Land Use and Soil Moisture effects.

Dissertation
to obtain the Ph. D. degree
in the Faculty of Agricultural Sciences,
Georg-August-University Göttingen, Germany

By

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Goettingen, February 2007

Bibliografische Information Der Deutschen Bibliothek
Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über http://dnb.ddb.de abrufbar.
1. Aufl. - Göttingen : Cuvillier, 2007
Zugl.: Göttingen, Univ., Diss., 2007

978-3-86727-143-1

D7

Referee: Professor. Dr. Holm Tiessen

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Date of Examination: 1st February 2007

Nonnenstieg 8, 37075 Göttingen
Telefon: 0551-54724-0
Telefax: 0551-54724-21
www.cuvillier.de

1. Auflage, 2007
Gedruckt auf säurefreiem Papier

978-3-86727-143-1

The process of scientific discovery is, in effect, a continual flight from wonder.

Science is the attempt to make the chaotic diversity of our sense-experience corresponds to a logically uniform system of thought.

Albert Einstein

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ACRONYMS AND ABBREVIATIONS.

ANOVA	Analysis of variances
CITMA	Ministerio de Ciencia, Tecnología y Medio Ambiente, Cuba
FAO	Food and Agriculture Organization of the United Nations
GmbH	Abbreviation used in the name of German companies that are legally established
Inc.	Abbreviation for Incorporated, used in the name of U.S. companies that are legally established
OMNILAB	Name of the company that provide laboratory equipments
PCA Ltd.	Name of the company that provide the ion exchange resins in sheet form
SPSS	Software for statistical analysis of data and name of the producer company
UNESCO	United Nations Educational, Scientific, and Cultural Organization
UNIDO	United Nations Industrial Development Organization
U.S.	United States of America

CHAPTER 1. SOIL FERTILITY IN CALCAREOUS TROPICAL SOILS: THE CASES OF YUCATAN, MEXICO, AND VILLA CLARA, CUBA.

1.1. INTRODUCTION

Soil fertility studies in the semiarid tropics, and particularly of calcareous tropical soils, are limited. Specifically, in semiarid regions exist an increasing pressure due to the population increase and the impacts of economic policies on land tenure. The assessment of the nutritional conditions of these soils may contribute to improve soil management. Suitable and sensitive techniques, which combine the influence of climatic factors and biochemical processes in the soil, permit a better understanding of these semiarid ecosystems.

This thesis deals with the problematic of semiarid calcareous soils from Yucatan, Mexico and Villa Clara, Cuba, which have low productivity. Problems related to phosphorus availability, cation imbalances, and water availability, have been reported in the literature as probable limiting factors in these soils (Weisbach et al., 2002, Vargas et al., 2003).

The aim is to establish the main chemical indicators of soil quality for these calcareous soils and evaluate the effect of management on soil fertility. More specifically, the work in this thesis focuses on the following points:

- Determine soil carbon and nitrogen contents, as well as the amounts of exchangeable calcium (Ca), magnesium (Mg), and potassium (K), in these calcareous soils under three different land uses from the semiarid tropic.
- Characterize phosphorus (P) in these soils based on its bioavailability to plants and microbes in these soils under contrasting managements.

- Evaluate the influence of soil moisture on the availability of five main nutrient ions (Ca, Mg, K, nitrate (NO_3^--N) and phosphate (PO_4^{2-}-P)) in these calcareous soils with different agricultural uses through incubation studies with ion exchange membranes.

1.2. LITERATURE OVERVIEW

1.2.1. Environmental concerns of calcareous soils in the semiarid tropics

The warm arid and semiarid tropics encompass very large areas of sub-Saharan Africa, Asia, and Latin America and the Caribbean, where populations are often relatively high (Sivakumar and Valentin, 1997). Semiarid ecosystems have soils that are considered to be problem soils, being highly susceptible to degradation. The phenomenon of land degradation involves an unfavorable alteration in one or all of soil's physical, chemical and biological properties and processes leading to loss of sustainable use (Abubakar, 1997), such as loss of organic matter, erosion, crust formation, structural decline, and sometimes salinity. Together they may be more significant than decreases in rainfall (Sivakumar and Valentin, 1997). Syers et al. (2002) considered soil degradation is an important factor affecting the sustainability of agricultural systems and remarked that nutrient depletion is one of the most important chemical processes involved in it, because nutrient supply is vitally important for crop production. A decreasing nutritional status of the soil has major implication for the sustainability of agriculture systems and future food supplies.

Calcareous soils are common in semiarid and arid climates, and occur as inclusions in more humid areas. The total extent of Calcisols is estimated at 800 million hectares worldwide, mainly concentrated in arid or Mediterranean climates. However, the total area of calcareous soils is difficult to estimate because many are salinized and do not key out as Calcisols (FAO, 2000).

Limestone soils are identified by the presence of the mineral calcium carbonate in the parent material, accumulation of lime, pH usually above 7 and may as high as 8.5. When these soils contain sodium carbonate, the pH may exceed 9. In some soils, $CaCO_3$ can concentrate into very hard layers, termed caliche (hardpan), that are impermeable to water and plant roots (Leytem and Mikkelsen, 2005). They are also characterized by high concentrations of bicarbonate ions in the soil solution and almost no exchangeable H^+ (Misra and Tyler, 1999).

The presence of free carbonates may cause nutrient deficiencies, excess nutrients, and nutrient imbalances resulting in losses of productivity (Kishchuk et al., 1999). High pH results in unavailability of phosphate, frequently the most limiting nutrient in these soils, and also reduces micronutrient availability, e.g. boron, manganese, zinc and iron. Availability of phosphorus is often the most limiting factor for plant growth in these soils (Leytem and Mikkelsen, 2005). The amount, nature and reactivity of carbonate minerals affect phosphate reactions in calcareous soils. Phosphorus is geochemically fixed in soils through its interactions with Ca, Al, and Fe, to form phosphate minerals or surface complexes. In arid ecosystems carbonate controls P retention and fixation in calcic horizons (Carreira et al., 2006).

Not only phosphorus is a limiting nutrient in calcareous soils, potassium and magnesium nutrition may be also problems as a result of the nutritional imbalance between these elements and calcium (Kishchuk et al., 1999 and FAO, 2000). Available Mg and K are sometimes in inadequate supply due to an imbalance between plant available Ca, Mg, and K ions. In these soils, the proportion of Ca to other exchangeable cations exceeds 80% and a low proportion of exchangeable Mg (less than 4%) and low exchangeable K, may lead to Mg and/or K deficiencies in crops (Hagin and Tucker, 1982 and Marschner, 1995 in Imas, 2000). In tropical soils, exchangeable K accounts for a variable percentage (0.5 - 50%) of total K of the soil (Baligar and Bennett, 1986).

The land use of calcareous soils is highly variable; ranging from deserts to intensively cultivated irrigation areas (FAO, 2000). They can be extremely productive for agricultural purpose when they are managed properly (Leytem and Mikkelsen, 2005). However, land management practices can also affect ecosystem function mainly due to their effects on microbial population or by temporal changes of chemical properties of the soils. For instance, slash-and-burn agriculture can induce an increase in plant-available nutrients through release from biomass and transfer into the soil environment with the ashes (Juo and Manu, 1996; Twosend et al., 2002). The quantities of the nutrient elements gained by the soil after burning depend not only upon the amount of each element in the ash but also the capacity of the soil to retain and store these nutrients in forms that are readily available to plants (Juo and Manu, 1996). Soil heating is a secondary mechanism of nutrient release in soils that experience slash-and-burn processes (Giardina et al., 2000). The heat can induce pyromineralization of the organic bound soil P causing the transformation of more resistant forms into plant available forms (Saa et al., 1993 in Lawrence and Schlesinger, 2001). Other studies have shown the effect of contrasting land-use systems on soil P fractions. Buehler et al. (2002) assessed P in a Colombian Oxisol under four treatments (two of them with fertilizer additions), and found that all fractions were strongly dependent on total P content of the soil, which was affected by the amount of P added as fertilizer and removed by plant uptake. In the two P-fertilized treatments most of the P was stored in the resin-Pi, Bicarbonate-Pi, and NaOH-Pi fractions, whereas in the two unfertilized the transfer of labeled ^{33}P into these inorganic pools was less clear suggesting that the soil Pi was much less exchangeable and the transference of labeled P into organic fractions was more important. Guo et al. (2000) reported the effect of exhaustive cropping on P fractions in eight Hawaiian soils. Their results suggest that resin Pi and $NaHCO_3$-Pi were the most sensitive fractions to plant removal in all soils. NaOH-Pi was the dominant fraction in the highly weathered soils, and also declined with plant removal. In contrast, residual P in the highly weathered soils is accumulated with plant removal, suggesting that it was unavailable to plants.

The erratic nature of the rainfall exerts a direct effect on soil moisture, and subsequently on nutrient availability. Limestone soils are commonly found in semiarid and arid regions, so, supplemental irrigation water is often the first barrier for crop production (Leytem and Mikkelsen, 2005). There are many recent studies on the relationships between precipitation and ecosystem processes in the semiarid tropics.

Phosphorus uptake by plants is influenced by soil moisture, being largely controlled by diffusion rates and P depletion in the rhizosphere (Gahoonia et al., 1994 in Misra and Tyler, 1999). Because phosphorus diffusion occurs in water-filled pore spaces within the soil, the volumetric soil water content is an important factor controlling diffusive flux (Kovar and Claassen, 2005), so the diffusive flux of phosphorus increase significantly as the soil moisture increases. Misra and Tyler (1999) studied the influence of soil moisture on soil solution chemistry in a limestone soil (Rendzic leptosol) and reported that phosphate concentrations increased with soil moisture, but most of this increase occurred above 70% water holding capacity (WHC). At low soil water content, the diffusion path is impeded, making phosphorus less available to plants, which was reflected also in nutrient content in biomass of calcicole plants according to the results obtained in this research.

Carbon (C) and N mineralization rates are highly susceptible to changes in soil moisture and drying-rewetting cycles (Fierer and Schimel, 2002). Schwinning et al. (2004) summarized the experimental approaches used to examine the implications of the seasonality in the semiarid tropics and its erratic rainfall in land degradation and nutrient cycling. They explained that soil moisture regimes regulate the mechanism of nutrient gain and losses in these environments where mineral and organic substrates tend to accumulate during dry periods. In these conditions, there is little nutrient demand, whereas the onset of the wet season leads to an excess of mineralization and denitrification increasing the losses of carbon and nitrogen from soil pools.

1.2.2. Climate, land uses, and soil fertility studies from Yucatan, Mexico and Villa Clara, Cuba

Yucatan, Mexico

The Yucatan peninsula, in southeastern Mexico, is completely south of the Tropic of Cancer. Throughout the peninsula a range of climatic vegetation complexes can be distinguished by the Köppen system, but the majority of the peninsula is considered a tropical dry forest (Aw) due to long periods of little to no precipitation. Annual precipitation ranges from 500-1500 mm (Benjamin, 2000), with the lower values in the North-West coast of the peninsula and values above 1200 mm in the South-East (Duch, 1988). Temperature in some moths may reach more than 40 ºC (Benjamin, 2000). The annual mean temperature is 26ºC (Duch, 1988).

The Yucatan peninsula, due to its physical and geographic characteristics, differs from the rest of Mexico because its biogeographycal relationships with the Antilles and the Caribbean region (Chiappy and Gama, 2004). The landscape of the peninsula can be described as unusual due to the dominant limestone bedrock found underneath a shallow soil surface layer, the lack of surface water and the presence of underground caves and rivers, but also sinkholes or cenotes, which are formed when limestone shelf collapses due to the dissolving process and expose the water below, throughout the peninsula (Benjamin, 2000).

The Yucatecan soils are formed from tertiary limestone on a typical karstic landscape of flat rocks outcrops and shallow depressions, giving a mosaic of black lithosols, which occur mainly on slightly elevated areas (<0.5m), and red rendzinas, which occur in depressions and are deeper (>20 cm) with a low gravel content. The differences in depth, stone content and high calcium carbonate content are closely related to their chemical properties (Weisbach et al., 2002).

Since pre-Columbian times, an assortment of agricultural and forestry systems have been used and adapted by Mayan settlements throughout the peninsula. Current Maya production systems include milpa farming, a shifting agriculture that co-exists with secondary forest, and homegardens (Benjamin, 2000). In Yucatan, one third of the soils (800 000 ha) is dedicated to the milpa, the traditional agriculture for maize associated with sweet potato, pumpkins, beans, and other legumes, and usually are cultivated for two years. Most of the areas need fallow periods between 15 and 25 years for restoration of soil fertility, but increasing population, changes in land tenure, and limited allocation has reduced fallow periods from around 20 years to less than 7, threatening the sustainability of the milpa ecosystems (Moya et al., 2003; Benjamin, 2000; and Weisbach et al., 2002).

Homegardens have been important to Maya cultivation for centuries. Nowadays, in the Maya villages in Yucatan, houses are surrounded by homegardens that mimic a complex structure of a mature forest with plants growing in multiple strata, and often, animals for household use. This ecosystem has been shown to be a productive use of the areas that surround people’s houses, providing fruits and vegetables for household consumption and also, for sale at a market (Benjamin, 2000). The constant inputs of resources in form of food, manure, “rich” soil “tierra de sarteneja” from the secondary forest, and human dwellings, and also, water management enrich the system as a site for plant growth. For this reason, Yucatecan homegardens could be described as a trap of nutrients (Andrist, 2003).

Soil fertility studies in Yucatan are limited mainly focused on the decline of soil fertility by cropping, but most of them present analytical problems and the quality of data is negatively influenced by the high heterogeneity of the soils (Weisbach et al., 2002).

Total soil carbon and nitrogen are very high in Yucatecan soils (Benjamin, 2000; Weisbach et al., 2002). Soil organic matter in Yucatecan forests averaged over 20%, which is higher than values (0.5 to 5%) for other tropical regions, and also N and P are much higher than those of other tropical dry forests (Ceccon et al., 2002). Weisbach et al. (2002) reported higher C and N content, and also a much greater accretion of soil organic matter in black soils, about twice that in red soils, even when both soils were under similar plant residue inputs explaining that this can be caused by a delayed decomposition of the plant residues or its concentration in the thin soil layer of the black soils. Higher organic matter content in black soils has been also reported by Bautista et al. (2003). These soils also differ in carbonate content, effective cation exchange capacity, primary P mineral and total P content. Red soils present lower content of all nutrients, indicating a more advance development (Weisbach et al., 2002).

Villa Clara, Cuba

The climate is tropical with a humid summer (Aw), prevailing in nearly the whole island with an alternating moisture regime. The rainy season starts in April-May and ends in November. Annual rainfall varies between 1000 and 1200 mm. Mean temperature is about 25 degrees and the hottest months are July and August and the coldest is January. Relative humidity is usually about 80% and can be near to 90% (Diaz Cisneros, 1989 cited by Villegas et al., 1994; CITMA, 2004).

Cuba, the largest island in the Greater Antilles, presented a complex geomorphology derived of its geological history (Russel et al., 2000; Soza et al., 2004; Kerr et al., 1999). The big island, where a limestone plain cover almost three quarter of its total surface (UNIDO et al., 2004), is part of a limestone platform related to the limestone areas of Florida, the Bahamas and the Yucatán (Chiappy et al, 2001).

In Cuba, agricultural surface is 62.7 % of all lands in the country, of which 76.8 % have diminished their fertility to very low levels. This has reduced potential crop yields at least in 30%. At the same time, desertification affects 14% of the country, principally in coastal areas (CITMA, 2004). Soil fertility is affected by erosion, sodicity, salinity and acidity problems, bad drainage and losses of organic matter (García and Perera, 1997; CITMA, 2004; Urquiza, 2002).

Brown calcareous soils [Orthi-Calcaric Cambisol in the FAO/UNESCO system according to Villegas et al. (1994) and Aleman et al. (2002)] account for 16% of the area of soils in Cuba (Urquiza, 2002). They have a great importance in Cuban agriculture and economy, because they cover a large area well distributed all over the island, and frequently have been used for sugarcane production; e.g. in Villa Clara they represented 32% of the area dedicated to sugarcane monoculture (Villegas et al., 1994).

The parent materials of these soils are calcareous rocks and sedimentary rocks with different carbonate content. In Santa Clara region, brown calcareous soils are developed from soft limestone and tend to contain residual carbonates and the presence of dolomite, differing from others developed in dryer areas of the country (east part), which present secondary carbonates (Cairo and Fundora, 1994). There are also serpentine minerals in the Santa Clara valley, which is surrounded by serpentinitic low hills with fersialitic soils developed over this serpentine rocks (Fundora, 1979; Torrecilla, 2005). Serpentine soils are characterized by the presence of lithogenic iron oxides, high magnesium and low calcium (Bonifacio and Barberis, 1999; Koide and Mooney, 1987).

Humus rich soils (Hyper-Calcaric Phaeozem in the FAO/UNESCO system according to Marin et al.,1994) represent 2 % of Cuban soils (Urquiza, 2002) and occur in different landscapes ranging from mountain to almost plains with an undulating relief, slopes from 5 to 10%, and frequently are associated with Cambisols (Brown calcareous soils). In mountain regions with slopes up to 20% the soils are associated with Ferrasols and Cambisols (Marin et al., 1994). These soils are formed from clay-marl (potter’s clay), and contain primary minerals through out the soil profile (Cairo and Fundora, 1994).

The original vegetation that covered these soils consisted of semi-deciduous tropical forests, but as a result of the deforestation at the beginning of the twentieth century, most of these areas are at present used for agricultural crops such as grains, vegetable, sugarcane and pasture, or converted to anthropogenic savannah with isolated patches of original vegetation and a degraded secondary vegetation consisting of semi-deciduous shrubs (Marin et al., 1994, Villegas et al., 1994), identified as woodlands. These formations appear together with grassland areas as agroforestry and silvicultural systems with multi-strata distribution (Vargas et al., 2003).

Cairo et al. (2004) studied the fertility of inceptisols under different tobacco-production systems in mountain areas in Villa Clara province. Tobacco has been cultivated under conventional agriculture systems for more than 60 years which has degraded the soils. These authors studied the change in physical and chemical soil properties in tobacco fields under conventional and ecological soil managements and found that those areas where the second management was applied physical and chemical properties improved, such as higher organic matter, water retention, and potassium availability, which was reflected in a yield increase of 0.23 t/ha.

In a preliminary evaluation of chemical fertility in a cattle agro-ecosystem on brown calcareous soil, Vargas et al. (2003) studied the effect of three treatments in soil fertility (silvicultural ecosystem formed by legume trees and gramineous grasses, natural grassland, and sugarcane monoculture). They measured organic matter content, phosphorus and potassium availability among other factors at two soil depth (0-10 cm and 10-20 cm) in brown calcareous soils from Santa Clara. These researches reported higher phosphorus content in a silvicultural ecosystem formed by grasses and legume trees compared to natural grassland and sugarcane monoculture, whilst potassium was superior in both pasture areas probably due to the enrichment with manure inputs. On the other hand, organic matter showed significant differences among the compared land uses at the lower depth, but the increase was significant only for the silvicultural ecosystem.

Other studies have been focused on efficiency of both inorganic and organic fertilizers. Aleman et al. (2002) evaluated the responses of different sunflower varieties to different fertilization doses with ammonium nitrate on brown calcareous soil from Santa Clara and reported that seed yield, as well as oil content and oil yield, do not vary with an increase of nitrogen fertilizers suggesting that annual mineralization of these soils, perhaps influenced by organic matter content and environmental conditions, produce enough nitrogen to fulfill sunflower nutritional demand. In another investigation, Caballero et al. (2001) tested the effect of manuring combined with chemical fertilizers on pepper yields growing in brown calcareous soils reporting an increase in yield at higher doses of combined organic and inorganic fertilizer.

1.2.3. Organic carbon and carbonates removal

Carbon is stored in oceans (38 000 Pg), atmosphere (730Pg) and terrestrial ecosystems, where 1500Pg are found in soils and 500 Pg in plants. By far, soil C stock is the largest “active” terrestrial carbon pool on Earth (John, 2003). Carbon in soils is present in two forms: inorganic and organic carbon (IC and OC, respectively). Calcareous soils present high amounts of carbonate minerals (IC) (Leytem and Mikkelsen, 2005), which have a great influence on soils because their solubility, their alkalinity, and their pH-buffering properties (Bisutti et al., 2004).

OC is present in the SOM in about 48-60% of the total weight (Bisutti et al., 2004). Soil fertility and nutrient availability are closely connected to the SOM content and its mineralization (Glaser et al., 2001). Therefore, several SOM studies focused in OC stocks (Caravaca et al., 1999; Glaser et al., 2001; John, 2003; Rudrappa et al., 2006). OC measurement is achieved indirectly or directly. In the indirect method, OC is obtained by mathematical subtraction of the IC from the TC content. However, this method is not suitable in soils rich in IC or poor in OC, because in such cases the result is derived from the subtraction of two large numbers. The direct method measure OC in two ways. In the first way a chemical oxidation is used to determine the OC content. The second one is based on IC removal by means of acid treatment prior measuring the OC. The goal of acid treatment is to eliminate IC from the matrix by decomposition of the carbonates. Carbonate mineralogy influences the time needed to complete the reaction between carbonates and acid. The acids generally used to remove IC are HCl, H_3PO_4, and H_2SO_3. HCl is generally used to estimate carbonate content in soils, because this acid reacts quantitatively with all carbonate present, except for siderite. Concentrated acid reacts quickly with calcite and aragonite, but slowly with dolomite (Bisutti et al., 2004).

The impacts of land use conversion on soil fertility in the semiarid tropics are largely unknown (Glaser et al., 2001). However, land use and soil cultivation can change the amount of SOM storage in the soil, because these storages are largely dependent on the amount and quality of the residue inputs (John, 2003). Therefore, OC and N stocks in soils may be good indicators of soil fertility in the semiarid ecosystems.

1.2.4. Phosphorus fractionation procedures.

Phosphorus (P) is an essential nutrient for plant growth and functioning. P biochemistry in soils is complex (Pierzynski, 2000) and is regulated by both biological and geochemical processes. In most natural ecosystems, the geochemical processes determine the long-term distribution of P in the soil, whereas in the short term, biochemical processes influence the distribution since most of the P available to plants is derived from the soil organic matter (Solomom and Lehmann, 2000).

In semiarid soils, when calcium carbonate ($CaCO_3$) is abundant in the soil profile, P availability is dominated by geochemical processes because of ligand exchange between P and carbonate minerals, and also due to the precipitation of phosphate with calcium (Lajtha and Schlesinger, 1988; Lajtha and Bloomer, 1988). Plant availability of P is determined by labile, surface absorbed or precipitated rather than by crystalline forms of phosphate. In calcareous environment, the availability is reduced by the low surface area of calcium phosphate, which is mainly present in sand and silt-sized particles (Stewart and Tiessen, 1987).

Only a small portion of the total soil organic matter may be biologically active (Stewart and Tiessen, 1987). This fraction is often overlooked, even when it may determine the availability of P to plants and exert a strong influence on the biochemical P cycle (Cross and Schlesinger, 2001).

The study of P transformations in soils has been facilitated by sequential extractions which separate Pi and Po into major chemical groupings, and into pools of different bioavailability (Agbenin and Tiessen, 1994). Since Hedley et al (1962), different procedures have been developed based on the bioavailability of P, which have been adapted to the specific conditions where they were applied. Pierzynski et al. (2000) compiled the techniques and methods using for P analysis in water, residuals and soil.

The Hedley et al. (1982) sequential extraction separates soil P into organic and inorganic fractions that vary their availability to plants. Exchangeable Pi is removed first with an anion exchange resin. Then, 0.5 M $NaHCO_3$ is used to remove “labile” inorganic and organic forms. At this step, inclusion of a second sample submitted to a chloroform treatment permits estimation of P originating from lysed microbial cells. Stable P forms are removed by stronger extractants as NaOH for Fe- and Al- phosphates, HCl for occluded phosphorus and H_2SO_4 for highly stable insoluble mineral P (Stevenson and Cole, 1999).

However, in tropical soils the efficiency of this sequential extraction has been limited by the large proportions of plant available P that remain unextracted and appears in the residual fraction. This required a modified sequence to characterize the residual P, which constitutes a substantial part of the total P (P_T) in tropical soils (Guo et al., 2000). Tiessen and Moir (1993) added a hot concentrated HCl extract to remove chemically resistant Pi and Po fractions, which are tightly bound to Fe and Al minerals and probably unavailable to plants and microbes.

Resin P is defined as freely exchangeable Pi, since the resin extract does not chemically modify the soil solution (Tiessen and Moir, 1993). The weakly sorbed organic and inorganic P removed using 0.5 M $NaHCO_3$ (pH 8.5) is likely to be plant available P, since the chemical reactions tend to mimic root respiration. Hydroxide-P extract is thought to remove P that is associated with the surface of Al- and Fe- minerals. Dissolved P from the $NaHCO_3$ and NaOH extracts is further separated into organic (P_o) and inorganic (P_i) forms through digestion of the organic matter and calculating P_o by subtracting the P_i value from the measured total P in the extracts (Cross and Schlesinger, 2001). The dilute HCl (1MHCl) is clearly defined as Ca-bound P (Tiessen and Moir, 1993). The concentrated HCl represent the stable pool that does not readily participate in P transformations (Agbenin and Tiessen, 1995) and the remaining P extract (H_2SO_4) represent the highly recalcitrant or inert fraction (Tiessen and Moir, 1993) that could be available to plants only over long time periods (Cross and Schelsinger, 2001).

Ruttenberg (1992) developed a method to fractionate the soil P. In this case, Pi forms were classified into three parts: (1) loosely bound by agitating the soil in 50 ml of 1 M $MgCl_2$ during two hours, centrifuging the soil and removing the supernatant through 25 mm filters, (2) Fe-bound P extracted with CDB (sodium citrate-sodium dithionite-sodium bicarbonate) (3) Ca-bound P extracted with 1M HCl shaking during 16 hours. Organic P is determined on residual material after ashing the sample at 500ºC (Levy and Schlesinger, 1999).

The contribution of soil biological processes to deliver plant-available P may be more important when availability of Pi is low. The decomposition of soil organic matter and plant residues is indeed often the main source of plant nutrients in low input small-scale farming systems in tropical areas (Bünemann et al., 2004). In tropical environments, organic P may provide a major source of available P, playing a substantial role in nutrient recycling (Linquist et al., 1997 in Cardoso, 2002). So, a fractionation of this pool could be advisable for characterization and interpretation of the P cycling. Nuclear magnetic resonance spectroscopy (NMR) is a relatively new approach for characterizing soil P. The major advantage of this technique is that information regarding organic forms can be obtained without resort to complex and time-consuming chromatographic procedures (Stevenson and Cole, 1999). Although promising, the technique still faces several methodological problems, such as the influence of paramagnetic ions (iron and manganese), which are especially important in tropical soils (Cade-Menun and Preston, 1996 in Cardoso, 2002). This technique has showed that most of the organic P that can be extracted from soils is present as monoesters (Duxbury et al., 1989).

All these procedures have been used widely and adapted or combined in function of the researches' interests and the specific conditions of the countries where they have been applied. For instance, Lathja and Schlesinger (1988) used the Hedley et al. (1982) procedure to characterize P fractions along a desert soil chronosequence using ground and unground soil. The aim was to determine if mineral surfaces that are exposed upon grinding contribute phosphorus that would not ordinarily be available to the soil solution. Only inorganic fractions were determined using this technique and the organic and microbial P was measured using the dry-ashing technique of Saunders and Williams (1955). They found that P fractions in ground and unground soil were very similar with no significant differences between the absolute amounts of both. Ca-bound pool was the largest fraction of the total P throughout the chronosequence. The organic and microbial P represented only a very small fraction of the total P, below the detection limits of the dry-ashing technique.

Sui et al (1999) utilized a modification of the methods of Hedley et al. (1982) and Tiessen and Moir (1993) to evaluate the effect of continuous biosolids amendments in a Mollisol. They used H_2O as the first extractant instead of equilibrating the soil sample with an anion exchange resin. The substitution was based on a preliminary study in the same soils that reported that an anion exchange resin was not required to extract detectable level of labile P from the studied soils. These researchers considered that water extract would be more closely related to bioavailable P in surface runoff from a soil than would resin-exchange. They avoided also the chloroform step from the Hedley et al. method (1982) used for estimating microbial P and followed the digestion procedure from Tiessen and Moir (1993) to determine organic P. Their results showed an increase in the concentrations of all P fractions at the 0-5 cm depth. However, at 5-20 cm depth some inorganic P fractions (H_2O-P, $NaHCO_3$-Pi, NaOH-Pi, and HCl-P) increased with depth as a result of biosolids amendments, but other pools decreased. No fraction was affected by biosolids amendments below 20 cm depth.

The effects of three different doses of chemical fertilizers (one-third, two-thirds and full recommended doses) and also, different combinations of chemical fertilizers and organic materials (ash and cow dung) on phosphorus fractions in wetland rice soils in Bangladesh was studied by Saleque et al (2004) using the modification of Sui et al. (1999) but they substituted the water extraction by 0.05 M $CaCl_2$ and maintained the digestion from Hedley et al. (1982) to determine organic pools. The distribution of P into the different pools was different for each treatment. An increment in the labile pools was reported for the treatments in which a combination of ashes and cow dung was applied together with chemical fertilizers, suggesting that manure application increase P lability in these soils.

Schlesinger et al. (1998) selected the Tiessen and Moir (1993) methodology to isolate P held in inorganic and organic pools, and bio-available and unavailable forms, in soils developing in volcanic ash deposited in Indonesia. Their results showed that most of soil P was retained in the HCl-extractable form, representing apatite. However, they detected a marked accumulation of organic P (especially in the OH-pool), which caused a shift from HCl-extractable form toward organic pools. Cross and Schlesinger (2001) also used Tiessen and Moir (1993) procedure to characterize phosphorus biochemistry in semiarid soils under grassland and shrubland in New Mexico, U. S. These authors reported that most of soil inorganic P was found in the 1M HCl- and concentrated HCl-extractable forms in both the grassland and shrubland soils, indicating that $CaCO_3$ dominate P cycling in these soils. Organic P accounted for 13.3 % of the total soils phosphorus in the grassland and 12% in the shrubland. However, these researches remarked that this small fraction is also important because of its influence on P availability by contributing to the labile inorganic pool.

The adoption of one of these methods is always based on the characteristics of the environment where the researches are working and also, the selected objectives for each research. Levy and Schlesinger (1999) compared Hedley and Ruttenberg fractionation effectiveness in 16 soils from undisturbed ecosystems. They found that when an index of plant-available P is desired the Hedley's procedure is effective in differentiating among soils and among organic fractions, which are recognized as controlling plant-available P in soils. On the other hand, Ruttenberg fractionation offers a useful separation of Ca-bound and apatite-bound P, which may be useful in arid lands containing both of these forms in high proportion.

Guo et al. (2000) studied the changes of P fractions induced in eight Hawaiian soils with different levels of weathering and under intensive agriculture. They followed the Tiessen and Moir (1993) method with slight modification in the resin strip step. They used a Fe-impregnated filter paper instead a resin in bicarbonate form. Resin-P and bicarbonate-Pi were identified as the most sensitive pools to plant withdrawal in all soils. NaOH-Pi also declined with plant P removal in all cases. In the less weathered soils HCl-P and residual P were the major P fractions, whilst in the highly weathered soils the dominant fractions was hydroxide-Pi. The results of this study revealed a strong interaction between cropping, weathering and P distribution into the different pools.

Cardoso (2002) estimated the effect of agroforestry systems and conventional coffee plantations on P pools in an Oxisol from Minas Gerais, Brazil. The Tiessen and Moir (1993) fractionation method was used with this purpose and also, a ^{31}PNMR (^{31} phosphorus nuclear magnetic resonance) study was included to identify the various compounds of Pi and Po. Based on the results of the different compounds, they reported that the agroforestry systems influence the dynamics of P through the conversion of part of the inorganic P into organic P, the effect being greater in the deeper layers than in the surface horizons.

Buehler et al. (2002) combined a sequential fractionation by Tiessen and Moir (1993) with isotopic techniques. They studied P fractions of a ^{33}P-labeled Oxisol under contrasting agricultural systems (native savanna, grass-legume pasture alternated with rice, continuous rice, and rice and green manure (cowpea) rotation). The recovery of ^{33}P in the treatments with annual fertilization (rice cropping) exceeded P outputs indicating that resin-P, bicarbonate-P and hydroxide-P represented most of the exchangeable P. The organic forms contained almost no exchangeable P. In contrast, in soils with low (rice-green manure) or no fertilization (native savanna) more than 14% of ^{33}P was recovered in NaOH-Po and HCl-Po fractions, showing the importance of organic P dynamics in these soils.

1.2.5. Ion exchange membranes.

Ion exchangers are insoluble inorganic or organic synthetic materials that contain labile ions that can exchange with other ions in the surrounding medium. Cation and anion exchangers are available in the form of resin beads, membranes or capsules (Salisbury and Christensen, 2000). For more than 40 years, ion exchange resins have been used to characterize nutrient bioavailability in terrestrial and aquatic ecosystems with general acceptance as a method for detection of soil nutrient levels, although methods of use and interpretation of their results are not uniform to date (Sherrod et al., 2003).

According to Qian and Schoenau (2000), the earliest use of ion exchangers to measure nutrient availability goes back to Pratt in 1951 and Amer et al. in1955. They explain that the first studies were conducted using ion exchange resins in bead form; however, the use of ion exchange resins in sheet or membrane form has also attracted researches' interest, since the work of Saunders in 1964, due to its simplicity in handling and use, and the ability to measure flux to an easily defined surface area. It also has the advantages of cost-effectiveness, because resin extraction is always a multi-nutrient extraction, and applicable in soils of different regions and in multiple-purpose agricultural and environmental studies. Saggar et al. (1990) developed a simplified resin membrane technique for determining the amount of phosphate extracted by membranes and compared the procedure with the common use of resin beads in nylon mesh bags, testing the technique with four New Zealand soils. They concluded that phosphate extracted by resin membranes is closely correlated with that extracted by the resin bags, and that the results were in proportion to the solubility of the P sources in each soil, and they also realize that the resin membrane procedure is simpler, more convenient, and less time consuming that the resin bead method. These authors combined the P elution and colour development steps together. They found that this effort was convenient for the resins-strips, but the resin-bags had to be eluted prior analysis thereby involved an extra step in the analytical procedure that they used.

Compared to conventional chemical extractions, which provide a static measure of the potential nutrient supply, ion exchange resins are effective for measuring nutrient bioavailability in both terrestrial and aquatic ecosystems providing integrated nutrient dynamics sensitive to environmental conditions (Sherrod et al., 2003). Moreover, resins offer a way to eliminate problems inherent to chemical extraction of soil. Nutrient recovery by *in situ* exchange resins, acting like plant roots, integrate nutrient availability and diffusion rates as affected by soil temperature, water content and biological activity (Salisbury and Christensen, 2000). Greer et al. (2003) explained that *in situ* ion exchange resins provide a dynamic measure of ion flux with climatic factors and could provide superior data on which to build an integrated soil-climate-plant model. Several resin methods have been developed for agricultural and environmental purposes, but in general, they can be grouped in two main categories: batch procedures and diffusion-sensitive systems in soil research.

In the first group are all the techniques where a certain amount of soil and resin (beads or sheet form) are mixed with abundant water and shaken for extended periods. The results of these techniques are strongly dependent on temperature, extracting time, and type and ionic saturation of the resin. In this category can be classified the techniques used for the sequential fractionation of phosphorus, also those used for assessing the bioavailable fraction of herbicides and their phytotoxicity in different soils types, and some microbiological studies for estimating soil microbial biomass and more recently, to sample soil microorganisms by shaking fresh soil with Na chelating ion-exchange resin in 0.1% NaCl solution to disperse soil and dissociate microorganisms from the soil particles (Qian and Schoenau, 2000).

Tiessen and Moir (1993) gave a detailed description of the batch extraction procedure using resin strips as the first step on a sequential phosphorus fractionation scheme. Mallarino and Atia (2005) also used this method for calibrating the phosphate absorption with corn yield response in U.S soils, comparing the results obtained with other routine soil tests. These calibrations are necessary to be able to use ion exchanger technique to predict crop response to phosphoric fertilization and environmental studies.

The diffusion-sensitive procedures measure both rates of release ions from different soil surfaces and their diffusion through the bulk soil. They integrate both chemical and biological transformations as well as diffusion to a sink into the measure of nutrient availability. Size, exchange capacity, resin type, time of exposure, soil moisture content, and soil temperature are some of the factors that affect adsorption kinetics in this technique. These techniques have been used for several purposes, such as, short-term and long-term measurement of nutrient supply rate in soil, assessing soil nutrient transformations, nutrient movement, and soil testing for fertilizer recommendations (Qian and Schoenau, 2000).

Soil moisture exerts a direct influence on soil solution chemistry and on nutrient availability to plants and microbes. Arid and semiarid ecosystems represent an extreme in which water availability creates a seasonal pulse on nutrient availability (Schwinning et al., 2004). As the soil becomes drier, the diffusion path becomes longer and more tortuous, as the large pores are no longer filled with soil solution. So, soil moisture is an important factor to consider in fertility studies in semiarid tropical soils (Qian and Schoenau, 2000).

Zeng and Brown (2000) examined the effects of soil moisture on mobility and fixation of K, maize growth and K uptake. A pot experiment was conducted during 16 days using two moisture regimes: constant moisture and wetting-dry cycles. Soil K mobility increased with soil moisture content, presenting a positive curvilinear relationship between gravimetric water content and diffusion coefficient, which suggest that more K can diffuse to the plant roots under sufficient moisture conditions. At the same time, they found that wetting-drying cycles enhanced K fixation and reduced available K pools in the soil, which was reflected in less K uptake by plants and a reduction in root and shoot growth.

In a field simulation study in the Chihuahuan desert, Fisher and Whitford (1995) measured nitrogen net mineralization using resin bags under wet and dry conditions. In one of the treatments, considered as control, soil water content was not manipulated. Rain exclusion reduced ion capture by resin bags. After allowing precipitation, ammonium capture was increased to more than double that in the cool-dry season, suggesting an increment in its availability. A hot, dry period was followed by a three to fourfold increase of NO_3^- and NO_2^- in the subsequent warm-wet season. They also performed laboratory incubations that suggested that N availability increase in dry conditions.

Pampolino and Hatano (2000) compared two soils under unsaturated (0.32 kg per kg of soil) and saturated moisture conditions (0.65 kg per kg of soil), in a laboratory incubation study with resin capsules for measuring phosphorus, potassium and nitrogen availability. They found that phosphorus and potassium availability were significantly lower under unsaturated conditions than when soils were saturated, showing a similarity to the absorption of these two nutrients by plant roots. However, although nitrogen availability was greater in saturated soils, the distribution of nitrate and ammonium forms varied with soil moisture, nitrate being the dominant ion under unsaturated conditions. Ammonium was mainly found when soil was at full saturation, probably because of the lack of oxygen in the soil. These authors also reported the influence of texture and its interaction with soil moisture in nutrient availability. Soil texture modifies ecosystem responses to precipitation through controlling infiltration depths, water holding capacities, and hydraulic conductivity for water (Schwinning et al., 2004).

The physical and chemical properties of both resin and soil are important factors influencing performance of the technique. Effectiveness of resins in soil studies are related to: (1) type of resin used, (2) chemical stability in the process of extraction and desorption, (3) counter-ion on/in the resin for ion exchange, which should be selected considering the pH of the soil, (4) moisture and temperature effects, (6) time of contact with soil, etc. (Qian and Schoenau, 2000). Some of these factors can be managed by researches in order to obtain better and more reliable results. Many commonly used counterions, such as H^+, HCO_3^-, and OH^-, can affect pH in the vicinity of the resins, which will in turn influence the solubility and /or soil release of certain elements (Sherrod et al., 2003). Both, the H-form for cation resin as well as the OH-form for anion resin, have been shown to work well because they have the lowest affinity to the resin. However, in calcareous soils the H-form is not suitable due to the formation of CO_2 and HCO_3^- when resin H reacts with $CaCO_3$. Another counter-ion widely used for anion exchange membranes is HCO_3^- because it mimics to a certain extent the HCO_3^- produced in the rhizosphere due to the respiration by plant roots and microorganisms (Qian and Schoenau, 2000). However, these authors reported that Kjønaas (1999) suggested HCO_3^- may not be a suitable counterion in acid soils with pH below 4.5. McLaughlin et al. (1994) chose Cl^- as counterion to study acidic soils in Australia. They explain that Cl^-, as bicarbonate, does not affect solution Ca concentrations. Besides, bicarbonate ions increase supernatant pH, which precludes extraction of Al and Mn from soils. Finally, for re-use, bicarbonate form required the regeneration from Cl^- form to the HCO_3^- form of the resin membrane after desorption and with the Cl^- this step is avoided.

Other aspects such as the length of resin exposure to soils should be selected considering the exchange capacity, nutrient availability, and the properties of the resin. Resin in membranes has generally lower exchange capacity than that of the same type of resin in bead form. Usually, a shorter residence time is applied in laboratory than in field conditions (Qian and Schoenau, 2000).

CHAPTER 2: SOIL ORGANIC MATTER INDICATORS AND EXCHANGEABLE CALCIUM, MAGNESIUM AND POTASSIUM.

2.1. ABSTRACT

Soil organic matter (SOM) and exchangeable base cations may identify a basic status of soil fertility. In our study, total and organic carbon (TC and OC), as well as total nitrogen (N) were measured by dry combustion with a CHNS analyzer (Model VARIO EL III, Elementar Analysensysteme GmbH, Hanau, Germany). Prior to OC determination, carbonates were removed by acid treatment with HCl by the methodology described by Echenique (2005). Exchangeable cations were determined through an extraction with 1M NH_4Cl *and a subsequent correction of this one with a water extraction. Our results showed that the interaction between the land use and soil type was a determining factor for IC, OC and total N contents in these ecosystems. Mexican black soils from forests and milpas presented the highest IC, OC, and N, followed by the black soils from homegardens. Red soils had less IC, OC and N compared to the black ones. In the Cuban sites, the woodland from the brown calcareous soil presented the highest IC, OC, and N contents, followed by the woodland and the pasture area in the humus-rich calcareous soil. Yucatecan black soils from forests presented the highest concentrations of exchangeable Ca followed by the black soils from milpa. However, Mg was affected only by land use, being higher in soils under forest use. In Cuban soils, Ca was higher in the sugarcane area from the humus-rich calcareous soil. As well, exchangeable Mg was higher in all sites from the brown calcareous group than in the humus-rich calcareous soil. On average, the difference was around 78% more exchangeable Mg. These differences between both soils were strongly marked by their mineralogical properties. In addition, exchangeable K was determined by management; although their levels were too low as much in Cuban as in the Mexican ecosystems. The highest K content was found in homegardens and pasture, respectively, suggesting that soil enrichment in K was due to manure and organic amendments. Moreover, the low levels of exchangeable K may be a limiting factor in these calcareous soils. Summarizing, we can affirm that land use, soil type, as well as the interaction between both factors influenced SOM and exchangeable Ca, Mg and K levels in these calcareous soils.*

Keywords: *carbon, nitrogen, calcium, magnesium, potassium, calcareous soil, semiarid tropic.*

2.2. INTRODUCTION

The understanding of nutrient cycling in dry tropical regions is far from complete (Campo et al. 2000). However, there is a clear evidence that land use change can alter soil fertility (Shang and Tiessen, 2000; Glaser et al., 2001; Echenique, 2005; Breuer et al., 2006). Soil organic matter (SOM) plays a crucial role in the development and maintenance of soil fertility, mainly through the cycling, retention, and supply of plant nutrients (John, 2003). Changes in agricultural practices often influence both the quantity and quality of SOM and turnover rates (Rudrappa et al., 2006). Traditional soil properties as carbon (C) content has been considered as sensitive to land use change as sophisticated physical fractionation schemes. As both C and N cycles are tightly coupled, a change in one has a direct influence on the other (Breuer et al., 2006), and therefore, both may affect the SOM status.

Basic cations such as Ca, Mg, and K play important roles in a variety of plant functions. Soil fertility and productivity may be limited by low availability of these cations (Campo et al. 2000). Weisbach et al. (2002) reported low levels of K in the Yucatecan soils limiting their productivity. In calcareous soils, exchangeable Mg and K are usually low, due to an imbalance between plant available Ca, Mg, and K ions. The proportion of Ca related to the others base cations may be more than 80%, whereas exchangeable Mg could be found at levels as low as less than 4% (Hagin and Tucker, 1982 and Marschner, 1995 in Imas, 2000), and exchangeable K accounts for a variable percentage (0.5 - 50%) (Baligar and Bennett, 1986).

The objective of this research was to estimate how land use influences on IC, OC, and N content as indicators of the SOM in these soils. In addition, we assessed the levels of exchangeable Ca, Mg and K. Both measurements permitted to establish a base line of soil fertility in these calcareous tropical soils.

2.3. MATERIALS AND METHODS

2.3.1. Site selection and soil sampling.

For this study, four tropical calcareous soils were selected. Two of them were collected in Mexico and the other two in Cuba.

Mexican sites.

In Mexico, the study sites were located in Yucatan. The Yucatan peninsula is completely south of the Tropic of Cancer (23° 27’ N latitude) and has a tropical climate Aw due to the long periods of little to no precipitation. Annual mean temperature is 26ºC. The hottest period is from April to June, in which temperature may have maximum temperatures of more than 40° C (Duch, 1988). Annual precipitation for the greater part of the peninsula ranges from 500-1500 mm. Precipitation throughout the year is uneven and can be highly unpredictable. Average rainfall probability is never more than 50% and ranges from 31-49% (Benjamin, 2000).

Samples were collected in Xmatkuil and Dzibilchaltun, near Merida, the capital city located in the northwest of the peninsula, and Hocaba municipality. Hocaba is 56 km south of Merida. The mean temperature in Merida and surrounding areas, as well as in Hocaba, is 26° C. The mean annual rainfall is 1000 mm in the Merida zone and 980 mm in Hocaba. The dry season lasts from October to May and rainfall is erratic both spatially and temporally (Duch, 1988; Weisbach et al., 2002).

The soils were Kankab and Tzekel according to the Maya classification. These are calcareous soils derived from limestone, with red and black color respectively. Kankab series are known in the FAO classification as a luvisol or redish brown rendzina (Benjamin, 2000, Weisbach et al. 2002). They are high in calcium carbonate from the limestone parent material and generally found at the bottom of the slopes. Tzek’el soils are very thin and contain many rocks. There are considered inferior for agriculture activities and are derived from the decomposition of organic and residual materials on surface outcrops of limestone bedrock. In the FAO classification, they are known as Lithosols, and as Entisols in the USDA systems classification (Benjamin, 2000, Weisbach et al. 2002).

Three land-use managements were selected for these soils: forest, milpa and homegarden systems. Three areas of each land-use were sampled, and 10 soil samples were collected in each land-use area (5 red and 5 black soils) using a randomized design stratified on soil color. Sampling depth was 10 cm. In total, 90 samples were collected (Table 2.1).

Table 2. 1. General description of the Mexican ecosystems.

Land-use	Soil Type	pH	Location	Time under this land-use	Vegetation
Milpa	Red	7.8	Xmatkuil Hocaba	2 - 4 years	Maize and beans, and pumpkins
	Black	7.9			
Homegarden	Red	8.2	Hocaba	>15 years	Native tree species, shrubs and herbs
	Black	8.2			
Forest	Red	8.5	Xmatkuil Hocaba Dzibilchaltun	15 - 25 years	Deciduous vegetation with native species
	Black	8.0			

Forest areas were located in Xmatkuil, Dzibilchaltun and Hocaba. Milpa sites were chosen in Xmatkuil (2 sites) and Hocaba (1 site). All the homegardens were selected in Hocaba town. Vegetation varied in function of the land use. Different combinations of maize with beans and vegetables were found in milpas. Homegardens presented multi-strata vegetation formed by native trees, shrubs and spices. The secondary forests showed typical semi-deciduous vegetation composed of native trees and shrubs in different stages of growth. In the particular case of Hocaba forest, isolated henequen plants remained from former henequen plantations in this area.

Cuban sites.

The Cuban climate is tropical with a humid summer (Aw) and dry winter (Diaz Cisneros, 1989, cited by Villegas et al., 1994). The rainy season starts in April-May and ends in November. Annual rainfall varies between 1000 and 1200 mm. Mean temperature is 25 degrees. The hottest months are July and August and the coldest is January. Relative humidity is usually about 80% and could shows higher values near to 90% (Marin et al., 1994; Villegas et al., 1994).

The Cuban sites were located at the Villa Clara province, in the center of the island. The soils were identified as brown calcareous and humus-rich calcareous soils, both derived from limestone. These brown calcareous soils were classified as Orthi-Calcaric Cambisol in the FAO/UNESCO system (1989) and Typic Eutropept in the USDA/SCS Soil Taxonomy (1992), according to Villegas et al. (1994) and Aleman et al., 2002). In the case of the Humus–rich soils, the FAO/UNESCO (1989) system classified them as Hyper-Calcaric Phaeozem and in the USDA/SCS Soil Taxonomy (1992) they are identified as Entic Haplustoll, as mentioned Marin et al. (1994). Both have great importance in Cuban agriculture and economy because they cover a large area of the island and also are well distributed through out the country. They are frequently used for sugarcane, a wide number of minor crops, and animal husbandry (Marin et al. 1994, Villegas et al. 1994) Brown calcareous soils were located in Santa Clara valley and the humus-rich calcareous soils in rural areas of Ranchuelo municipality. A description of the vegetation, as well as other data, is presented in Table 2.2.

Table 2. 2. General description of the Cuban field sites.

Land-use	Soil type	Soil pH	Location	Time under this land-use	Vegetation
Sugarcane monoculture	Brown calcareous	6.2	Santa Clara	>30 years	Sugarcane monoculture
	Humus-rich calcareous	8.0	Ranchuelo	>30 years	Sugarcane monoculture
Pasture	Brown calcareous	8.1	Santa Clara	2 years, previous used for intensive agriculture.	Leucaena leucocephala L. and stargrass (Cynodon spp.).
	Humus-rich calcareous	7.9	Ranchuelo	>40 years	Natural grassland with few native trees.
Woodland	Brown calcareous	6.6	Santa Clara	52 years	Native secondary vegetation mixed with exotic trees (Woodland from the Botanical Garden).
	Humus-rich calcareous	8.0	Ranchuelo	30 years	Cedar, Majagua, Mango, guava, lemon, royal palm, and coconut.

For each soil, three different land-uses were sampled: Sugarcane monoculture, Pasture (abandoned and artificial grasslands), and Woodland (the isolated patches of natural and secondary vegetation). Sampling was done following a random design, at a number of 10 samples per site (replications) for a total of 60 samples. Sampling depth was 10 cm.

All Cuban and Mexican samples were air dried; 2-mm sieved and packed in hermetic plastic bags for shipping to Germany. In Germany, the preparation for the laboratory analyses consisted in grinding the samples in a ball-mill, drying in the oven at 40°C and storage in the oven at 26°C until the analyses to avoid the re-moistening of the samples under the German climatic conditions.

2.3.2. Laboratory analyses

Samples were analyzed for total and organic carbon, total N and exchangeable Ca, Mg and K.

Total (TC) and organic (OC) carbon, as well as, total nitrogen (N) were measured by dry combustion with CHNS analyzer (Model VARIO EL III, Elementar Analysensysteme GmbH, Hanau, Germany). For TC and N, 60-mg air-dried soil, ground in the ball-mill, were placed into tin caps. The tin caps were closed hermetically and stored in dry conditions until measurement. OC content was determined after removal of carbonates by acid treatment with HCl following the methodology described by Echenique (2005). HCl is generally used to estimate carbonate content in soils. This acid reacts quantitatively with all carbonate present, except for siderite. Concentrated acid reacts quickly with calcite and aragonite, but slowly with dolomite (Bisutti et al., 2004). Inorganic carbon (IC) was determined indirectly, as the difference between TC and OC.

For removing the carbonates, a 2-g sample of dry soil was placed in a petridish and moistened with pure water to field capacity and placed in desiccators (7 samples per desiccator). Before, small beakers with concentrated HCl (30%) in a proportion of 8.6 ml acid/g soil were placed in the bottom of three desiccators, so only acid vapors reacted with soil particles. The desiccators were left overnight in 40°C water-baths. After overnight treatment, samples were tested pouring a drop of 2M HCl and observing the appearance of bubbles indicating the presence of carbonates. If this happened, sampled were left 6 hours more under acid vapor treatment and then checked again with 2M HCl before to continue with next step. In this case, samples were remoistened when was necessary. After the acid vapor treatment, soil samples were transferred into 100-ml flasks and washed with 50 ml of 2MHCl for removing residual carbonates in some samples. If foam thickness exceeded 2 cm the procedure was repeated from the beginning. The suspensions were hand shaken and caps were removed for releasing pressure and finally caped flasks were placed in the mechanic shaker and shaken for 2 hours at 150 rpm. After that, the samples were dried in the oven at

40°C and prepared in the same way that the samples for total carbon and nitrogen and measured in the CHNS analyzer (Model VARIO EL III, Elementar Analysensysteme GmbH, Hanau, Germany).

For the effectiveness of this methodology, the good moistening of the soil samples was considered as essential by Echenique (2005). So, field capacity (FC) was determined gravimetrically prior to carbonate removal. For that, 10g of soil were placed into a bottomless glass-tube and pressed gently. Then, deionized water was added until reach saturation (15 ml for red soils, 25ml for black soils, and 20ml for both Cuban soils). The bottom of the tube was covered with one layer of parafilm still permitting soil drainage. Then, deionized water was added until saturation. Samples were let stand overnight for water infiltration. At the second day, soil samples were weighed every two hours until the variances in weight were too small. The weight difference between this saturated point and dry conditions were considered as the volume of water needed to reach field capacity in these soils.

Exchangeable Ca, Mg and K were determined by an extraction with 1M NH_4Cl and a correction with a separate water extraction. The 2g-soil samples were mixed with 20 ml 1M NH_4Cl and shaken in an oscillatory shaker during one hour. Then, the samples were centrifuged during 4 minutes at 3000 rpm and decanted into 100-ml flasks. This procedure was repeated 3 times and finally more 1M NH_4Cl was added to make volume. The extracts were kept at 4°C until the analyses. The same procedure was repeated for the extraction with deionized water instead of 1M NH_4Cl. Afterward, the results from the water extraction were subtracted from the 1M NH_4Cl extractable cations to obtain the exchangeable ones. Ca^{2+} and Mg^{2+} were determined by atomic absorption and K^+ by flame emission spectroscopy in the NOVAA 315 stand alone Flame AAS (Analytic, Jena AG, Germany).

2.3.3. Data processing and statistical analyses

OC was determined using the formula developed by Echenique (2005). TC data of the carbonate-free samples were converted into OC g kg^{-1} by the following formula:

OC (g kg^{-1}) = [soil free of $CaCO_3$ (g)/ whole soil (g)] x TC of $CaCO_3$-free samples (g kg^{-1})

IC was calculated as:

IC (g kg^{-1}) = TC (g kg^{-1}) of the sample – OC (g kg^{-1}) determined as described above.

For all cations, the readily exchangeable value was determined using the next formula:

Exc.Cation (mmol kg^{-1}) = NH_4Cl extractable cation (mmol kg^{-1}) – H_2O extractable cation (mmol kg^{-1})

Cuban and Mexican soils were analyzed independently considering the differences in soil management and land uses between both countries. For the analyses, data was arranged by soil type and land uses.

Statistical analyses were done with SPSS 9.0 (SPSS Inc., Chicago). Data were tested by two-way ANOVA with the factors land use and soil type, for determining the possible interaction between both factors. Subsequently, whenever the two-way ANOVA indicated significant interactions for $P<0.05$, the results were analyzed by one-way ANOVA for red and black soils independently. If the interactions were not significant, the analyses were done for the significant factor (land use and/ or soil type) without distinctions regarding soil type or land uses. Differences between red and black soils were confirmed by T-test. The same procedure was done for humus-rich calcareous and brown calcareous soils from Cuba. Comparisons were performed using Fisher protected LSD test (FPLSD).

2.4. RESULTS AND DISCUSSION

2.4.1. Carbon and Nitrogen.

IC, OC, and N content in Mexican and Cuban soils were influenced by land use and soil interaction (Table 2.3). In the Mexican group, the black soils from forests and milpas presented the highest OC and N, followed by the black soils from homegardens. Red soils had less IC, OC and N compared to the black ones, independently of the land use adopted. No significant differences were found among land uses for OC, but total N was also higher in forest than in the other two land uses. Carbonate content in Mexican soils was about 70% higher in black soils than in the red group. Especially in milpas and forest the differences in IC were above 70%. In homegardens, the differences were less pronounced, only 40%. In addition, N was 59%, 54%, and 32% for milpas, forests, and homegardens, respectively. The C/N ratios for OC varied among the different sites, ranging from 7.1 to 11.6. The highest C/N ratio was found in red soils from homegardens and the lowest in black soils from milpas.

The larger OC and N content in forests agreed with other studies in calcareous soils from the semiarid and other regions. In Yucatan, red soils are preferred by the farmers for cropping because they are easier to work than the black ones (Weisbach et al., 2002), so they had more losses in OC and N compared to black soils. As well, homegardens presented less OC and N stocks. Benjamin (2000) described Yucatecan homegardens are small areas, used as intensive agroecosystems, where yields are increased based on inputs from other areas such as milpas, forest, and household garbage. In contrast with other ecosystems and agroecosystems with the same plant diversity and structure, litter input to soil in Yucatecan homegardens is low. One probable reason may be the continuous sweeping and burning of litter, which made inefficient the nutrient cycling. Also, the management of vegetation, improving fruit production with less investment in leaf biomass may be considered for explaining these results (Benjamin, 2000). Caravaca et al. (1999) reported high differences in C content at the first 20 cm in calcareous soils under cultivation and forests from the

Mediterranean zone in Spain. Cultivated soils ranged from 4.4 to 18.1 g kg^{-1}, whereas the areas covered by forests presented TC contents from 34.7 to 61.1 g kg^{-1}. Glaser et al. (2001) compared the effect of land use changes on C and nitrogen mineralization in soils from the semiarid region of Northern Tanzania. They found that OC and N contents were significantly higher in soils of the native savanna woodland than at any other site apart from the soils amended with manure. OC decreased by 56% within 3 years after conversion from natural savanna to agricultural lands. However, the degraded woodlands and the recently cleared fields showed high nitrogen mineralization in comparison with the native savannas due to the large stable nitrogen pools despite the strong reductions of the labile N pools. Since residues are burned or decomposed in the field, a flush of nutrients and C are released into the soil during the post-burning phase (Garcia-Montiel and Neill, 2000, in Echenique, 2005).

Land use not only controls the magnitude of SOC stocks, but also influences the composition and quality of SOM. Helfrich et al. (2006) compared the quality of the residues from spruce, maize, and grassland areas and found that the maize residues contained the largest proportion of easily decomposable carbohydrates. This may suggest high bioavailability and fast turnover of the SOC in the milpa areas. On the other hand, Vitousek (1984) summarized several studies of nutrient cycling and litterfall in tropical forests. He found high rates of mineralization reported and also realized that N was not limiting in most lowland forests. The relative abundance of leguminous trees in the tropical flora was identified as the probable explanation for this. Moreover, in lowland forest, the decomposition rates are high enough for organic N to be returned to the forest floor for several times in a year.

Table 2. 3. Carbon and Nitrogen in Mexican and Cuban ecosystems.

Mexico

Land use	**Soil**	**OC**	**CO_3**	**N**	**OC/N**
			------------------------ g kg^{-1} --------------------------		
Milpa	Red	52	15	6.3	8.3
	Black	109	71	15.3	7.1
Forest	Red	61	18	7.4	8.2
	Black	133	56	16.0	8.3
Homegarden	Red	55	29	5.1	10.8
	Black	73	48	7.5	9.7
FPLSD	Red	ns	3	0.7	
	Black	15	8	1.6	
P		0.001	0.000	0.000	

Cuba

Land use	**Soil**	**OC**	**CO_3**	**N**	**OC/N**
			------------------------ g kg^{-1} --------------------------		
Sugarcane	Humus-rich calcareous	20	10	2.6	7.8
	Brown calcareous	21	5	2.5	8.2
Pasture	Humus-rich calcareous	25	15	3.3	7.6
	Brown calcareous	15	9	1.8	8.5
Woodland	Humus-rich calcareous	24	19	3.4	7.1
	Brown calcareous	36	33	4.4	8.1
FPLSD	Humus-rich calcareous	2	2	0.2	
	Brown calcareous	1	1	0.1	
P		0.000	0.000	0.000	

Within the same column and considering the same soil type, differences > FPLSD are significant at $P<0.05$. Abbreviation “ns” means not significant differences at $P<0.05$. In the last row, is reported the significance of the interaction between land use and soil type.

Our results also evidence strong differences between both Yucatecan soils. Beach (1998) reported large differences between red and black soils from northwest Yucatan. This author reported 0.7% $CaCO_3$ and 0.24% $CaMg(CO_3)_2$ content in red soils, whereas the black group presented 28.% $CaCO_3$ and 7.6% $CaMg(CO_3)_2$ content. Weisbach et al. (2002) studied the effect of fallow cycle on soil fertility in these Mexican soils. They also reported differences between black and red soils in OC, N, and carbonate contents. On average, black soils presented 54% more OC, 48% more N, and 69% more carbonates than red soils. These authors also found that organic matter content was reduced in both Yucatecan soils after the end of the fallow cycle (12 yr). This depletion accounted for 30% of OC and 20% of N in red soils, whereas in the black group OC and N were reduced by 26 and 21%, respectively. They also observed that, under similar plant inputs, the increment of SOM in black soils was twice as high as the red group. The large accumulation of SOM in black soils under fallow indicated that decomposition may be limited in these soils. It has been assumed that, even in semiarid areas, rates of SOM turnover and mineralization are generally greater in tropical than in temperate soils (Shang and Tiessen, 2000). However, Echenique (2005) suggested that the extremely high carbonate content in these soils may be acting as a factor of the SOM stabilization impeding its mineralization, which may influence negatively on nutrient availability for plants and productivity.

In the case of the Cuban soils, the woodland from the brown calcareous soil presented the highest OC, and N contents, followed by the woodland and the pasture area in the humus-rich calcareous soil (Table 2.3). Both sugarcane areas and the planted grassland in the brown calcareous soils showed less content of total N and both C forms. OC presented a complex picture where land use and soil interaction did not show a clear trend. The highest OC content was found in the woodland from the brown calcareous soils. This was followed by the woodland and pasture from the humus-rich calcareous soil in this order. However, sugarcane areas from both soils did not present any difference and the pasture area in the brown calcareous soil had the lowest OC content. The carbonate content varied among sites with lower amounts in sugarcane areas from both soils and in the pasture and woodland areas from the brown calcareous soil. On average, humus-rich calcareous soil presented 42% more carbonate than the brown calcareous group. On the other hand, N was significantly higher in the woodland from the brown calcareous soil, followed by woodland and pasture areas in the humus-rich calcareous soil. The pasture in the brown calcareous soil showed the lowest N content, as a consequence of degradation from previous land uses. The

C/N ratios for OC in Cuban areas ranged from 7.1 to 8.5 and varied among land uses within the same soil type, although in the humus-rich calcareous the variation is greater than in the brown calcareous group.

The higher C and N contents in woodlands areas may be attributed to litterfall. In woodlands, litterfall accumulation is higher than in the pasture and sugarcane areas. Litterfall has been recognized as the main pathways for nutrient cycling in semiarid forests, because its nutrients may be decomposed and cycled several times in a year (Vitousek, 1984). However, Markewitz et al. (2004) explain that, in some tropical ecosystems, grass turnover may substitute litterfall return as the predominant pathway of nutrient cycling. Neil et al. (1997) found similar amounts of C and N in the top 10 cm pasture and forest soils in the southwestern Brazilian Amazon Basin. But the evidence of changes in soil organic matter stocks caused by conversion from forest to pasture are variable, increasing in some areas and decreasing in others (Neil et al., 1997; Echenique, 2005). The grassland in the humus-rich calcareous soil presented similar OC and total N that the woodland in the same soil type. The pasture area in the humus-rich calcareous soils has been used with this purpose for more than 30 years (Table 2.2). In contrast, the pasture area in the brown calcareous soil presented the lowest amounts of OC, and total N. This area was severely degraded due to its use for intensive agriculture during more than 20 years. Two years before this study, it was converted to grassland with the purpose of reclaiming the soil. These differences in previous land use and the time under the present farming systems explain the contrast between these sites. In some cases, pasture implementation may have a minimal impact or can increase SOM content. The amount and quality of both above- and below-ground biomass incorporated to the SOM can contribute to maintain OC content with time (Echenique, 2005). Vargas et al. (2003) studied OM content at two depths (0-10 am and 10-20 cm) in brown calcareous soils from Santa Clara with different land uses (sugarcane, pasture, and legume-forage fields). They found that the natural grassland and the legume-forage field had higher OM content than the sugarcane area at both depths. Their results suggested that either natural or artificial grassland may preserve higher SOM and OC stocks than areas under intensive agriculture.

The intensive agriculture in sugarcane areas in Cuba, as well as in the pasture area from the brown calcareous soils that is degraded from previous uses, may lead to depleted OC and N in soils. Shang and Tiessen (2000) studied the turnover and stabilization of SOM in semiarid tropical Haplustox derived from marine sediments in northeastern Brazil. They found that, after twelve years of cultivation, C content was reduced 28% compared to the initial levels in the natural forests. Helfrich et al. (2006) explain that cultivation of virgin soils results in a decrease in soil organic carbon (SOC) and total nitrogen (N) content because tillage breaks up large macro-aggregates and exposes some labile organic matter to microbial attack. Six et al. (1999) reported that C sequestration in no-tillage areas was greater than in fields with conventional tillage due to tillage influence on the stability of the micro- and macro-aggregates. In addition, inorganic amendments may lead to an increase in SOM. Mineral fertilization changes the amount of C allocated beneath the ground, but the relative amount of belowground assimilated C decreased due to N fertilization. This indicates that measures to optimize aboveground plant growth and total fixed C (total dry mass production) result in a decrease of belowground translocated portion of assimilated C (John, 2003).

The differences between both soils are mainly influenced by their mineralogy. Humus-rich soils are shallow soils (Marin et al., 1994), forming from clay-marl (or potter’s clay) and have primary carbonates through out the soil profile (Cairo and Fundora, 1994). In contrast, brown calcareous soils from the central Cuba range from moderately deep to deep soils (Villegas et al., 1994) and present mainly residual carbonates (Cairo and Fundora, 1994). Also, humus-rich calcareous soils may have double the organic matter content compared to brown calcareous soils (Cairo and Fundora, 1994). Humus-rich calcareous soils are distinguished by the presence of a humus-rich horizon as result of humus accumulation, which is one of the dominant soil forming processes in these soils. This process is strengthened by the seasonal moisture regime and high calcium and clay content due to the sialitization inherited from the carbonate rock (Marin et al., 1994)

Table 2. 4. Exchangeable cations (NH_4Cl extractable cations – H_2O extractable cations) in Mexican and Cuban sites.

Mexico

Land use	**Soil**	**Ca**	**Mg**	**K**	**Ca:Mg:K**
		----------------------- mmol kg^{-1}	------------------------		
Milpa	Red	4.2	0.44	0.19	20:2:1
	Black	5.9	0.62	0.17	40:4:1
Forest	Red	4.7	0.65	0.18	28:4:1
	Black	6.8	0.78	0.14	54:6:1
Homegarden	Red	3.8	0.57	0.26	14:2:1
	Black	4.0	0.51	0.29	16:2:1
FPLSD	Red	ns	0.06	0.02	
	Black	0.4	0.11	0.05	
P		0.000	ns	ns	

Cuba

Land use	**Soil**	**Ca**	**Mg**	**K**	**Ca:Mg:K**
		----------------------- mmol kg^{-1}	------------------------		
Sugarcane	Humus rich calcareous	8.5	0.23	0.16	38:1:1
	Brown calcareous	4.5	0.88	0.06	70:14:1
Pasture	Humus rich calcareous	6.8	0.35	0.30	20:1:1
	Brown calcareous	5.8	0.67	0.14	45:5:1
Woodland	Humus rich calcareous	7.2	0.31	0.20	46:2:1
	Brown calcareous	2.0	2.54	0.07	36:36:1
FPLSD	Humus rich calcareous	0.2	0.04	0.04	
	Brown calcareous	0.1	0.09	0.01	
P		0.000	0.000	ns	

Within the same column and considering the same soil type, differences > FPLSD are significant at $P<0.05$. Abbreviation “ns” means not significant differences at $P<0.05$. In the last row, is reported the significance of the interaction between land use and soil type.

2.4.2. Exchangeable Ca, Mg, and K.

The levels of exchangeable Ca in Mexican soils were influenced by soil type and land use interaction (Table 2.4). Black soils from forests presented the highest concentrations of exchangeable Ca and were followed by the black soils from milpa. Homegardens showed the lowest values of exchangeable Ca. No significant differences were found among land uses in the red group. As well, Mg and K were determined by the single factor land use (Figures 2.1 and 2.2). No significant interactions between land use and soil were found for these two nutrients. Mg concentrations were higher in soils under forest use, whereas K showed the higher concentrations in homegardens. Weisbach et al. (2002) reported significant differences between black and red soils in exchangeable Ca and Mg, but not for exchangeable K. However, these authors assessed the soils under different periods of fallow, but they did not evaluate the incidence of different farming systems as in our case.

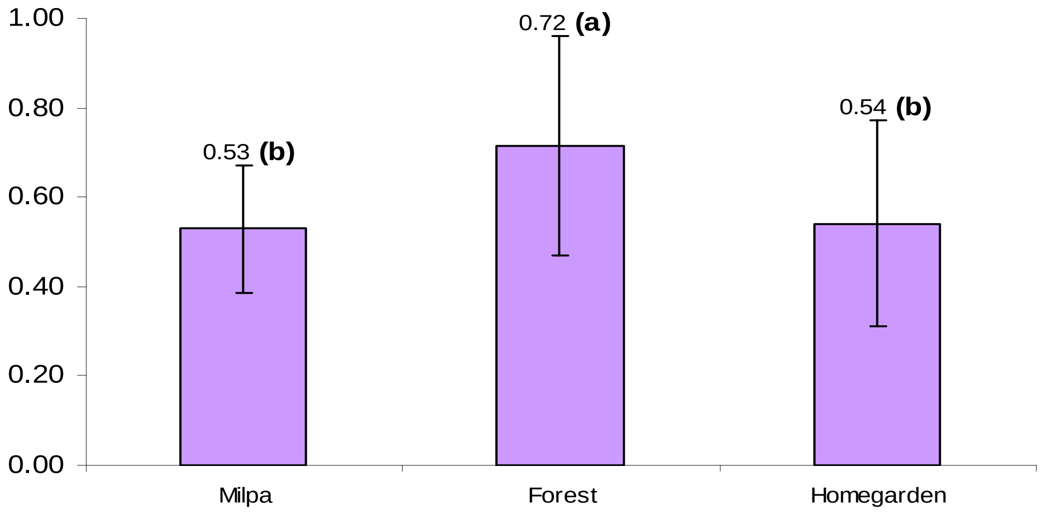


Figure 2. 1. Exchangeable Mg grouped by land uses in the Yucatecan ecosystems independently of soil type. Numbers followed by the same letter are not significantly different by FPLSD = 0.10 at P<0.05.

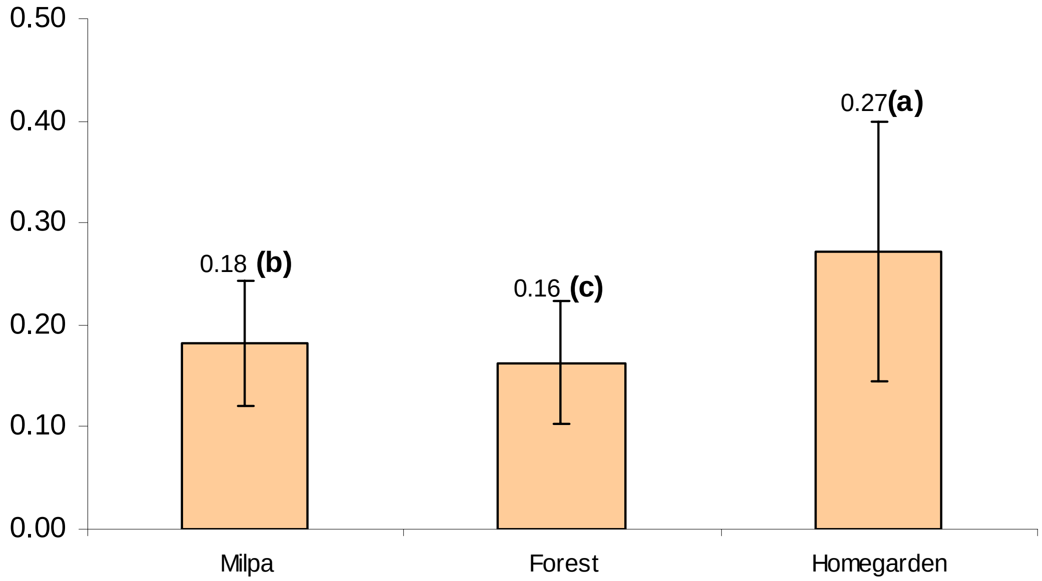
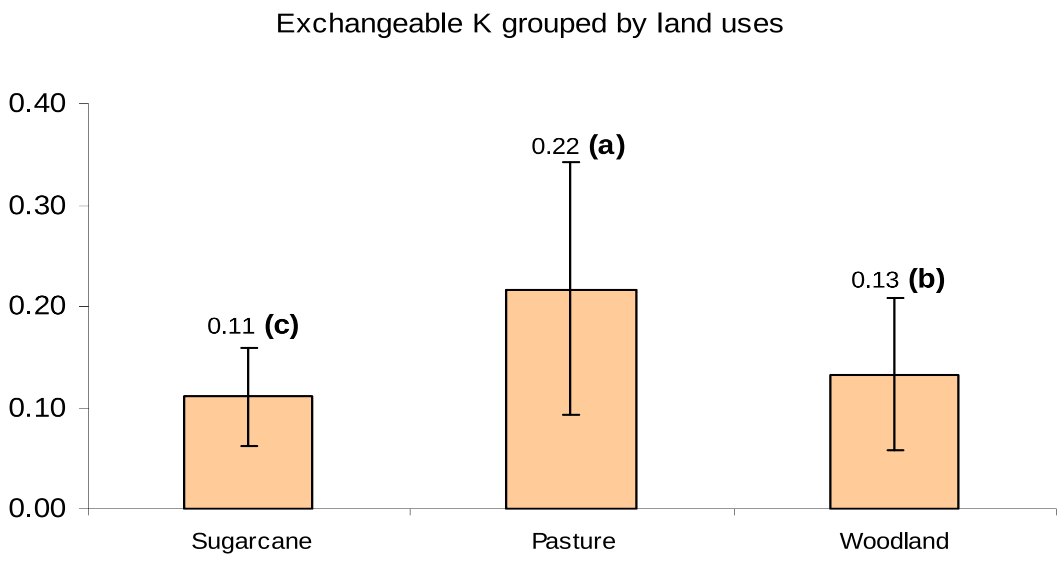


Figure 2. 2. Exchangeable K grouped by land uses in the Yucatecan ecosystems independently of the soil type. Numbers followed by the same letter are not significantly different by FPLSD = 0.05 at P<0.05.

The higher concentrations of Mg in forest may be attributed to litterfall contribution in nutrient cycling. Campo et al. (2000) found litterfall as the main pathway for Ca and Mg return to the soil in a tropical dry forest from Chamela region, on the Pacific coast of Mexico. Of the total aboveground return, 99% of Ca and 84% of Mg occurred in the litterfall. These authors concluded that Ca, Mg, and also, K are held tightly within the ecosystem. However, K was significantly higher in homegardens compared to the other two land uses. Yucatecan homegardens have been identified as intensive agricultural systems, in which fertility is maintained through the addition of household refuse and animal manure (Benjamin, 2000). Andrist (2003) explained that Yucatecan homegardens are sustained at the expense of nutrients from the surrounding lands (forests and milpas), household residues, and animal manure. Glaser et al. (2001) did a pair-wise comparison between native and cultivated savanna plots in Northern Tanzania. They observed that the soils from the homesteads were enriched in basic cations (apart from Mg). They remarked that, after 3 years of animal manure applications, the soil enrichment in K was higher than with other cations.

In Cuban soils, the interaction between land use and soil defined the concentrations of exchangeable Ca and Mg (Table 2.4). Ca was 45% more in the humus-rich calcareous soil than in the brown calcareous soil, with the highest values in the sugarcane area from the first soil type. Brown calcareous soil had 78% more exchangeable Mg. The greatest differences were found in the woodland from the brown calcareous soil, followed by the sugarcane and the pasture areas from the same soil group. These differences between both soils were strongly marked by their mineralogical properties. In the central region of Cuba, brown calcareous soils have only residual carbonates, whilst humus rich calcareous are derived from marine sediments and contain high amounts of clay-marl (Cairo and Fundora, 1994; Marin et al., 1994). Additionally, in the Santa Clara valley the effect of serpentine soils that surround the calcareous areas has been reported. In the woodland ecosystem, the inclusion of a fersialitic strip into this area accentuated the differences in the amounts of exchangeable Ca and Mg. The main consequences of this vicinity are higher amounts of magnesium and low calcium contents (Fundora, 1979; Torrecilla, 2005).

The independent effects of land use and soil type explain the differences in exchangeable K in Cuban soils (Figure 2.3). K was higher in pasture than in the other two land uses. The constant manure inputs in grassland areas are the main cause for these results. Animal manure is a good source of K, because it contains much more K than Mg and Ca. Also, almost all of total K from manure application will be available to the plants during the year it is applied (Johnson and Eckert, 1995). Vargas et al. (2003) emphasized that about 90% of K consumed by animals can be recycled again through excretions. This has a rapid effect on K content in soils because this element is readily released in the process of dung decomposition.



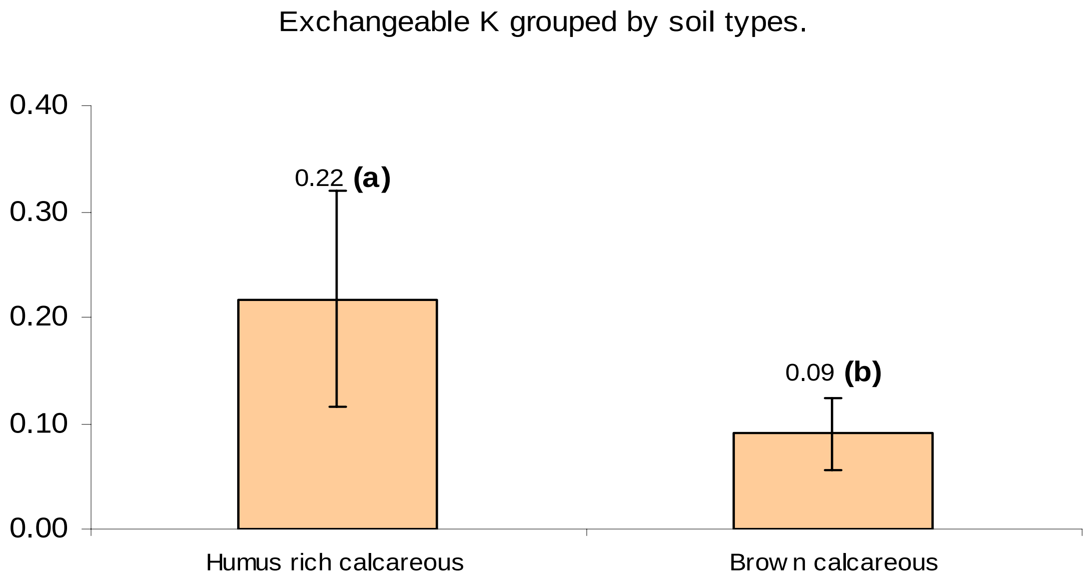


Figure 2. 3. Exchangeable K in Cuban sites grouped separately by land use and soil type. Numbers followed by the same letter are not significantly different by FPLSD = 0.04 in the case of land uses and FPLSD = 0.03 for the aggregation by soil types at P<0.05.

On the other hand, humus-rich calcareous soils presented 50% more K than brown calcareous soils. Vargas et al. (2003) found high K content in those land uses where soils presented also higher SOM content. Cairo and Fundora (1994) reported that humus rich calcareous soil may presented double amounts of SOM compared to the brown calcareous group. However, our results were not so conclusive due to the influences of previous land uses in the pasture area for the brown calcareous soil and specific mineralogical properties and more prolonged woodland use in the area of the same soil type.

In general, the Ca:Mg:K ratios show that Ca is the dominant cation in both groups, Yucatecan and Cuban soils. Even in the brown calcareous soil (45:15:1), which had high Mg content compared to the other soil groups, Ca was still the dominant cation. Vestin et al. (2006) studied the influence of alkaline parent material on the concentrations of exchangeable cations in soils. With this aim alkaline and non-alkaline plots were compared analyzing the concentrations of Ca, Mg, K, and sodium (Na). They found that exchangeable Ca and Mg in the solid phase were three times higher for Ca and twice as high for Mg in alkaline plots compared to the non-alkaline soils. In the soil solution, also Ca and Mg were higher in the alkaline plots than in non-alkaline group. Their results suggested that exchangeable Ca and Mg are strongly correlated to parent material. However, K was not correlated with the parent material and was found in similar amounts in both alkaline and non-alkaline plots. K is the second most concentrated nutrient in plant leaves and shoots after N. The retention of K by ecosystems is relatively greater than that of other cations (Jobbágy and Jackson, 2001). So, in natural and low-inputs agricultural ecosystems, the enrichment in K should be expected from plant cycling (Jobbágy and Jackson, 2001), whereas in grassland and homegardens, K will increase due to constant manure and residues inputs (Johnson and Eckert, 1995; Glaser et al., 2001; Benjamin, 2000; Andrist, 2003).

2.5. CONCLUSIONS

OC and total N were determined by the interaction between the land use adopted and the mineralogical properties of the soil type. IC was also related to the combined effect of land use and soil type. Probably, prior choices of land use or some specific agricultural practices could influence the carbonate content in these soils. The exchangeable cations were not always determined by this interaction, but also by the independent effect of one single factor. Ca was always dependent on this interaction for the soils of both countries. However, Mg was affected by land use only in the Mexican group. In both, Yucatecan and Cuban ecosystem, K content was very low and was highly influenced by management, specifically, by manure and residues inputs in the ecosystems. The highest K content was found in homegardens and pasture, respectively. Summarizing, we can affirm that land use, soil type, as well as the interaction between both factors influenced SOM and exchangeable Ca, Mg and K levels in these calcareous soils. Moreover, the low levels of exchangeable K may be a limiting factor in these calcareous soils.

CHAPTER 3: PHOSPHORUS FRACTIONS IN CALCAREOUS SOILS FROM THE SEMIARID TROPIC UNDER DIFFERENT LAND USES.

3.1. ABSTRACT.

Phosphorus (P) was assessed in four tropical calcareous soils from Yucatan, Mexico, and Villa Clara, Cuba. In Mexico, the soils were classified as redish brown redzinas and black lithosols. Both soils presented three main land uses: milpa, forest, and homegardens. In Cuba, the selected soils were brown calcareous (Orthic-Calcaric Cambisol) and humus-rich calcareous (Hyper-Calcaric Phaeozem) soils. The land uses considering in the study were: sugarcane monoculture, pasture and woodland (isolated patches of secondary vegetation). P fractionation was done following the sequential extraction procedure from Tiessen and Moir (1993). The results evidenced that P availability and P distribution into the different pools were directly influenced by land use and soil type, as well as the interaction between both factors. In the Mexican ecosystems, black soil presented higher amount of total phosphorus (Pt) than most tropical soils. The inputs of manure, plant residues and human dwellings increased Pt in both red and black soils from homegardens. In Cuban ecosystems, pasture in the humus rich soil had the highest Pt content. Humus rich calcareous soils showed more Pt than the brown calcareous. However, in all Mexican and Cuban ecosystems most of Pt (around 60%) was comprised in unavailable forms. The organic fraction (Po) was 10% of Pt in homegardens and 30% in forest and milpas for the Mexican group. As well, the organic pool comprised 16% of Pt in sugarcane, whilst in pasture and woodland represented 38 and 38% of Pt, respectively. Even when small, Po seemed to be an important P source in these soils and may determine P availability, considering that most of Pt is comprised in unavailable forms.

Keywords: *phosphorus fractionation, semiarid tropics, calcareous soils, Mexico, Cuba.*

3.2. INTRODUCTION.

Phosphorus (P) is an essential nutrient for plant growth and functioning, which frequently appears as the first limiting element in many agricultural systems, independently of their management.

The chemistry of the P in soils is complex, because inorganic P (Pi) can react with Ca, Fe and Al to form discrete phosphates and organic P (Po) is found in different forms with varying resistance to microbial degradation. The study of P transformations in soils has been facilitated by sequential extractions which separate Pi and Po into major chemical groupings, and into pools of different bioavailability (Agbenin and Tiessen, 1994). Hedley et al. (1982) introduced a sequential extraction procedure whereby biologically available Pi is removed first with an anion exchange resin; following a mild eluent (0.5 M $NaHCO_3$) is used to remove “labile” inorganic and organic forms. At this step, inclusion of the chloroform treatment permits estimation of (Po) originating from lysed microbial cells. Stable P forms are removed by stronger extractants as NaOH for Fe- and Al- phosphates, HCl for occluded P and H_2SO_4 for highly stable insoluble mineral P (Stevenson and Cole, 1999). But, in tropical soils the efficiency of this scheme has been limited by the large proportions of plant available P that remain unextracted and are lumped in the residual fraction (Agbenin and Tiessen, 1994; Guo et al., 2000). This required a modified sequence to characterize the residual P, which constitutes a substantial part of the total P (Pt) in tropical soils. Tiessen and Moir (1993) developed a sequential extraction procedure modifying the Hedley et al (1982) scheme following the dilute HCl extraction by an additional hot concentrated HCl to remove chemically resistant Pi and Po fractions, which are tightly bound to Fe and Al minerals (Tiessen and Moir,1993) and probably unavailable to plants and microbes.

In the Tiessen and Moir scheme (1993), resin-P represents an easily exchangeable inorganic fraction (Pi) dissolved in the soil solution from solid phases in the soil. The bicarbonate extract simulate the activity of plant roots; together, both resin- and bicarbonate-P are considered to be available to plants and microbes in the short term (Cross and Schlesinger, 2001). The labile organic P (Po) in the bicarbonate extract is derived from organic compounds and readily mineralized by microbes and contributes to plant-available P (Tiessen and Moir, 1993). The NaOH-P is thought to remove P associated with some Al- and Fe- minerals and is moderately available to plants, while Po in the hydroxide extract represents more stable P involved in the intermediate-term P transformations in soils. The other extracts represent the unavailable P fractions, perhaps available in a long term. The dilute-HCl pool is associated with calcium carbonate minerals, and the concentrated HCl removes Pi and Po bounded inside Fe- and Al- minerals and apatite. Residual P is the most stable form of P (Cross and Schlesinger, 2001).

Land management practices also affect the ecosystem functioning mainly due to their effects on microbial populations that are closely related to P cycling or by changing of chemical properties of the soils. For instance, slash-and-burn agriculture can induce an increase on the plant-available nutrients, including P, through the release of pools held in biomass and transferred into the soil environment with the ashes. Burning and subsequent ash depositions not only create a nutrient pulse, but also elevate the pH, which decreases the strength of P sorption and occlusion reactions in acid soils, although this initial pulse of fertility is short-lived, and significant P losses can occur during and after deforestation (Towsend et al., 2002). Other studies have shown the effect of contrasting land-use systems on soil P fractions. Buehler et al. (2002) assessed P in a Colombian Oxisol under four treatments (two of them with fertilizer additions), and found that all fractions were strongly dependent on total P content of the soil, which was affected by the amount of P added as fertilizer and removed by plant uptake. In the two P-fertilized treatments most of the P was stored in the resin-Pi, Bicarbonate-Pi, and NaOH-Pi fractions. In the two unfertilized soils the transfer of labeled ^{33}P into these inorganic pools was lower suggesting that the soil Pi was much less exchangeable and organic fractions were more important.

Guo et al. (2000) reported the exhaustive cropping effect on P fractions in eight Hawaiian soils. Their results suggest that resin-Pi and $NaHCO_3$-Pi were the most sensitive fractions to plant removal in all soils. NaOH-Pi was the dominant fraction in the highly weathered soils, and also declined with plant removal. In contrast, residual P in the highly weathered soils is accumulated with plant removal, suggesting that it was unavailable to plants.

Based on the consulted literature, we tested the hypothesis that ecosystem management and farming systems influence the cycle of P, which is reflected in the distribution of P fractions, in calcareous soils from the semiarid tropics in the Caribbean area. For this purpose, we studied the distribution of P in four soils (two from Yucatan and two from Villa Clara, in the central part of Cuba) under three representative land uses of each country

3.3. MATERIALS AND METHODS.

3.3.1. Site selection and soil sampling.

For this study, four tropical calcareous soils were selected. Two of them were collected in Mexico and the other two in Cuba.

Mexican sites.

In Mexico, the study sites were located in Xmatkuil and Dzibilchaltun, near to Merida, the capital city of Yucatan State, at the northwest of the peninsula. There were also sites located in Hocaba municipality at 56 km south of Merida. The area has a tropical climate (Aw) due to the long periods of little to no precipitation. Annual mean temperature is 26ºC, but in the hotter season temperatures may reach more than 40° C (Duch, 1988). Precipitation throughout the year is uneven, available for only certain months of the year, and can be highly unpredictable. Average rainfall probability is never more than 50% and ranges from 31-49% (Benjamin, 2000). The mean annual rainfall is 1000 mm in the Merida zone and 980 mm in Hocaba. The dry season lasts from October to May and rainfall is erratic both spatially and temporally (Duch, 1988; Weisbach et al., 2002).

In the Mayan classification the selected soils are known as Kankab and Tzekel, with red color and black color respectively. Both are calcareous soils derived from limestone. Kankab series are identified in the FAO classification as a luvisol or redish brown rendzina and Tzek’el group are distinguished as Lithosols and Entisols in the USDA systems classification (Benjamin, 2000, Weisbach et al. 2002).

For our study three main land-uses were identified: forest, milpa and homegarden. For each land-use were sampled three sites. A total of 10 soil samples at 10-cm depth were collected per site (5 red and 5 black soils) following a randomized design stratified on soil color for a total of 90 samples (45 of each soil types).

Forest areas were selected in Xmatkuil, Dzibilchaltun and Hocaba. Two of the milpas were chose in Xmatkuil village and the third one and all the homegardens were selected in Hocaba town. The vegetation in milpas was maize combined with pulses and vegetables. In homegardens different strata formed by native trees, shrubs and spices was more usual. Forests are characterized by semi-deciduous vegetation formed by native trees and shrubs in different stages of growing, and, in the particular case of Hocaba forest, isolated henequen plants remained from former henequen plantations in the area.

Cuban sites.

Cuban climate is tropical (Aw) with a rainy summer and dry winter (Díaz Cisneros, 1989, cited by Villegas et al., 1994). Mean temperature is 25 degrees. Annual rainfall varies between 1000 and 1200 mm. The relative humidity is high with more than 80% (Villegas et al., 1994).

Two calcareous soils from Villa Clara province were selected for the study: brown calcareous and humus-rich calcareous soils, both derived from limestone. Both are widely used in Cuban agriculture, especially for sugarcane, a wide number of minor crops, and animal husbandry (Marín et al. 1994, Villegas et al. 1994). Brown calcareous soils were collected in Santa Clara, and the humus-rich calcareous soils in Ranchuelo municipalities, respectively.

Three different land-uses were selected in both soils: sugarcane monoculture, pasture, and woodland. Sampling was done at 10 cm depth following a random design, at a number of 10 samples per site, for a total of 60 samples.

The vegetation of the sites varied in function of the land use. In the monoculture areas, sugarcane was the only crop. Pasture presented different combinations. In the grassland from the humus rich soil a wide number of different grasses and legumes were found combined with few disperse trees. In the artificial pasture from the brown calcareous, a combined plantation of Leucaena leucocephala L. and star grass (Cynodon spp.) represented the vegetation of the area. The Ranchuelo woodland was distinguished as one of the typical savanna isolated patches of secondary vegetation, but in Santa Clara, this area is part of the Botanical Garden and presented a mix of Cuban and foreign species.

All Cuban and Mexican samples were air dried, sieved at 2 mm and packed in hermetic plastic bags for shipping to Germany. After their reception in Germany, samples were ground in a ball-mill, dry in the oven at 40°C and kept stored in the oven at 26°C until the analyses to avoid the re-moistening of the samples because of the high air humidity under the German climatic conditions.

3.3.2. Laboratory analyses.

P-fractions of these soils were obtained using the sequential fractionation scheme from Tiessen and Moir (1993) (Figure 3.1). A 0.5g-soil sample was placed into a 50-ml plastic centrifuge tube with 30 ml of deionized water and two anion exchange membranes (PC Acid 35, PCA Ltd., Germany), cut into strips (9 X 62 mm), and previously converted to bicarbonate form. Samples were shaken overnight (16h). The resin strips were removed from the tubes, and P retained on the membrane was eluted placing the strips in a clean tube with 30 ml of 0.5M HCl and shaking overnight. Soil suspensions were centrifuged at 5000 rpm, and the water was decanted through a millipore filter (pore size 0.45 µm). Water was discard and the remaining soil was extracted with 30 ml of 0.5M $NaHCO_3$ (pH 8.5) solution. The suspension was shaken overnight. This procedure was repeated with 0.1M NaOH and 1M HCl to remove P pools more strongly retained in the soil and less available to plant and microbes. Subsequently, soil residue was heated with 10 ml concentrated HCl in a water bath at 80°C for 10 minutes. Tubes were vortexed to mix soils and acid, and caps were removed before putting into the hot bath. Temperature of the mixture was checked until it reached 80°C. Tubes were kept at 80 °C for 10 minutes and then, were removed from the hot bath and a further 5 ml of concentrated HCl were added, vortexed and allowed to stand at room temperature for 1 h. After this time, tubes were capped and the mixture was centrifuged at 4500 rpm and decanted into 50-ml volumetric flaks. Soil was washed with 10 ml of deionized water, centrifuged and decanted, repeating this process twice. Subsequently, the solution was diluted to volume.

Finally, soil residue was placed into a 75-ml digestion tube with 10 ml of deionized water. Then, 5 ml of concentrated H_2SO_4 and 4 boiling chips (order by OMNILAB, type resistant) were added. The tubes were vortexed and put on a cold digestion block (Gerhard, Kjeldalterm KT-40 S, Germany). Temperature was increased very slowly to evaporate water and when 360°C was reached tubes were removed, let cool to hand warm and 0.5 ml of H_2O_2 were added. Then, the sample was reheated for 30 minutes during which H_2O_2 was is used up. This step was repeated until the liquid was clear, when the tubes were removed and let cool. The solution was diluted to volume and transferred to plastic storage flask.

P-content in all fractions was determined by Murphey and Riley (1962), as described by Tiessen and Moir (1993). For this, a suitable aliquot of the sample was pipetted into a 50-ml volumetric flask. Because, samples required prior neutralization, two drops of paranitrophenol were used as indicator for adjusting the pH. At this point, 4M NaOH was added until the solution turned yellow, and then, 0.25M H_2SO_4 was dropped into the solution until turned clear. Then, 8 mL of color developing solution were added. Finally, deionized water was added to make volume, the solution was shook and the samples were read on spectrophotometer (UNICAM 8625 UV/VIS) at 712 nm after 10 minutes. The color solution was made mixing 250 ml 2.5M H_2SO_4 with, first, 75 ml ammonium molybdate solution (40g into 1000 ml H_2O), following by 50 ml ascorbate solution (26.4g in 500 ml H_2O), and finally, 25 ml of antimony tartrate solution (1.454g in 500 ml H_2O). After each addition, the contents were swirled throughoutly.

3.3.3. Data processing and statistical analyses.

For data processing, the results were grouped by land uses and soil type. No statistical comparisons between Mexican and Cuban soils were made because the management and land uses are different between both countries.

Each P fraction was analyzed independently. The inorganic fractions were summed to obtain the total inorganic phosphorus (Pi). The organic fractions were also summed and analyzed as one complete pool (Po). Finally, the sum of the results from both inorganic and organic pools was considered as total P (Pt). For all ecosystems these combined pools were analyzed statistically.

Statistical analyses were performed with SPSS 9.0 (SPSS Inc., Chicago). Data were tested by two-way ANOVA with the factors land use and soil and the possible interaction between both factors. Following this, the results were analyzed by one-way ANOVA for red and black soils independently, whenever the two-way ANOVA indicated significant interactions for $P<0.05$. If the interaction between both factors (land use and soil type) was not significant, the analyses were done by one-way ANOVA without differentiation of land use and/ or soil type, considering the significance of each. The same procedure was done for Cuban soils. Comparisons were performed using Fisher protected LSD test (FPLSD). The data reported are means of each individual or group.

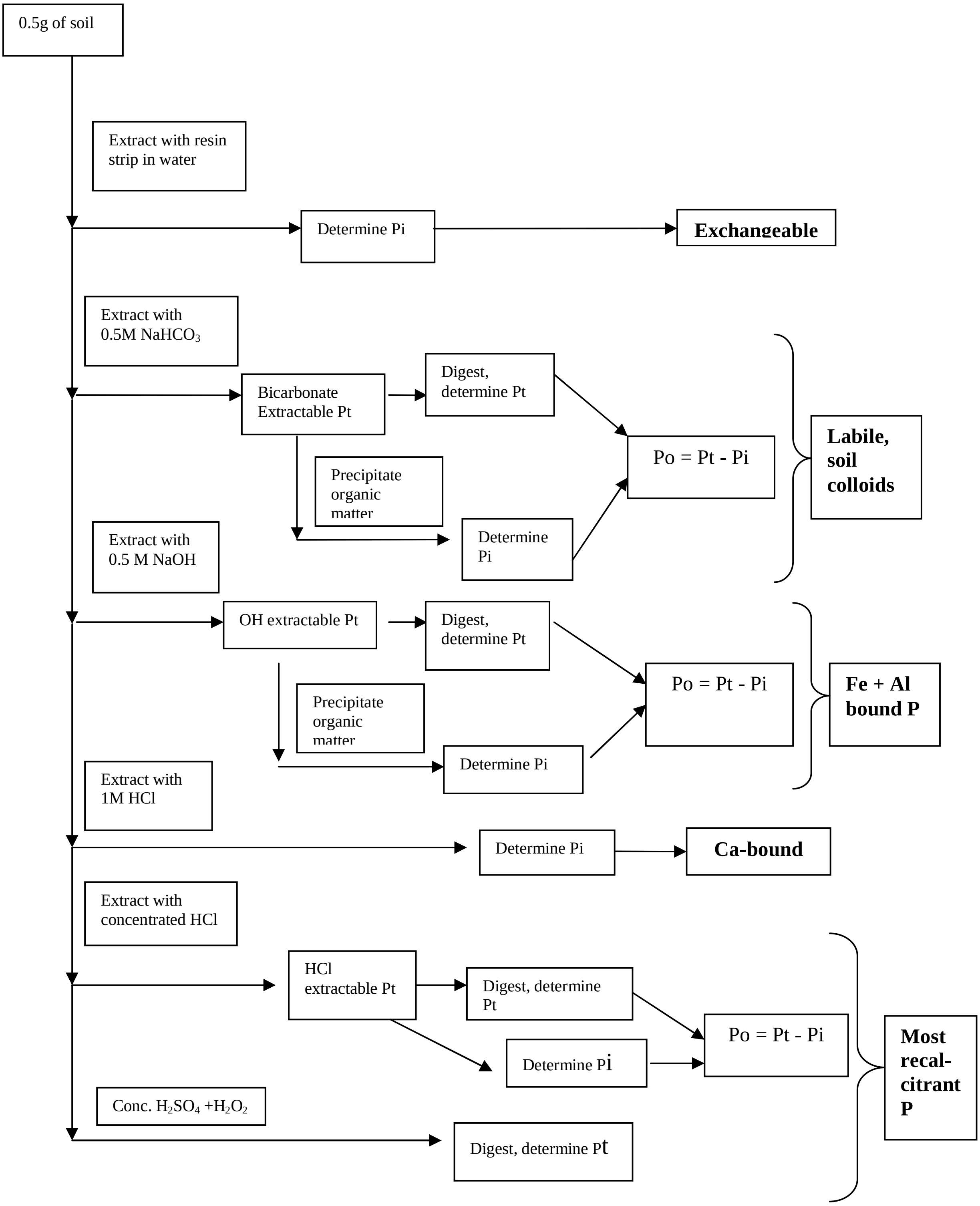


Figure 3. 1 Flow chart of the sequential P fractionation adapted from Tiessen and Moir (1993)

3.4. RESULTS AND DISCUSSION.

3.4.1. Total P

The total P (Pt) content in Mexican soils for the red soils was 779 mg kg^{-1} in forests and 675 mg kg^{-1} in milpas. In contrast, in homegardens red soils presented an average of 2690 mg kg^{-1} of Pt. Black soils of the three Mexican ecosystems presented more than 1000 mg kg^{-1}, with 1403 mg kg^{-1} in milpas, 1026 mg kg^{-1} in forest and the highest value in homegardens with 3658 mg kg^{-1}. Black soils from Yucatan presented more Pt than red soils, with an average of 25 and 26 % more for forest and homegardens, respectively, and 51 % for milpas, which is the land use that presented the highest contrast between the two soil groups. However, even in the homegardens and black soils, most of Pt is comprised in unavailable forms (Table 3.1).

The Yucatecan homegardens were described by Andrist (2003) as “a trap of nutrients”, explaining that a lot of resources in form of food, manure, water, residues are all brought to the homegarden, which is enriched with these inputs. This may explain the higher amount of Pt found in the homegardens above of the usual range in soils, which is in the order of 500 to 800 mg kg^{-1} (Stevenson and Cole, 1999).

On the other hand, Weisbach et al. (2002), in a prior soil study on areas under shifting cultivation representing different stages of fallow in Yucatan, reported Pt values between 491 and 523 mg kg^{-1} for the red soils, with an average of 514 mg kg^{-1}. However, they did not find values above 800 mg kg^{-1} for the black soils, presenting P data for this soil group in the range of 652 to 754 mg kg^{-1}, with an average of 680 mg kg^{-1}.

The values of Pt for all Cuban sites were between 503 and 875 mg kg^{-1} (Table 3.2). These results are around the normal range for most soils in the world according to Stevenson and Cole (1999). The pasture from the humus rich calcareous soil presented the highest Pt content (875 mg kg^{-1}), followed by the sugarcane (759 mg kg^{-1}) and the woodland (746 mg kg^{-1}) ecosystems in the same soil. No significant differences were found among the three ecosystems in the brown calcareous soils. Brown calcareous soils showed 34% less Pt than Humus-rich calcareous soils.

In both soils, approximately 60% of Pt was retained in the non-labile fractions. The inputs of manure and chemical fertilizers may enhance P concentrations in soils. Beck and Sanchez (1996) studied P fraction in unfertilized and fertilized plots in Peru. They found that P added as chemical fertilizer tended to accumulate mainly in all inorganic fractions in the fertilized plots, although, bicarbonate pool was also increased by fertilizer applications. Motavalli and Miles (2002) explained that over-application of animal manure and commercial fertilizers can lead to soil P accumulation in agricultural soils.

The influence of the soil type in these results is important, since all ecosystems in the humus rich calcareous had higher resin-P than the ecosystems from the brown calcareous soil. In the brown calcareous soil from the Santa Clara Valley, the influence of serpentine minerals (Fundora, 1979; Torrecilla, 2005) may reduce the levels of exchangeable P. Serpentine minerals are rich in iron oxides (Bonifacio and Barberis, 1999), which may react with P forming insoluble minerals. Vargas et al. (2003) found very low levels of P in calcareous soil under contrasting land uses.

3.4.2. Inorganic P fractions

Resin-Pi in Yucatecan ecosystems was not influenced by the interaction between land use and soil. However, it was determined by the independent action of each factor. Resin-Pi was significantly higher in homegardens than in milpa and forest ecosystems. Buehler et al. (2002) and Damodar et al. (2004) reported significant increments in resin-P after manure additions. On the other hand, black soils presented 31% more resin-Pi than the red ones (Figure 3.2). Weisbach et al. (2002) also found a similar trend in available Pi (resin-, bicarbonate- and hydroxide-Pi) in these Yucatecan soils. They reported that red soils had 64% less available Pi than the black group. The difference between both soils should be related to the organic matter content in both soils. Our own previous results showed that OC was, on average, 50% more in black soils than in the red one. Weisbach et al. (2002) also reported that black soils may double the organic carbon content compared to red soils. The importance of plant residues and other organic P sources is more relevant in tropical soils, where P availability often depends on the amounts and mineralization of organic P (Stewart and Tiessen, 1987).

Table 3. 1. P fractions in Mexican soils.

Land use	**Soil**	**P-resin**	**Pi-HCO$_3$**	**Pi-OH**	**Pi-1MHCl**	**Pi-HClc**	**P-residue**	**ΣPi**	**ΣPo**	**ΣPt**
		--------------------	--------------------	--------------------	--------------------	mg kg^{-1}	--------------------	--------------------	--------------------	--------------------
Milpa	Red	12	14	62	37	28	341	152	181	675
	Black	37	51	54	276	60	445	923	480	1403
Forest	Red	9	13	57	27	34	354	141	285	779
	Black	25	34	54	116	51	366	646	379	1026
Homegarden	Red	174	187	232	1228	76	506	1897	287	2690
	Black	219	273	247	1981	104	503	3326	332	3659
FPLSD	Red	28	27	18	169	5	39	221	42	202
	Black	21	15	26	119	9	42	167	69	188
Significant interaction Land use x soil		ns	0.044	ns	0.001	ns	ns	0.001	0.001	0.010

Differences are significant for those which their differences are higher than Fisher’s protected LSD (FPLSD) within the same column and for the same soil type for $P < 0.05$. Abbreviation “ns” means no significant differences at $P<0.05$.

Table 3. 2. P fractions in Cuban soils.

Land use	Soil	P-resin	Pi-HCO_3	Pi-OH	Pi-1MHCl	Pi-HClc	P-residue	ΣPi	ΣPo	ΣPt
		------------------------------	------------------------------	------------------------------	--------mg kg^{-1}	--------------------------	------------------------------	------------------------------	------------------------------	------------------------------
Sugarcane	Humus-rich calcareous	15	26	29	216	30	250	566	193	759
	Brown calcareous	19	11	42	52	14	236	373	161	534
Pasture	Humus-rich calcareous	37	26	43	272	32	267	677	198	875
	Brown calcareous	11	9	26	143	7	224	419	120	539
Woodland	Humus-rich calcareous	24	21	37	200	6	222	516	230	746
	Brown calcareous	32	12	34	45	15	221	359	143	503
FPLSD	Humus-rich calcareous	2	ns	2	20	4	19	26	15	35
	Brown calcareous	1	1	3	4	2	ns	14	11	ns
Significant interaction Land use x soil		0.000	0.005	0.000	ns	0.000	0.000	0.001	0.002	0.004

Differences are significant for those which their differences are higher than Fisher's protected LSD (FPLSD) in the significant interactions within the same column at $P < 0.05$. Abbreviation "ns" means no significant differences at $P<0.05$.

In Cuban ecosystems, resin-P was influenced by land use and soil type interaction. Within the humus-rich calcareous soil, the pasture showed the highest resin-P followed by the woodland area. In the brown calcareous group, the highest resin-P was also found in the woodland ecosystem. Within each soil type, all sites differed significantly in resin-P content. The ecosystems with the higher resin-P are the most stable and older of the six studied sites. In the grassland the inputs of manure, a P-rich amendment, may result in significant increases of readily available resin-P, as well as, other inorganic and organic fractions (Iyamuremye et al., 1996). Also, in some tropical ecosystems, grass turnover has replaced litterfall return as the predominant mechanism of nutrient recycling (Markewitz et al. 2004). Mineralization of Po sources, such as manure or plant residues, may increase Pi levels in soil solution (Tiessen and Moir, 1987).

The positive effect of tree and permanent grassland covers on resin-P has been reported in the literature (Günter and Lehmann, 2000, Lehmann et al., 2001, Vargas et al., 2003, Markewitz et al., 2004). Trees are considered especially suitable for land use under low-P-input conditions because litterfall and pruning improves soil P availability. P is returned to soil with litter, improving P availability through mineralization (Lehmann et al., 2001). Under Cuban conditions, as result of deforestation suffered at beginning of the twenty century, the woodlands and grasslands are similar to multi-strata agroforestry and silvicultural systems, respectively (Marín et al., 1994, Vargas et al., 2003). Vargas et al. (2003) reported higher values of available phosphorus in a silvicultural ecosystem formed by grasses and legume trees compared to natural grassland and sugarcane monoculture in brown calcareous soils from Santa Clara.

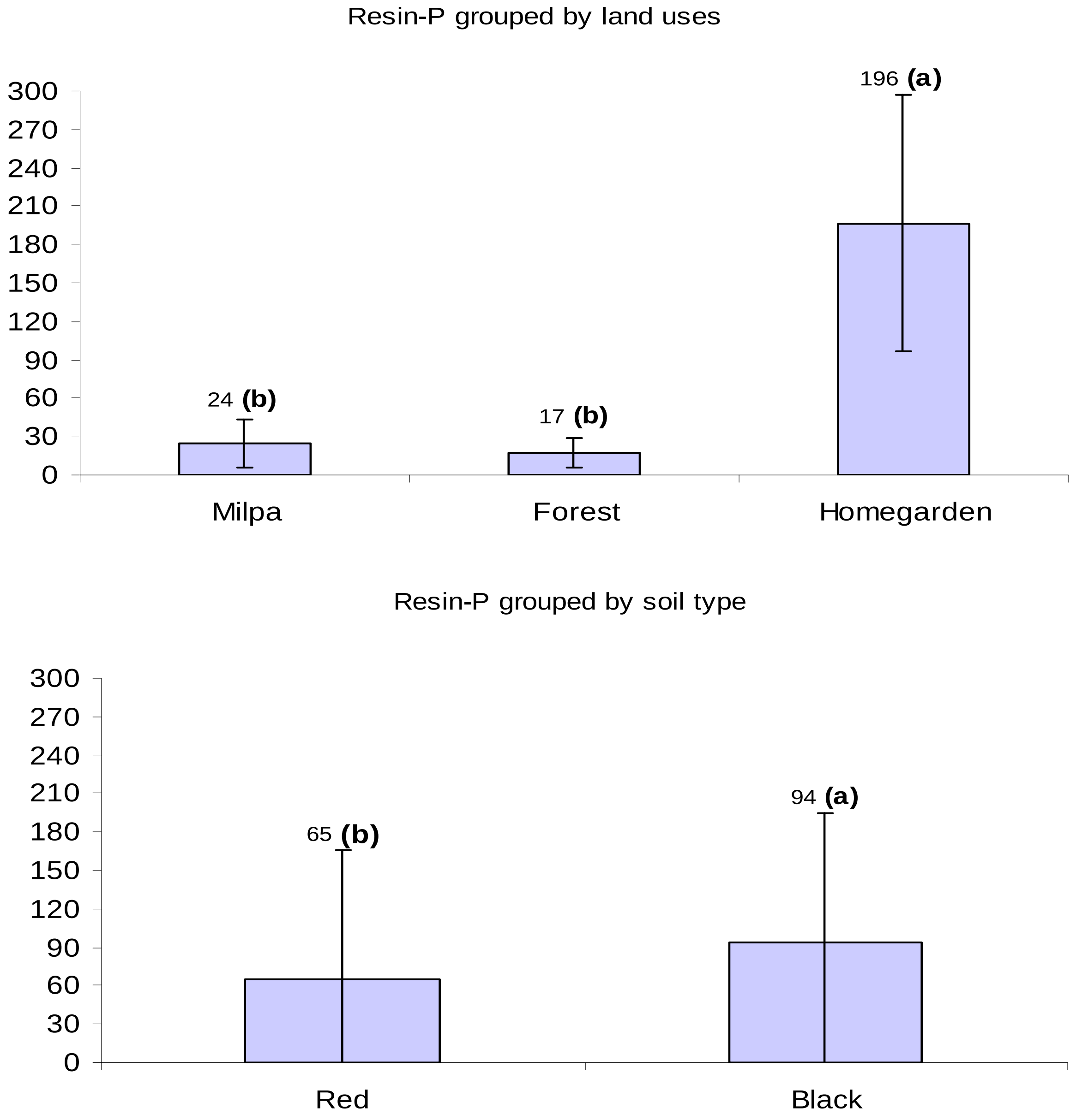


Figure 3. 2. Resin-P in Yucatecan ecosystems grouped by land uses and soil types independently. Numbers followed by the same letter are not significantly different by FPLSD = 30 for land uses and FPLSD = 24 at P<0.05.

Bicarbonate Pi was determined by land use and soil interaction. Homegardens showed higher bicarbonate Pi than all the other ecosystems, in both soil groups. At the same time, the differences between red and black soils were lower in homegardens compared to the other two ecosystems. Bicarbonate Pi was 32 % more in black soils from homegardens compared to the red soils under the same land use. In forests, bicarbonate Pi was 62% more in black soils than in the red one, whereas in milpas, black soils had 73 % more bicarbonate Pi than the red group (Table 3.3). The diverse and periodical inputs of “organic fertilizers” in homegardens (Andrist, 2003) may enhance the lability of P in these soils. Saleque et al. (2004) reported a positive correlation between P accumulation in the resin and bicarbonate fractions and the application of organic manure (cow dung and ash) at 0-15 cm soil depth in wetland rice soils. The differences between both soil groups under milpa and forest uses were similar to the results reported by Weisbach et al. (2002) in available Pi for these Yucatecan soils. Our results suggested that the differences between both soil groups were accentuated by their management. Milpas and forest are systems with low-P inputs, in which soil fertility depends only on the restoration of the nutrients during the fallow period. In these two ecosystems, the differences between both soils were higher than in the homegardens, where the constant inputs of plant residues, manure and household garbage may diminish these differences. Even when the P levels increased in both soils, the increment in red soils is high enough to reduce the differences with the black group.

In Cuban areas, bicarbonate Pi did not showed significant differences among land uses in the humus-rich calcareous soils, but it was higher in the pasture, followed by sugarcane and woodland (in that order). Within the brown calcareous group, bicarbonate Pi varied among land uses, with the highest concentration in the woodland area. P content in the bicarbonate fraction from the brown calcareous soil was significantly lower compare to the humus rich calcareous soil. The average difference between both soils was 55%. Saleque et al. (2004) demonstrated that bicarbonate P can be increased by the manure applications, with several fold greater results than the increase that occurred due to fertilizer, suggesting that constant inputs of manure during long periods may fully substitute for P supply. The pasture area in the brown calcareous soil, which was dedicated to different crops under conventional agriculture and converted to grassland farming 3 years ago to recover it, showed the lowest lability of P as result of the degradation from previous use. This suggested that the soil reclamation in this area will need much more time to reach similar levels that the 35-years grassland of the humus-rich soil. Guo et al. (2000) studied the distribution of P fractions under intensive plant growth and found that resin and bicarbonate P decline with cropping as reflection of plant removal. The presence of a P sink such as a plant root in the soil system lowers Pi concentration in the soil solution, promotes biochemical mineralization and minimizes the residence time of free Pi with a rapid turnover (Stewart and Tiessen, 1987).

However, Saleque et al. (2004) found that bicarbonate Pi build up also by fertilizer P additions and combining both, manure and fertilizer. P additions may imply an ample P supply for cropping. This explains the higher concentrations of P in the bicarbonate fraction from the sugarcane area compared to the woodland, considering that sugarcane areas are mono-cropping systems with large inputs of chemical and organic fertilizers.

On the other hand, humus rich calcareous soils presented higher organic matter content than brown calcareous soils. In Cuban conditions, organic matter in humus rich calcareous soils range from 5% in undulated relief to 13% in more plain areas. In brown calcareous soils, organic matter range from 3-6% only (Cairo and Fundora, 1994). These differences in organic matter content influence bicarbonate P pools.

The hydroxide Pi was significantly higher in homegardens compared to the other land uses (Figure 3.3). However, soil type did not present any influence on this fraction. The Fe- and Al-bound Pi was a small fraction in these soils (Table 3.3), perhaps due to the solubility of these minerals at high pH (Tiessen and Moir, 1993), which permits dissolution of the phosphate and release it to soil solution, thus contribute to the most labile Pi. In Cuban ecosystems, hydroxide Pi was higher in the pasture from the humus rich calcareous soil and in the sugarcane area in the brown calcareous soil, following by the woodland ecosystems in both soils. Saleque et al. (2004) found that the application of chemical fertilizer tended to accumulate in this pool. However, they also reported that the build up of hydroxide Pi was higher in the presence of manure and ashes application compared to chemical fertilizers.

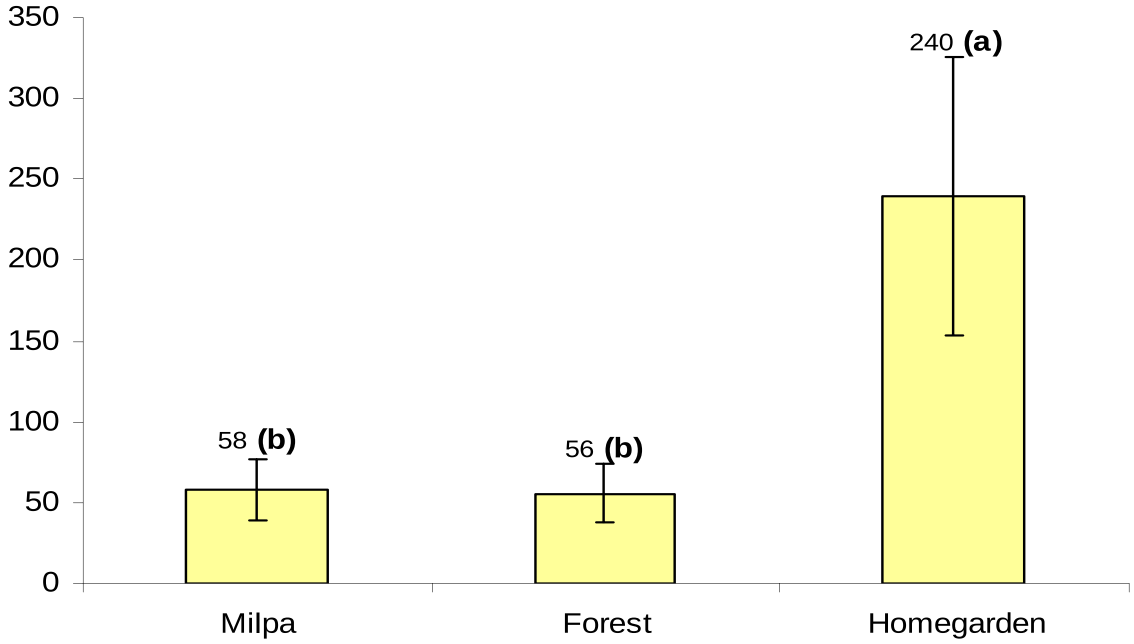


Figure 3. 3. Pi in the hydroxide fraction in Yucatecan ecosystems grouped by land use without distinction of soil type. Numbers followed by the same letter are not significantly different by FPLSD = 27 at P<0.05.

In Mexican and Cuban ecosystems, the inorganic hydroxide fraction made up only a small portion of Pt. This fraction tends to accumulate in soils with high Fe and Al oxides (Guo et al., 2000), but this is not the case of these soils, where calcium and magnesium carbonates prevail over the other soil minerals. However, it has been found that hydroxide Pi, as the other labile fractions, increase with P-fertilizer additions (Buehler et al., 2002). Damodar et al. (1999) realized that both application of fertilizer and manure increased bicarbonate- and hydroxide-P, as well as, Pt. They explained that the increment of P in these labile pools can be ascribed to resorption of P added as chemical fertilizers in excess of crop removal. This excess P may inhibit phosphorylase activity and, as a consequence, suppress mineralization. Manure additions also enhance the concentration of P in the labile pools. However, the manure applications play a beneficial role by retaining a major portion of added P in the form of Olsen P. Organic manure and its decomposition products are known to reduce P sorption/fixation, thereby enhancing the level of labile P in soils. Whalen and Chang (2001) also reported great increases on Pt and labile P on plots amended with manure annually for 16 years. The higher lability of P in homegardens and pasture ecosystems may be explain by the constant inputs of manure and residues throughout the years. Homegardens are old ecosystems in Yucatan, being one of the typical Mayan farming systems since pre-Hispanic times (Benjamin, 2000). In Cuba, the high labile P content in the pasture ecosystems can be explained also by the determinant role of the more than 40-years inputs of manure in the grassland from the humus-rich soil. In tropical environments, a summation of these three fractions (resin - , HCO_3 - , and OH - Pi) may be considered as “labile Pi pool” (Agbenin and Tiessen, 1994).

On the other hand, the differences between red and black soil, as well as between brown calcareous and humus rich calcareous soils, can be related to their strong differences in organic matter content. Humus rich calcareous soils may have double the organic matter content present in brown calcareous soils (Cairo and Fundora, 1994) and black soils in Mexico presented 54% more organic carbon and 48% more total N compared to the red soils (Weisbach et al., 2002). Even when only a small portion of the total organic matter is biologically active, it plays an important role in P turn over (Stewart and Tiessen, 1987).

In Yucatecan homegardens, 1MHCl-Pi comprised 45% in the red soils and 54% in the black group, being the largest fraction in this ecosystem. In Cuban ecosystems, the Ca-bound was determined by the independent effects of land use and soil, but the interaction between both factors did not influence this fraction. For all sites, this fraction was the second largest fraction. Grassland ecosystems had an average of 208 mg kg^{-1} in this fraction, which represented 36% more than sugarcane and 41% more than woodland areas. The presence of carbonates and other Ca salts may lead to the mineralization of Po from manure or other sources, and cause elevated Pi levels. This enrichment in Pi precipitated when react with carbonates to form insoluble salts and decreasing P solubility (Stewart and Tiessen, 1987). The large 1MHCl fraction in calcareous soils reflects the influence of geochemical processes on P cycling in soils with high concentrations of calcium carbonate minerals in the surface soils (Cross and Schlesinger, 2001). However, in milpas and forests, the Ca-bound fraction did not comprise the majority of P. No significant differences were reported between sugarcane and woodland land uses in Cuban ecosystems either. Perhaps, in these degraded ecosystems P may accumulate in less available pools (Stewart and Tiessen, 1987). Guo et al. (2000) also suggested the possibility that this fraction may act as buffer for the available P in slightly weathered soils. So, the decline in 1MHCl-P may be caused by the conversion from this pool to readily available P, assumed as resin-P and bicarbonate Pi.

Black soils from milpa had 86% more Ca-bound P than the red soils under the same land use. In forest areas, black soils showed 77% more Ca-bound P than the red soils. However, the difference between red and black soils in homegarden, although significant, was only 38%. Weisbach et al. (2002) found that black soils had 75% more Ca-bound P compared to the red group. Cuban soils also presented differences on P accumulation in this fraction. Humus rich calcareous soil had 65% more Pi-1MHCl than the brown calcareous soil. Undoubtedly, these results show the influence of soil mineral properties. It is well known that P distribution in the different pools is strongly dependent on soil properties such as, mineralogy of parent material, stoniness, and texture (Cross and Schlesinger, 2001). The influence of the parent material in these soils is the main cause for the differences in this fraction. Humus rich calcareous soils are formed from clay marl whereas the brown calcareous from this region often only presented residual carbonates. Also, the organic matter in the humus rich calcareous soils is of the calcic mull type (Cairo and Fundora, 1994). So, in the humus rich calcareous soils are present more carbonate minerals reacting with phosphate ions.

The sugarcane and woodland ecosystems from the brown calcareous soil presented a depleted acid P pool compared to the other sites. The intensive farming systems of the sugarcane monoculture have been practiced in these areas since several decades and still subsist. This may be causing the depletion of the Ca-bound P. In degraded soils under exhausting cropping, Guo et al. (2000) found that 1M HCl-Pi fraction is reduced due to the continuous and exhaustive cropping for a long term. These authors suggested that this fraction can be available to plants. Cross and Schlesinger (2001) also supported the theory that this fraction is available over long time periods. The dissolution of hydroxyapatite can be enhanced if protons are supplied or if P or Ca ions are removed from the soil solution (e. g. plant uptake), and also, because the adsorption of P ions by other soil constituents, favoring the dissolution of Ca-phosphate (Hinsinger, 2001).

The mineralogy of the brown calcareous soils in the Santa Clara valley may be a factor influencing P in these sites. In the west and central regions of Cuba, brown calcareous soils present residual carbonates, in contrast with the same soils in the east part of the country where present secondary carbonates throughout the profile (Cairo and Fundora, 1994). In the Santa Clara valley, the effect of serpentine soils surrounded the calcareous areas has been reported. In the woodland ecosystem, the vicinity with a fersialitic strip from serpentine soils and especially, the inclusion of a fersialitic strip into this area (Fundora, 1979; Torrecilla, 2005), may explain the low levels of Ca-bound Pi, even when this area has not been cropped for more than 50 years. Serpentine soils are characterized by the presence of lithogenic iron oxides, high amount of magnesium and low calcium in the soil solution (Bonifacio and Barberis, 1999, Koide and Mooney, 1987).

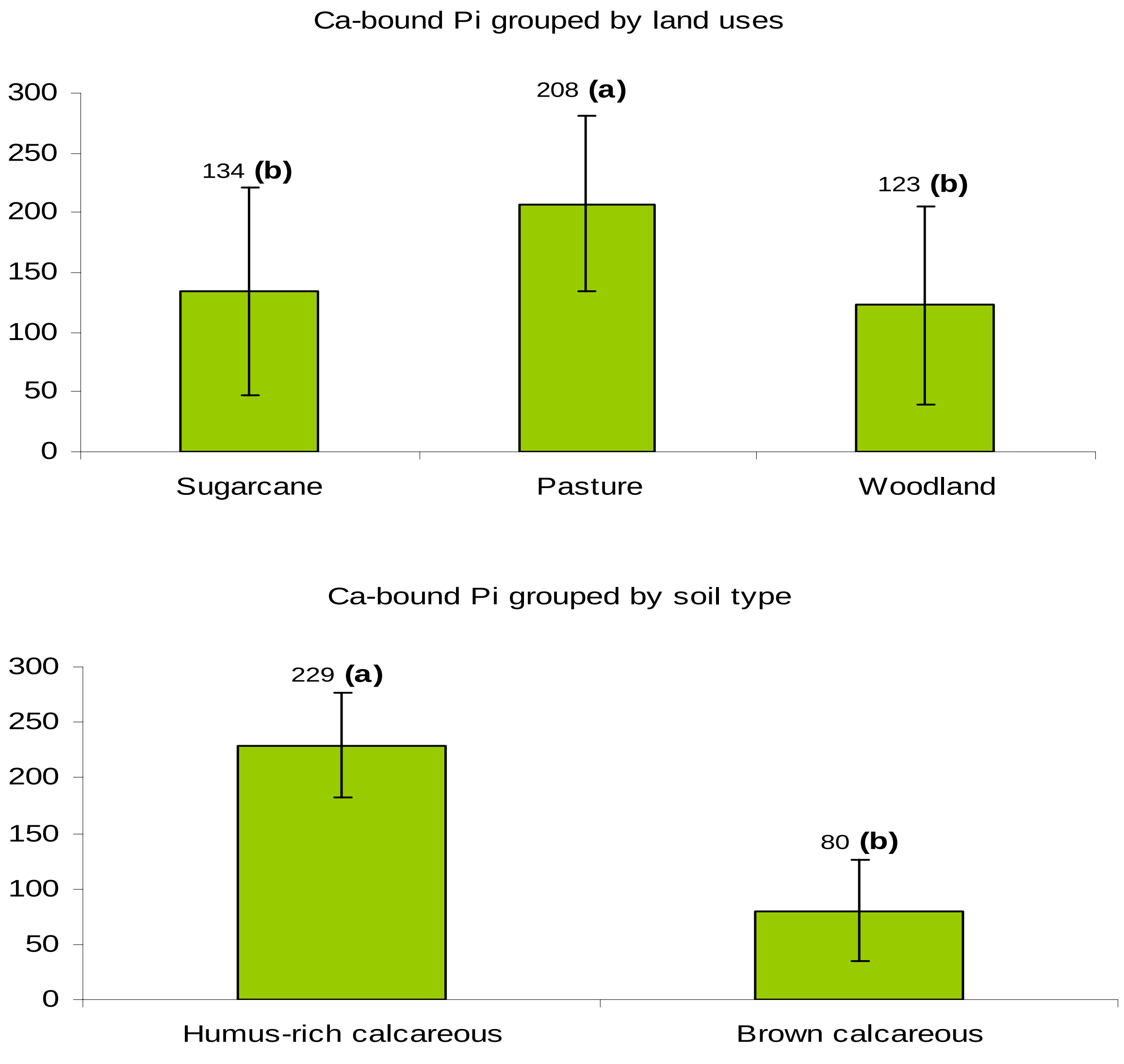


Figure 3. 4. Ca-bound P in Cuban soils grouped by land uses and soil types. Numbers followed by the same letter are not significantly different by FPLSD = 12 for land uses and by FPLSD = 14 for soil types at $P<0.05$.

HClc-Pi and P-residue, are the most recalcitrant forms of P, which in tropical ecosystems are designated as non-labile P (Agbenin and Tiessen, 1994). Homegardens showed higher Pi content in both fractions compared to the other two ecosystems (Figures 3.5 and 3.6). However, Pi-residue was the largest fraction in milpas and forest ecosystems (Table 3.1).

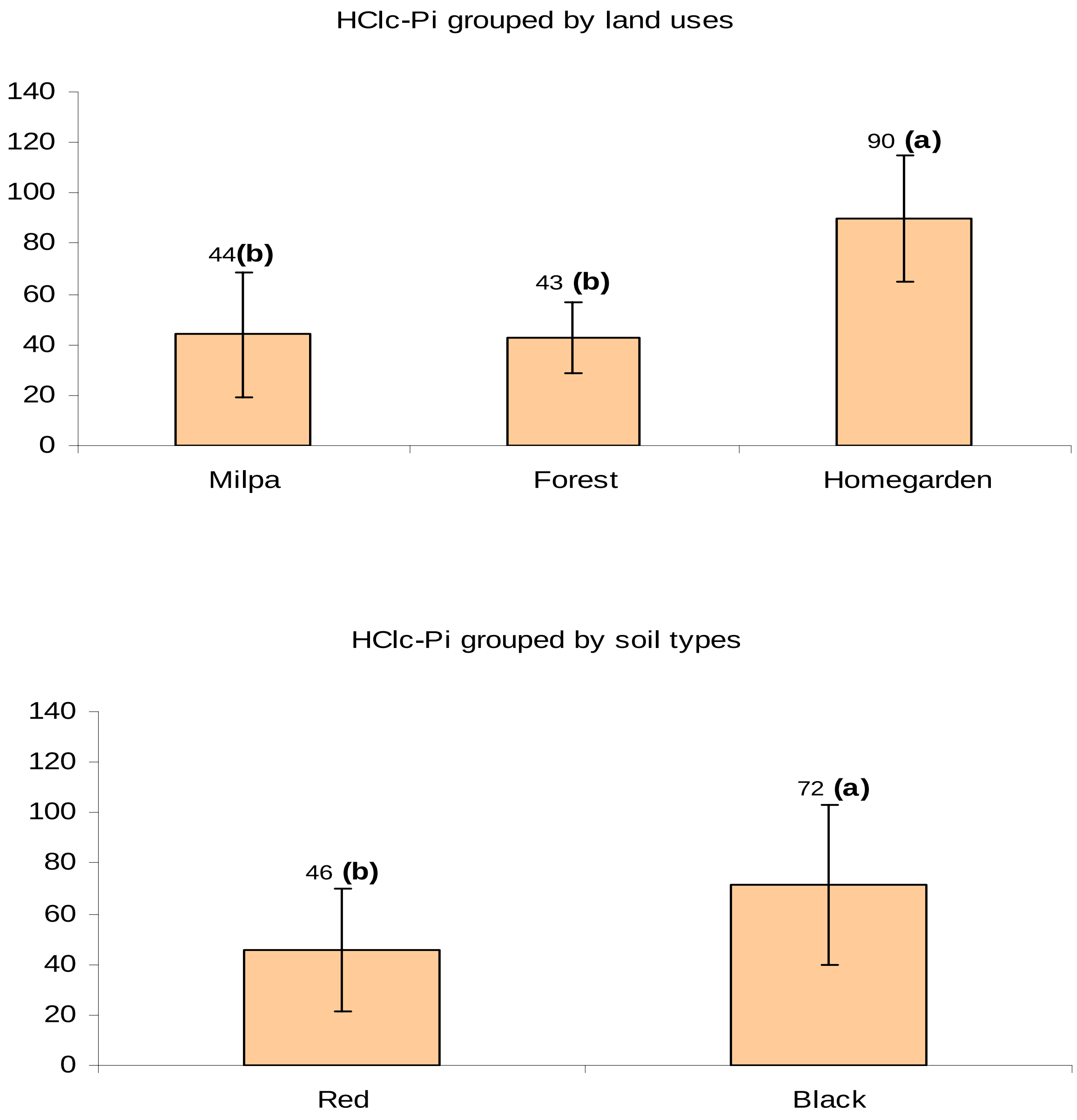


Figure 3. 5. HClc-P in Mexican ecosystems grouped by land uses and by soil types. Numbers followed by the same letter are not significantly different by FPLSD = 9 for land uses and by FPLSD = 7 for soil types at $P<0.05$.

The HClc-Pi fraction was influenced by land use management and soil type independently (Figure 3.5). Homegardens differed from milpas and forests, but these last two did not present differences between them. Black soils presented more Pi (36%) retained in this pool than red soils. Differences in P-residue were determined by land uses, specifically homegardens management. Forest and milpas did not differ significantly in this pool either.

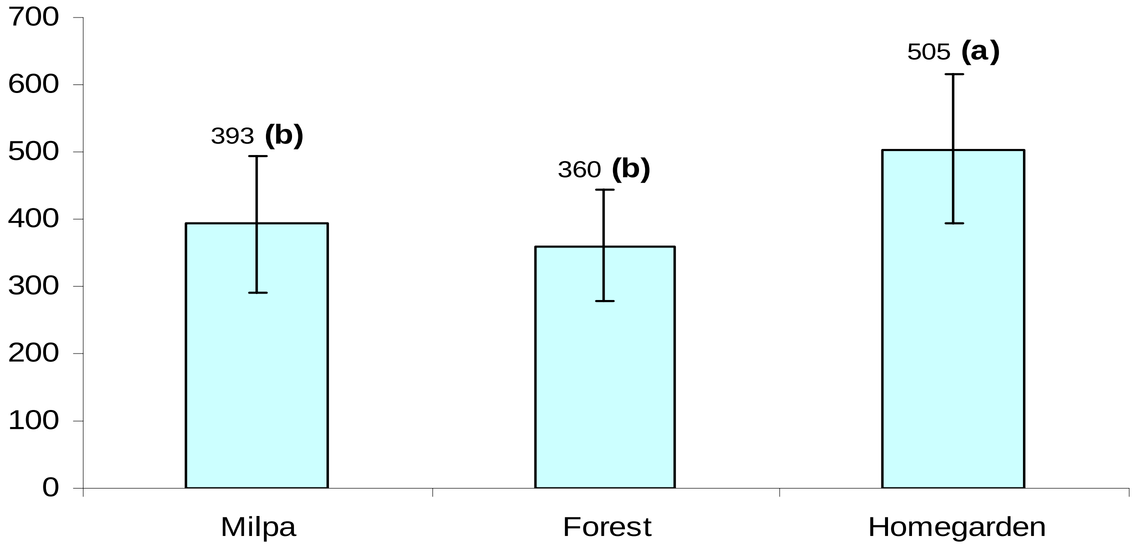
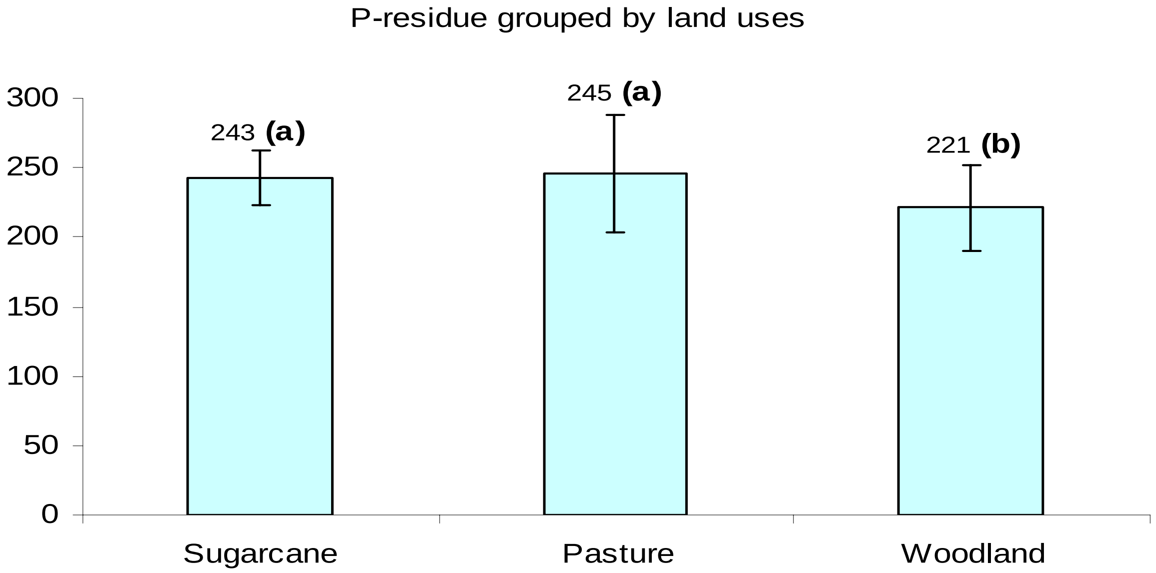


Figure 3. 6. Residual P in Yucatecan ecosystems grouped by land use without distinction of the soil type. Numbers followed by the same letter are not significantly different by FPLSD = 49 at P<0.05.

In Cuban ecosystems, the HClc-Pi and P-residue comprised around 35% in the humus-rich and 45% in the brown calcareous soils (Table 3.2). The largest fraction in all sites was P-residue (Figure 3.7), which implied that most of Pt is not available to plants. This, combined with the Ca-bound P, indicate that in this soils P cycling is strongly related to soil properties. It is well known that that phosphorus availability is directly dependent on soil mineral properties as mineralogy of parent material, leaching rates and texture (Cross and Schlesinger, 2001). Plant available P is determine by labile, surface absorbed or precipitated rather than by crystalline forms of phosphate, and in calcareous environment, the availability is reduced by the low surface area of calcium phosphate, which are mainly present in sand and silt-sized particles (Stewart and Tiessen, 1987).



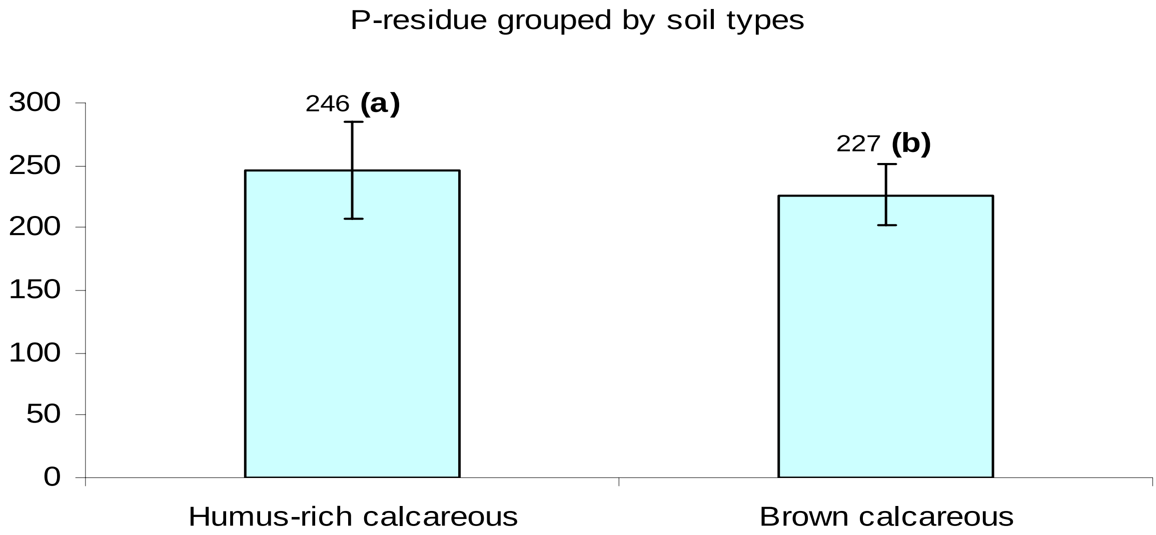


Figure 3. 7. P-residue in Cuban ecosystems (a) grouped by land uses, and (b) by soil types. Numbers followed by the same letter are not significantly different by FPLSD = 14 for land uses and by FPLSD = 16 for soil types at P<0.05.

The HClc-Pi fraction may be considered inactive because of its low solubility, and therefore it does not readily contribute to P availability (Agbenin and Tiessen, 1994). It will be possible that in these highly calcareous soils, some Ca-bound phosphate still remains after the extraction with 1MHCl. So, in this case, the results of HClc-Pi and residual P will be overestimated. Guo et al. (2000) postulated that some residual P in slightly weathered soils may be Ca-P, which was not removed in the previous fractionation steps.

3.4.3. Organic P.

In Yucatecan ecosystems, the total organic P (Po) (Table 3.1) made up more than 30% for forest and milpas in both soil types, but in homegardens was only 10% of Pt. Po distribution is showed in Table 3.3. In Cuban soils, the organic fractions comprised an average of 27% of Pt of each soil (Table 3.2). Under pasture and woodland land uses, humus rich calcareous presented 38 and 39 % more Po than the brown calcareous soils. However, the difference were much lower (only 16%) under sugarcane plantations. Our results agreed with other studies in Yucatan, where 30 and 37% of Pt from red and black soils, respectively, is comprised in the organic pool (Weisbach et al., 2002), and other tropical areas (Tiessen et al., 1994; Buehler et al., 2002). However, results from other tropical areas have accounted less than 5% of Pt in Po pool (Agbenin and Tiessen, 1994; Guo et al., 2000). Po may be mineralized to Pi by simple autolysis or enzymatic phosphorylation, and become plant available. This will be dependent on two factors: microbial activity and the pools of exchangeable and organic P in the soil (Cross and Schlesinger, 2001).

In Cuban and Mexican soils, Po was mainly NaOH-Po (Table 3.3), which is considered a resistant organic fraction as well as HClc-Po (Agbenin and Tiessen, 1994). Hydroxide Po represented 23% and around 31% of Pt in milpas and forests, respectively. In homegardens this fraction comprised around 8% only. The higher concentrations of Po in this pool were found in black soils from milpas and forests, whereas the lowest was found in red soils from milpas. In Cuban soils, hydroxide Po grouped an average of 22%, 17%, and 24% of Pt in sugarcane, pasture and woodlands, respectively. Hydroxide Po is considered as a more stable forms of Po involved in the long-term transformations of P in soils (Tiessen and Moir, 1993). In tropical ecosystems, the presence of rich carbon substrates (plant residues in milpas, animal manure in homegardens and litter in forests) stimulate microbial activity, which enhanced a shift toward Po in the hydroxide fraction and microbial biomass (Bünemann et al., 2004). In homegardens, the litter and plant residues are swept away daily and burn it, so, this residues are incorporated as ashes.

Although HCO_3-Po accounted for only a small portion of the total Po, bicarbonate Po is easily mineralized and contributes to plant available P (Tiessen and Moir, 1993). This fraction represents P that is held in the soil by adsorption to soil particles or soil organic matter. It has been correlated with high concentrations of organic carbon (OC), as well as hydroxide Po, and total nitrogen (N) content (Cross and Schlesinger, 2001).

HClc-Po is recognized as a very stable residual pool tightly bound to Fe and Al minerals. However, it may come from particulate organic matter that is not alkali extractable, but may become easily available to plants (Tiessen and Moir, 1993).

Although in the calcareous environment P cycle is dominated by geochemical factors, the small organic pool may determine in the availability of P (Cross and Schlesinger, 2001). Po is not a significant contributor of available P in high-P mineral soils (Guo et al., 2000). However, the contribution of soil biological processes to deliver plant-available P may become more important when availability of Pi is low. The decomposition of soil organic matter and plant residues is indeed often the main source of plant nutrients in low input small-scale farming systems in tropical areas (Bünemann et al., 2004).

Table 3. 3. Distribution of the organic P into its different fractions in Mexican (a) and Cuban (b) soils.

(a)

Land use (LU)	Soil (S)	Po-HCO$_3$	Po-OH	Po-HClc
Milpa	Red	25	152	5
	Black	20	325	135
Forest	Red	23	248	14
	Black	21	311	47
Homegarden	Red	12	260	15
	Black	9	244	80
FPLSD	Red	4	42	5
	Black	4	ns	33
	Significant interaction Land use x soil	ns	0.007	0.003

(b)

Land use (LU)	Soil (S)	Po-HCO$_3$	Po-OH	Po-HClc
Sugarcane	Humus-rich calcareous	9	178	6
	Brown calcareous	36	119	6
Pasture	Humus-rich calcareous	32	159	8
	Brown calcareous	23	93	4
Woodland	Humus-rich calcareous	30	193	6
	Brown calcareous	27	110	7
FPLSD	Humus-rich calcareous	4	15	**ns**
	Brown calcareous	2	10	2
	Significant interaction Land use x soil	0.000	ns	0.031

Differences are significant at $P<0.05$ for those which their differences are higher than Fisher's protected LSD (FPLSD) in the significant interactions within the same column. Abbreviation "ns" means no significant differences at $P<0.05$.

3.5. CONCLUSIONS

P is often the limiting nutrient in most tropical areas. Ecosystem management and agricultural activities alter the cycle of P in soils. Our results showed differences among the P fractions, which can be attributed to management and farming systems adopted in each case. Mayan slash and burn agriculture alternate milpa areas with secondary forest. The distribution of P into the different fractions in both ecosystems is very similar. However, in homegardens Pt was significantly higher for both soils compared to the other areas. Also, P had different partition into the inorganic fractions.

Cuban soils cropped under intensive agriculture since colonial times reported low Pt and also less available P compared to the other sites with woodland and pasture land uses. The pasture area from humus-rich soil presented the highest P content and also P availability, but in this case the processes are influenced by the stable inputs of manure in the system throughout decades. The pasture from the brown calcareous soil did not presented the same results as a consequence of severe degradation caused by previous uses. Woodlands are stable ecosystems in both soils, where biological and chemical processes depend on soil properties and nutrient turn over.

The organic P fraction was only a small portion of Pt. However, Po seemed to be an important P source in these soils and may determine P availability, since most of P is comprised in non-labile pools.

Finally, in these calcareous tropical soils geochemical processes dominates P cycling, enhanced by the influence of calcium carbonate. Nevertheless, biological processes should play an important role in P availability. Probably, the microbial activity is closely related to other factors such as, soil moisture fluctuations, suggesting the relevance of new studies which accounted the particular climatic conditions of the semiarid tropics.

CHAPTER 4: NUTRIENT AVAILABILITY AND SOIL MOISTURE INTERACTIONS IN CALCAREOUS SOILS FROM YUCATAN, MEXICO, AND VILLA CLARA, CUBA.

4.1. ABSTRACT

The strong seasonality in the semiarid tropics affects soil moisture. This is an important limiting factor for nutrient availability in calcareous tropical soils. In four calcareous tropical soils (two from Yucatan, Mexico and two from Villa Clara Cuba) under different land uses we assessed the interaction between two soil moisture levels [field capacity (FC) and one half of that the gravimetric moisture content at field capacity (HFC)] and the availability to plants of five nutrients (Ca^{2+}, Mg^{2+}, K^+, PO_4^{3-}, and NO_3^-) using in situ ion exchange membranes. Soil sampling was done following a random design, and in the case of the Mexican soils, it was stratified by soil color due to the extreme heterogeneity of the soil that is expressed as a mosaic of red and black soils. The experiment was conducted during 45 days under controlled laboratory conditions. Soils were placed in two caps with a cation exchange membrane (CEM) in between and joined with the help of clamps. The same procedure was repeated with anion exchange membranes (AEM). Resin membranes were replaced every five days, and the removed membranes were eluted in 0.5 N HCl. Eluates were kept at 4°C, and cations were analyzed by atomic absorption Ca^{2+} and Mg^{2+}, and K^+ by flame emission spectroscopy. Anions were measured by colorimetric analyses. The availability of all nutrients, except phosphorus, was lower at FC than at HFC in both soil types. For instance, nitrate decreased around 30% when soil water content reached full moisture. Phosphate availability increased around 95%. All the cations showed lower concentrations in the soil solution at full moisture. In the Mexican ecosystems, homegardens presented higher content of phosphate and potassium than the other land uses, while nitrate was more available in forests. Red soils presented less nitrate and phosphate availability compare to the black group, but higher magnesium levels. In Cuban soils, calcium, nitrate, and phosphate availability was higher in the humus-rich soils than in the brown calcareous. Magnesium concentrations presented an inverse trend compared to these elements. Our results suggest that in Mexican and Cuban ecosystems, soil fertility problems may be caused by low levels of phosphate and potassium, and their interactions with the available water.

Keywords: *nutrient availability, soil moisture, water content, ion exchange membrane, resin, calcareous tropical soils, Yucatan, Mexico, Villa Clara, Cuba.*

4.2. INTRODUCTION

Calcareous soils are typical soils of semiarid and arid climates (FAO, 2000) and are characterized by the presence of free calcium and magnesium carbonates and pH above 7 (Leytem and Mikkelsen, 2005), which cause a different nutritional environment for vegetation compared with non-calcareous soils (Kishchuk et al., 1999).

Water content is an important property of soils, influencing soil solution chemistry and nutrient uptake by plants. Moisture fluctuations regulate the availability of nutrients (Misra and Tyler, 1999). However, these fluctuations can not be assessed using traditional chemical extractions. Their measurements provide only a snapshot of nutrient availability. They are unable to measure fluxes that occur with changing environmental conditions (Knopp and Guillard, 2002).

For more than 40 years, ion exchange resins have been used to characterize nutrient bioavailability in terrestrial and aquatic ecosystems, and with general acceptance as a method for detection of soil nutrient levels (Sherrod et al., 2003) compared to the conventional soil tests, which measure the quantity of a nutrient at the time of sampling, but may not account for factors affecting subsequent availability of the same one (Salisbury and Christensen, 2000).

Ion exchangers are considered a promising method for estimating nutrient availability because resins eliminate problems inherent to chemical extraction of soil. Nutrient recovery by in situ exchange resins, acting like plant roots, integrate nutrient availability and diffusion rates as affected by soil temperature, water content and biological activity (Salisbury and Christensen, 2000). Greer et al. (2003) explained that ion exchange resins provide a dynamic measure of ion flux and scale the results with climatic factors, and therefore, could provide superior data on which to build an integrated soil-climate-plant model.

Cuba and Mexico are in the semiarid area with calcareous soils affected by degradation processes, reflected in decreasing productivity of the agricultural ecosystems and low fertility of these soils. The main objective of this experiment was to assess nutrient availability of four calcareous soils (two from Mexico and two from Cuba) under two levels of soil moisture and different land uses, characterizing the nutrient supply for five macro nutrients (NO_3^--N, PO_4^{2-}-P, Ca^{2+}, Mg^{2+}, and K^+) using ion exchangers .

4.3. MATERIALS AND METHODS.

4.3.1. Experimental field design.

Soil sampling in both countries was done during the dry season following a random design, and in the case of the Mexican soils, it was stratified by soil color due to the extreme heterogeneity of the soil. Two calcareous soils for each country were selected: from Yucatan, there were red and black soils identified as red Redzina and Lithosols (Weisbach et al., 2002), respectively; and from Villa Clara, brown calcareous and humus-rich soils classified as Orthic-Calcaric Cambisol (Villegas et al., 1994; Aleman et al., 2002) and Hyper-Calcaric Phaeozem (Marin et al., 1994).

In the Mexican ecosystems were identified three land uses: forest, milpa, and homegardens. Three sites of each one were considered for sampling for a total of 9 sites. Two soil types (red and black soils) were sampled collecting 5 replicates of each group per site of collection (10 samples per site). This gave us a number of 90 samples (45 of each soil type). In the case of the Cuban soils three land uses were chosen: sugarcane, pasture and woodlands. Two soil types were selected: humus-rich and brown calcareous soils. A number of 10 replicates per site were collected for a total of 60 samples.

Previous to the experiment in controlled conditions, samples were air dried and the field capacity was determined gravimetrically. With this purpose, 10g-soil samples, previously sieved at 2 mm and air-dried, were placed in bottomless glass-tubes and pressed gently. Previously, the bottom part of the tube was covered with a single layer of parafilm. Then, deionized water was added slowly until reached soil saturation (15 ml for red soils, 25 ml for the black ones and 20 ml for both Cuban soils). Following that, the upper part of the tube was covered with a single layer of parafilm for avoiding water evaporation. Especially for black soils, water infiltration was very slow. On the second day, samples were checked. Generally, black-soil samples took more than one day to be uniformly saturated. When the samples were uniformly wet and saturated, the parafilm layer at the bottom of the tube was removed carefully to avoid soil losses. Samples were left to drain and weighed every two hours to check the losses of moisture. When drainage ceased, the moisture content in soil samples was taken to be at field capacity (FC). The weight of the dried sample (10g) was subtracted from the weight of the sampled that reached FC. The resulting value was considered as the volume of water needed it for reaching FC for this weight of soil. For the second water treatment, the volume of water added to the soil was simply half of the quantity used for FC (HFC).

4.3.2. Preparation of the membranes.

The ion exchange membranes used for this research were synthetic resins commercially available (PC Acid 35 and PC SK, PCA Ltd., Germany). Both, anion (AEM) and cation (CEM) exchange membranes were bought in 500 cm^2 sheets. They were cut into circles of 3.2 cm diameter (Figure 4.1), which provide a reactive surface of 16.08 cm^2 per strip (both sides, i.e. twice the circle area) and a total of 225 strips per sheet.

During the preparation and extraction, AEM and CEM were kept in different beakers, in order to facilitate the differentiation of each type of resin strip.

4.3.3. Conversion and regeneration of AEM to HCO_3^- form and CEM to Na^+ form.

For the preparation and regeneration of the resins, 150 AEM and CEM disks were placed in 1000 mL beakers containing 0.5 N HCl, shaken for 1 hour and washed thoroughly 2 times with deionized water. The objective of this step was to clean the membranes before the AEM and CEM conversion to HCO_3^- and Na^+ form, respectively.

Next, membranes were placed again in 1000 mL beakers containing solutions of 0.5 M $NaHCO_3$ for AEM and 0.5 M NaCl for CEM, and shaken for another hour. This procedure was repeated 5 times in fresh solutions. At the end, the membranes were rinsed well with abundant deionized water.

After conversion/ regeneration, the membranes were stored in deionized water and kept at 4°C.

4.3.4. Experimental procedure in the laboratory.

Each air-dried sample of 20 g-soil was watered to FC and HFC and placed into two caps (10 g in each one) with an ion exchange membrane, previously converted to HCO_3^- (anion exchange membrane (AEM)) or Na^{2+} form (cation exchange membrane (CEM) placed in between. The caps were joined and pressed together with the help of a clamp to guarantee the full contact between membrane and soil (Figures 4.1 and 4.2).

For the laboratory experiment, the field sampling design was maintained and a water treatment with two levels of moisture (FC and HFC) was included, obtaining a tri-factorial interaction (land use-soil-water content). As the field design was kept, for each water treatment a total of 150 samples (90 samples from Mexican soils and 60 from Cuban soils) were prepared for AEM and for CEM, each.

The removal of the membrane was done carefully every five days, avoiding any loss of soil. Membranes were washed back with little deionized water into the soil before putting into the flask with the eluent (0.5 N HCl). The samples were checked for moisture losses and, when needed, more deionized water was added again until FC and HFC was reached. Before the experiment, test samples were prepared and weighed immediately after being hydrated to half or full moisture. Samples were kept in the same controlled conditions as for the experiment. After five days, the samples were weighed once more. The weight differences indicated losses of moisture. The losses of water were averaged for each combination: land use-soil type-moisture. The averages were used for re-hydrating the samples in every five-day cycle.

The absorbed anions and cations were recovered by shaking the membranes overnight in 25 mL of 0.5 N HCl. For that, resins were put into plastic flasks with the acid, and, after gas bubbles disappeared, flasks were caped and shaken overnight (16 hours). Eluates were kept at 4°C until analysis.

Figure 4. 1 "Sandwich" compositions: caps with soil, circular strip of ion exchange membrane, and clamp.

Figure 4. 2. Incubation experiment under controlled conditions with ion exchange membranes.

4.3.5. Analyses of the extracts.

Each extract was analyzed for the following five plant nutrients: Ca^{2+}, Mg^{2+}, K^+, NO_3^--N, and PO_4^{2-}-P. Ca^{2+} and Mg^{2+} were determined by atomic absorption and K^+ by flame emission spectroscopy in the NOVAA 315 stand alone Flame AAS from Analytic, Jena AG, Germany.

Nitrate was determined by colorimetric analysis using the technique described by Yang et al. (1998), and adapted for our case. This procedure is based on a single color development solution (TRI solution) obtained by dissolving 1g of sodium salycilate, 0.2g of sodium chloride (NaCl) and, 0.1g of ammonium sulfamate in 100 ml of 0.01M NaOH. The last two chemicals are useful to avoid interferences, since NaCl, at low concentration, masks Cl^- interference and ammonium sulfamate suppresses NO_2^- interferences. The other reagents used were H_2SO_4 and concentrated NaOH (40g in 100 ml deionized H_2O). The resin extracts required prior neutralization with 0.5 M NaOH before the addition of the color solution. One mL aliquots of standards and extracts were transferred into 50 mL volumetric flasks and, after neutralization by adding 1 mL of 0.5 M NaOH, 0.5 mL of TRI solution were swirled to mix. Next, the samples were placed in an oven at 65°C overnight to evaporate water. After drying, they were let stand to cool. Then, 1 mL of concentrated H_2SO_4 was added along the flask wall to wet the residues, which were dissolved by occasional swirling. The samples were let cool for 10 minutes after which 5 mL of H_2O were added slowly along the wall and swirled to mix well. As soon as the samples were cooled again, 5 mL of 40% NaOH were added slowly and mixed thoroughly, and during that, the yellow color was developed. Finally, the samples were cooled again and made to volume for measuring at 410 nm in the spectrophotometer (UNICAM 8625 UV/VIS).

Phosphate was measured using two methods. For the FC treatment, it was measured in a Technicon Autoanalyzer (Figure 4.4) at 420 nm using the method for total P adapted by substitution of the sulphuric acid by 0.5 N HCl, the same acid and concentration of the extracts. The yellow color solution used was prepared by dissolving 1 g of ammonium vanadate in 200 mL deionized water, stirred and heated at 200°C on the magnetic stirrer. After that, 20 g of ammonium molybdate was dissolved in 200 mL of deionized water and mixed in the magnetic stirrer. Finally, in 1L volumetric flask with 150 mL deionized water were added 150 mL concentrated HCl (37%), and then, first the ammonium vanadate solution, followed by the ammonium molybdate solution. As last step, water was added to volume.

In the case of the HFC, because of the very low P concentrations expected at this moisture, was used the Murphey and Riley (1962) method described by Tiessen and Moir (1993) in order to obtain more precise results. A suitable aliquot of the sample was pipetted into a 50-ml volumetric flask. Two drops of paranitrophenol were used as indicator for adjusting the pH. Then, 4M NaOH was added until the solution turned yellow, and then, 0.25M H_2SO_4 was dropped into the solution until turned clear. Finally, 8 ml of color developing solution were added, the solution was made to volume, shaken and read at 712 nm after 10 min on a spectrophotometer (UNICAM 8625 UV/VIS). The color solution was made mixing 250 ml 2.5M H_2SO_4 with, first, 75 ml ammonium molybdate solution (40g into 1000 ml H_2O), following by 50 ml ascorbate solution (26.4g in 500 ml H_2O), and finally, 25 ml of antimony tartrate solution (1.454g in 500 ml H_2O). After each addition, the contents were swirled throughoutly.

Both methods were cross calibrated. The samples with the lower concentrations were measured again with the blue method, and no significant differences were found with the results obtained with the yellow method.

4.3.6. Calculation and Data interpretation.

Based on the results obtained in the analyses described above, it was possible to calculate the nutrient supply rate (NSR) for each ion, defined as the total amount of nutrient ion adsorbed per unit surface of ion exchange membrane over the time of direct contact with soil as specific temperature and moisture conditions, which can be expressed as $\mu g/cm^2$/ time, based on the following formula:

$NSR = (C \times V)/ S$

Where,

C: concentration of an adsorbed ion (µg/mL)

V: Volume used of the extracting solution (25 mL)

S: surface area of the membrane strip (cm^2)

Cuban and Mexican ecosystems were analyzed independently given the differences in soil management and land uses between both countries. The NSR calculations were done for each change and for the total of the nutrient released.

Data processing was done with SPSS 9.0 (SPSS Inc., Chicago). The means of the concentration in the eluates for each membrane change were plotted to obtain the curves of nutrient release by land use-soil combination. Differences between the means were tested by one-way ANOVA of the single factor land use within the same soil type and moisture level. For the means of the total concentrations of the ions (sum of all 5-days extracts), the same procedure was used.

For the total amounts of the ions, data were also analyzed by three-way ANOVA with the factors land use, soil type, and water content. When the interactions between were significant, the analyses were performed by one-way ANOVA for red and black soils separately. With the two water treatments, the same procedure was done. The differences between soils, as well as between the two levels of moisture, were confirmed by T-test. Mean separation was accomplished using Fisher protected LSD (FPLSD) at $\alpha = 0.05$ of significance level.

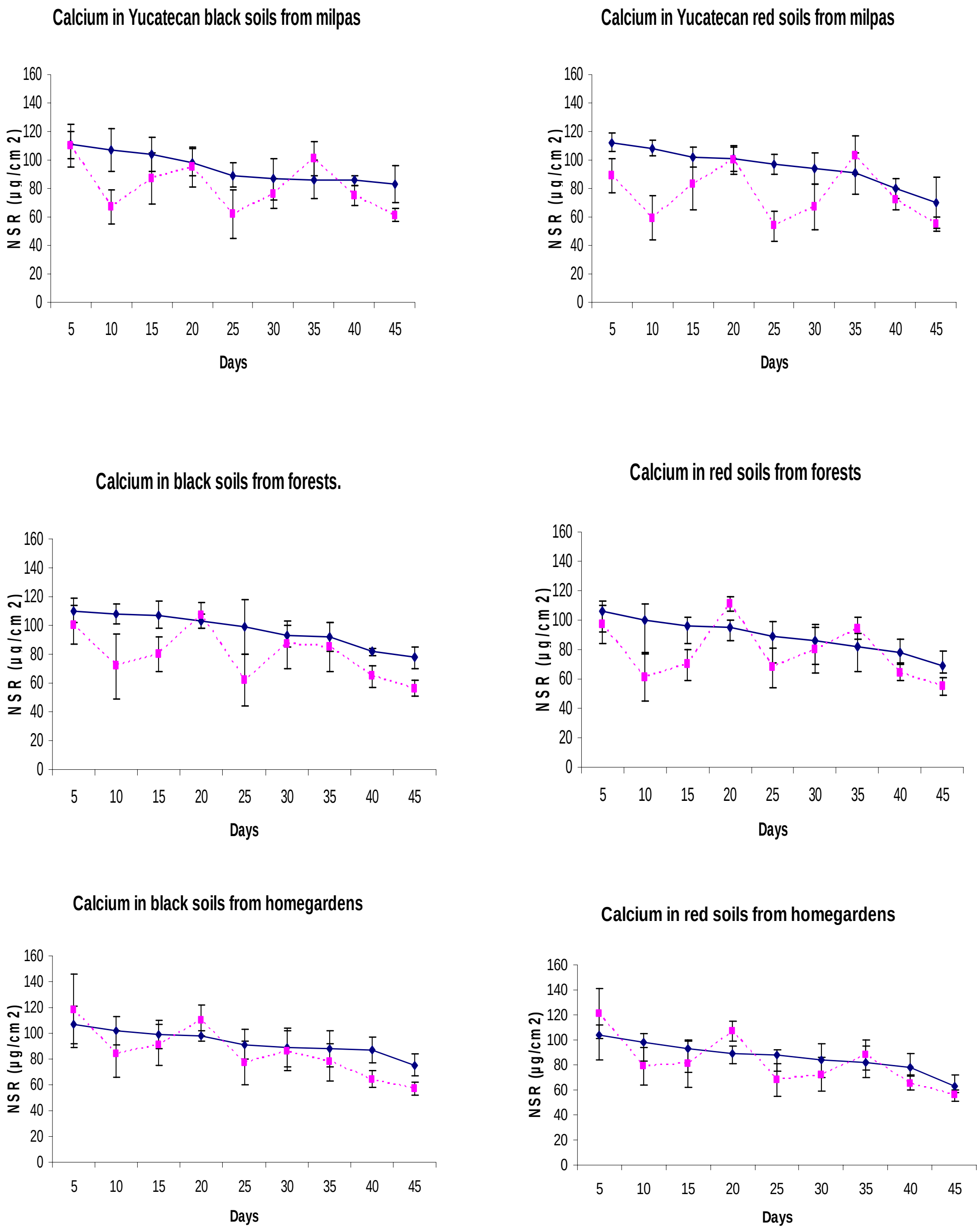
4.4. RESULTS AND DISCUSSION.

4.4.1. Incubation experiment with ion exchange membranes at FC and HFC.

The curves of nutrient release obtained at FC and HFC for the five nutrients are represented in Figures 4.3 to 4.12. At full moisture the release curves were uneven, whilst at half water content, they were smooth. The incubation experiments at FC and HFC were not done simultaneously. During the incubation at FC, specifically at 20 days, some technical problems were reported with the distilled water supply. Therefore, it is possible that the deionized water applied for re-watering the samples in every change could cause the peaks in the curves at FC due the inputs of some contaminant in the water.

In general, red and black soils from Mexican ecosystems and brown calcareous and humus-rich calcareous soils from the Cuban sites showed differences in nutrient availability. Within the same soil group, the differences were caused by the effect of land use. Water levels also affect the nutrient availability, phosphate being the nutrient ion with the more remarked response. The interactions among the three factors (soil type, land use and water content) showed that all soils did not respond identically to land use changes and different levels of soil moisture.

The release of the nutrients showed that the availabilities with time varied for each (Figure 4.3 to 4.12).Within the cation group, Ca availability with time stayed constant within the range for each site for Mexican and Cuban soils. At both levels of soil moisture, Ca availability did not present critical contrasts in the curves of nutrient release. Ca dominated over the other four nutrients even for the woodland in the brown calcareous soils where the highest Mg availability was found. The availability of Mg oscillated in a constant range until the 35 days for Mexican and Cuban soils. At this point, Mg availability declined and dropped to zero at days 40 and 45. In contrast with Ca that seemed to be constant throughout the incubation period, K availability dropped to zero at 30 days even when the released amounts were much lower than those for Ca and Mg. The only exceptions were the homegardens in the Yucatecan group and the pasture from the humus-rich calcareous soils, where K availability dropped to zero at 40 and 35 days, respectively. In the anion group, nitrate availability decreased strongly at 10 days compare to the concentrations found at 5 days. After that, although at low levels, nitrate availabilities were even dropping to zero at 40 days. Phosphate availability started to decline at 25 days in all sites. At 30 days, most of phosphate availability dropped to zero excepting for homegardens in the Mexican group and pasture areas in the Cuban soils. These results suggested that K and phosphate availabilities with time are lower than Ca, Mg and nitrate availabilities. Both nutrients dropped to zero at 30 days of the incubation experiment, which may be interpreted as a possible deficiency of these nutrients in these calcareous soils. There are several papers where it has reported problems with K and phosphate availabilities in calcareous soils due to carbonates interference and cation imbalances (Misra and Tyler, 1999; Kishchuk et al., 1999; FAO, 2000; Imas, 2000; Leytem and Mikkelsen, 2005; Carreira et al., 2006).



Calcium in Yucatecan black soils from milpas

Calcium in Yucatecan red soils from milpas

Calcium in black soils from forests.

Calcium in red soils from forests

Calcium in black soils from homegardens

Calcium in red soils from homegardens

Figure 4. 3. Calcium released from Mexican soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).

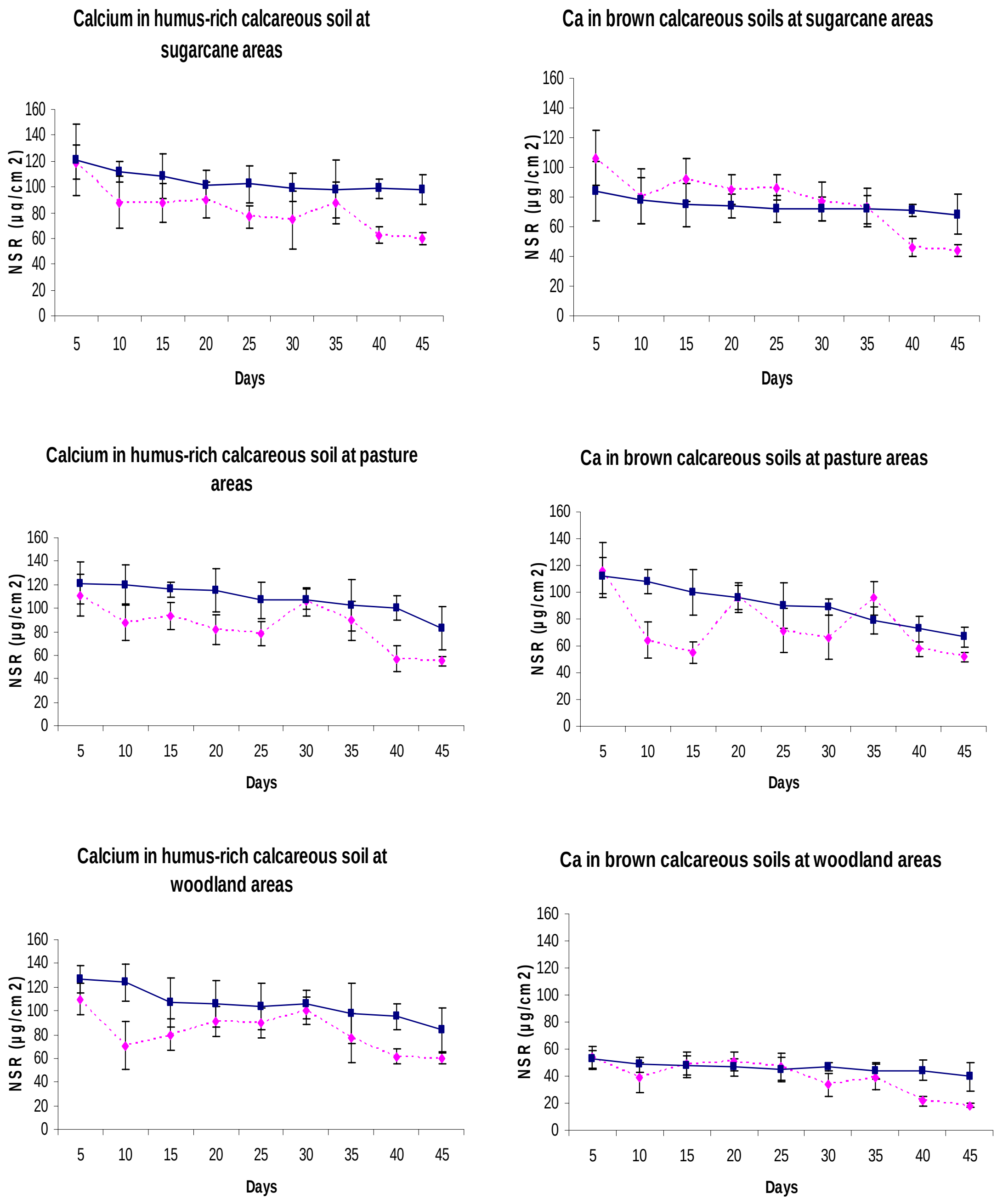
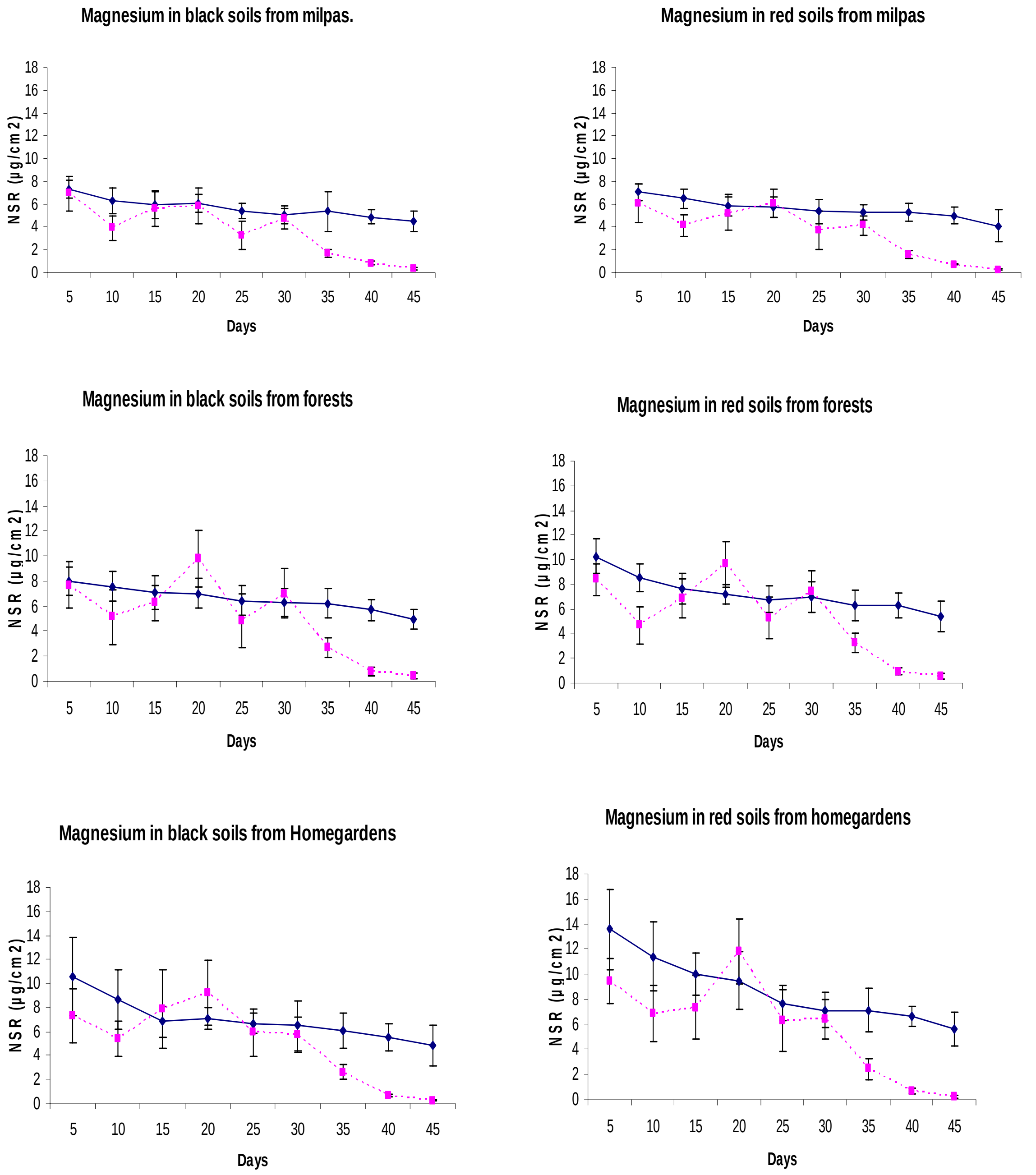


Figure 4. 4. Calcium released in Cuban soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).



Magnesium in black soils from milpas.

Magnesium in red soils from milpas

Magnesium in black soils from forests

Magnesium in red soils from forests

Magnesium in black soils from Homegardens

Magnesium in red soils from homegardens

Figure 4. 5. Magnesium released in Mexican soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).

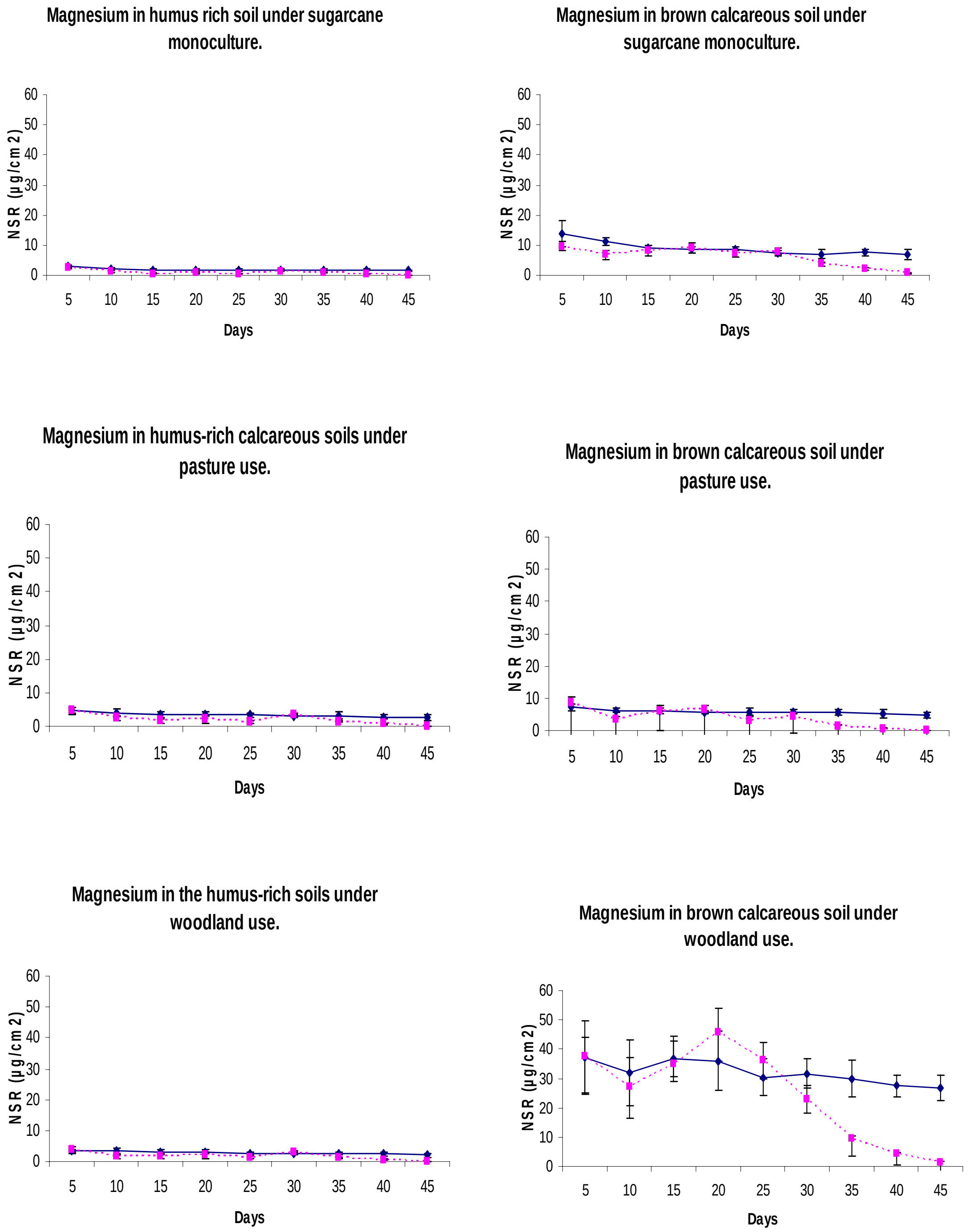


Figure 4. 6. Magnesium released in Cuban soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).

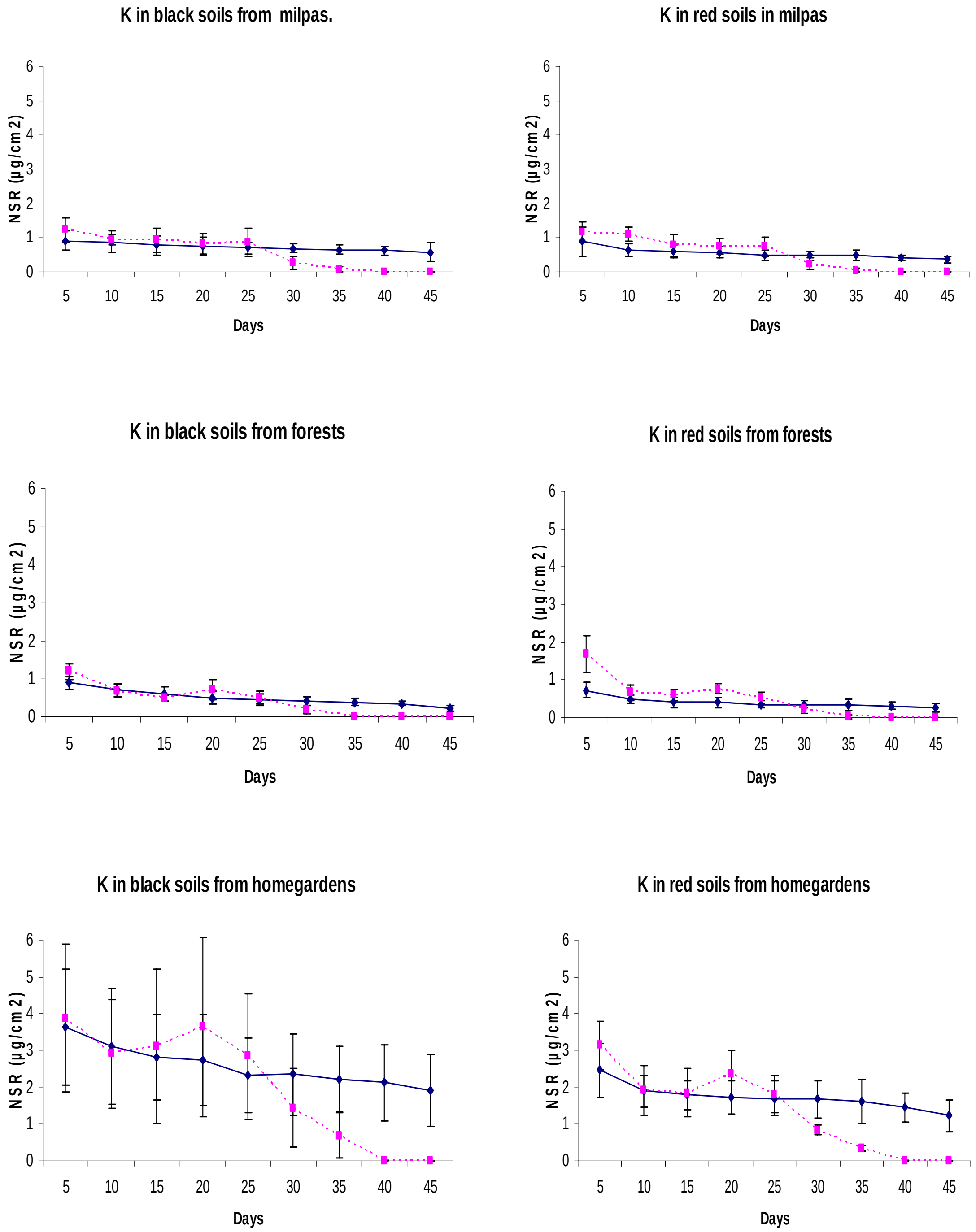


Figure 4. 7. Potassium released in Mexican soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).

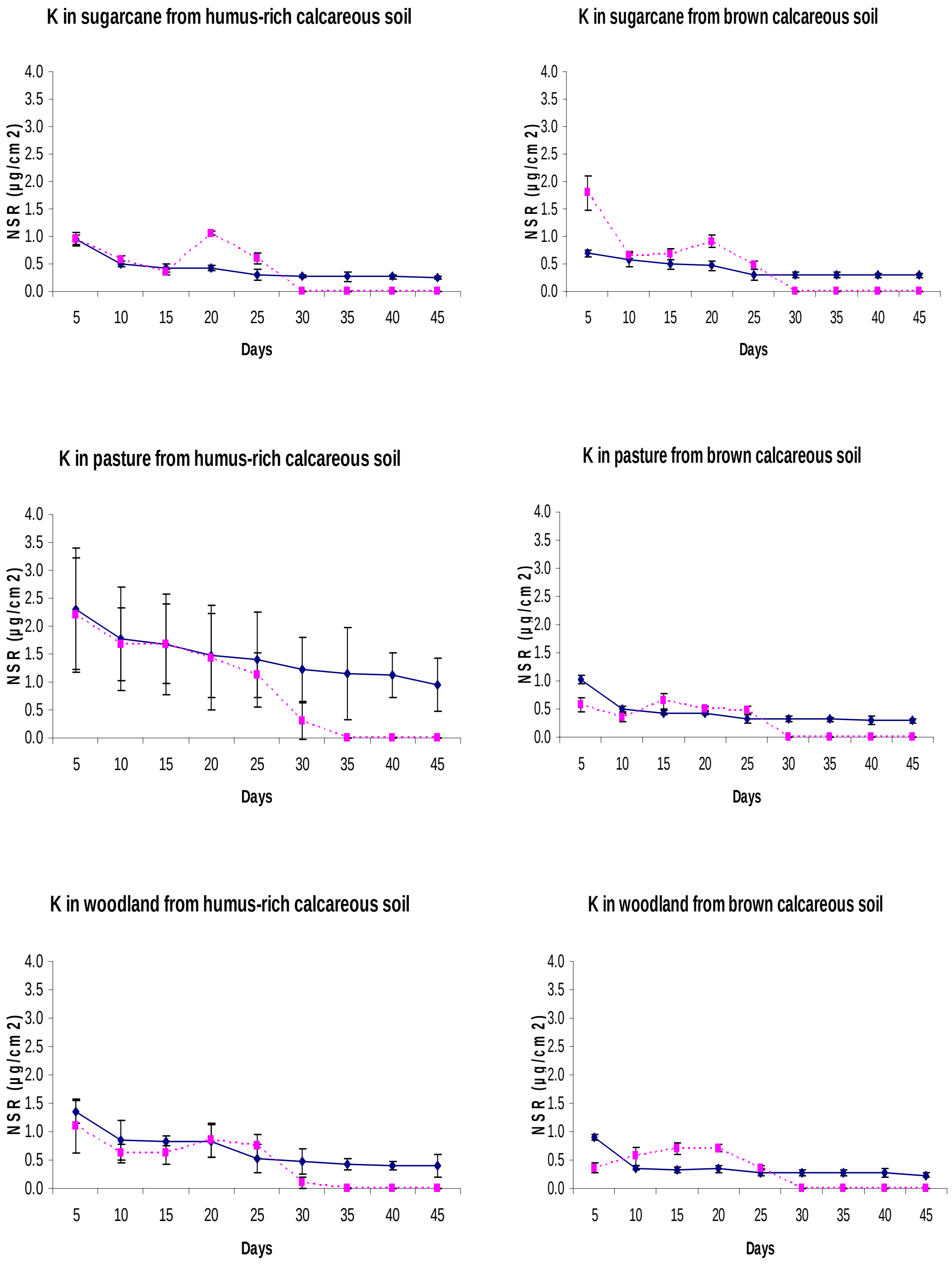


Figure 4. 8. Potassium released in Cuban soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).

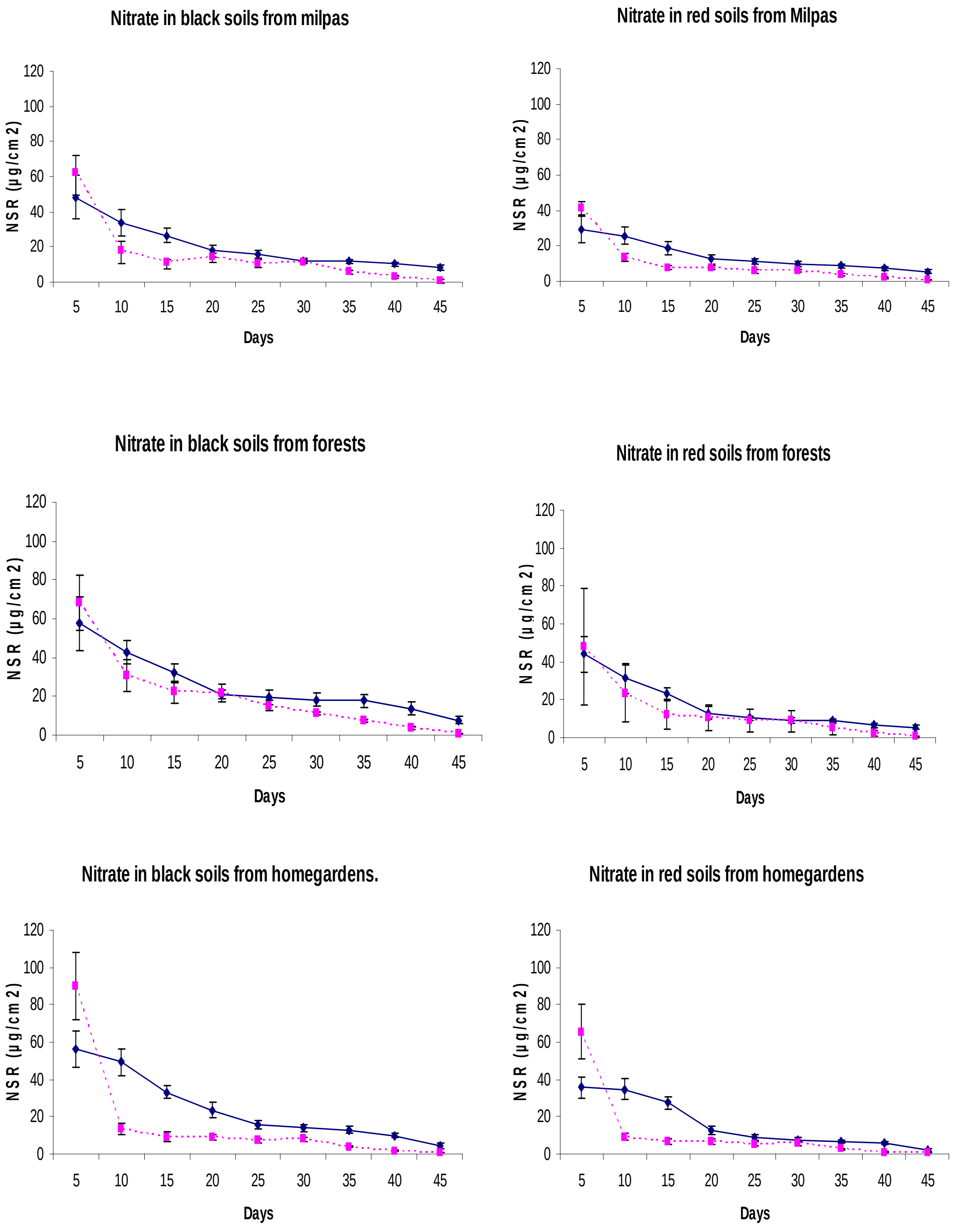
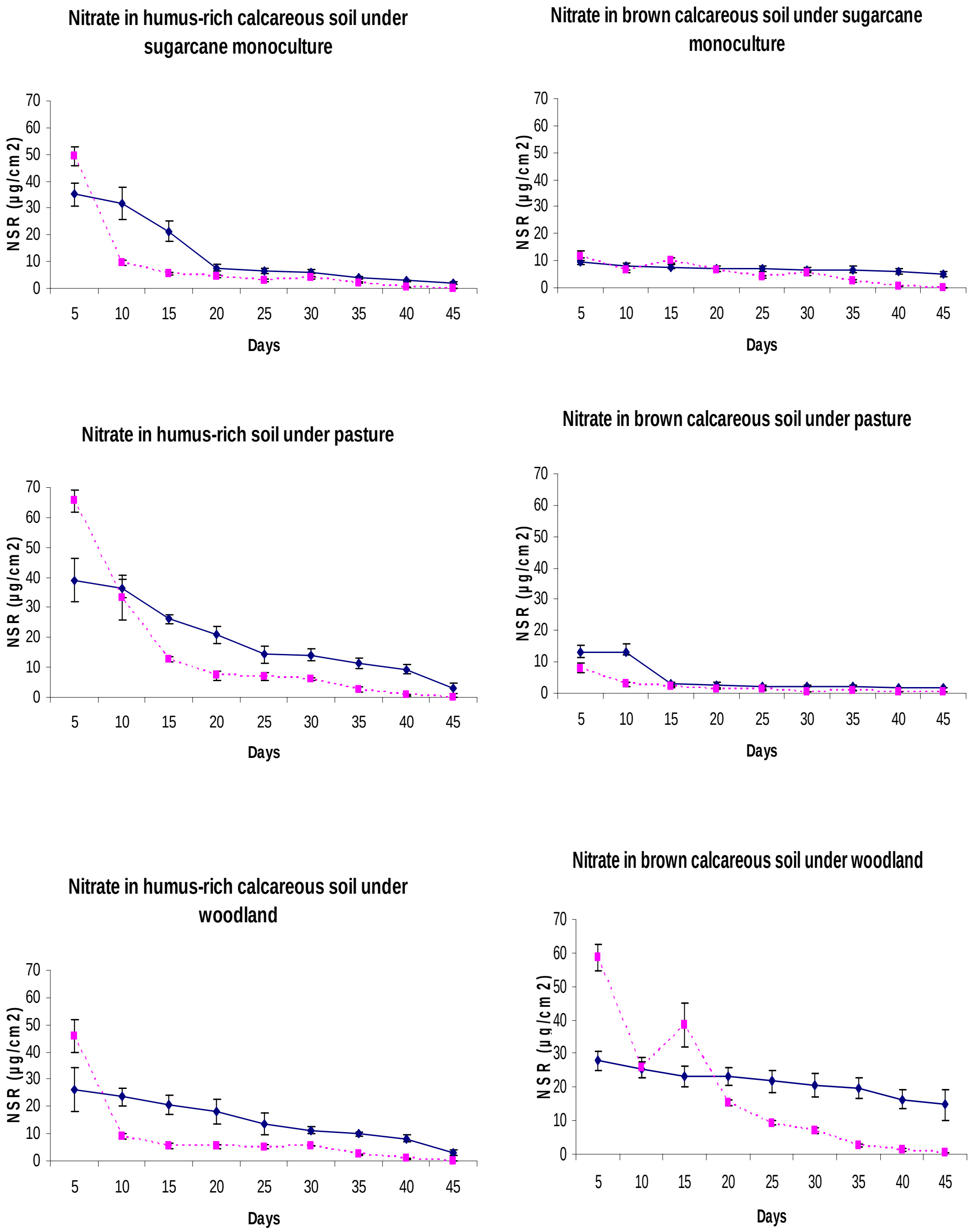


Figure 4. 9. Nitrate released in Mexican soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).


Nitrate in humus-rich calcareous soil under sugarcane monoculture

Nitrate in brown calcareous soil under sugarcane monoculture

Nitrate in humus-rich soil under pasture

Nitrate in brown calcareous soil under pasture

Nitrate in humus-rich calcareous soil under woodland

Nitrate in brown calcareous soil under woodland

Figure 4. 10. Nitrate released in Cuban soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).

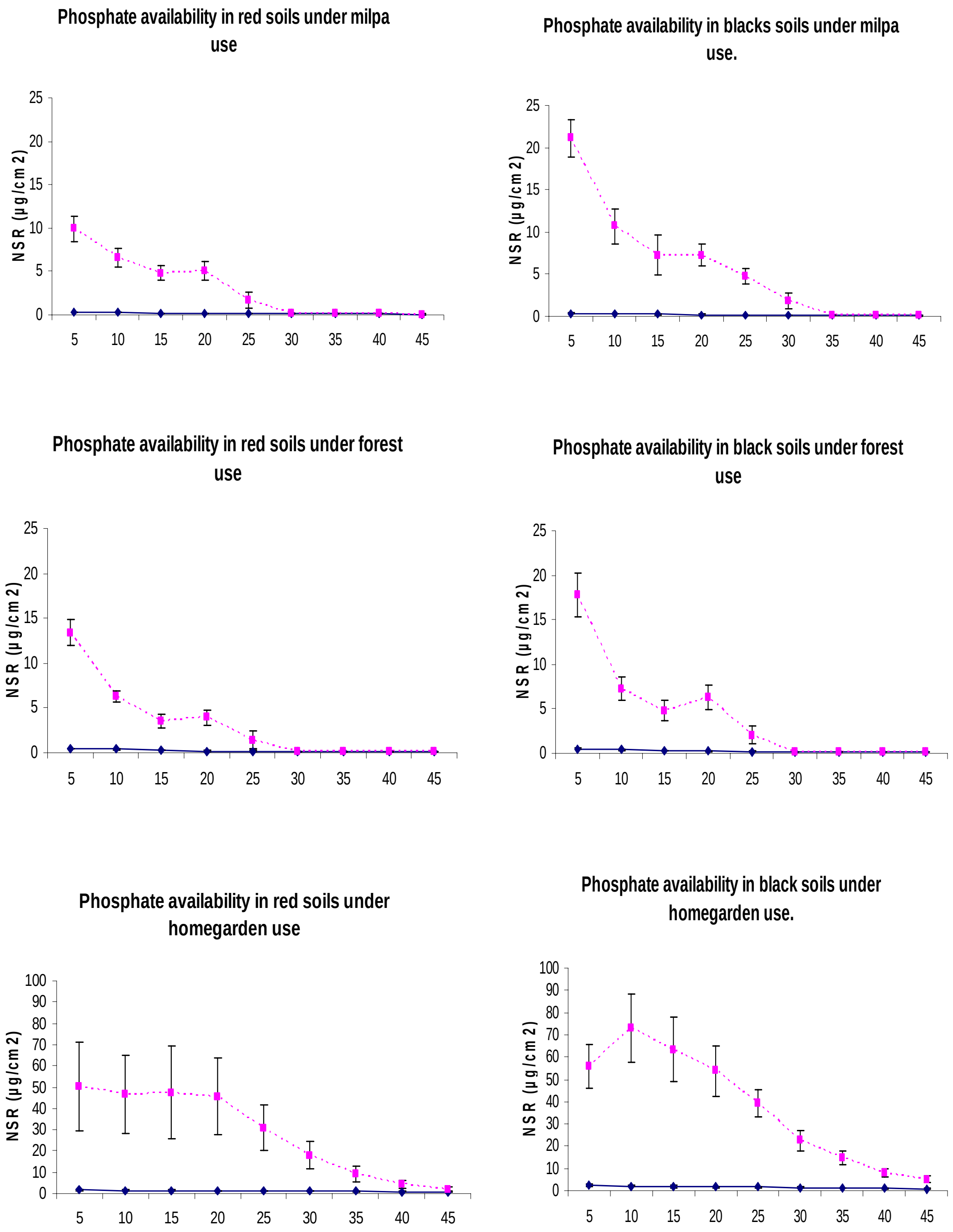


Figure 4. 11. Phosphate released in Mexican soils at two levels of moisture: HFC (continuous line) and FC (discontinuous line).

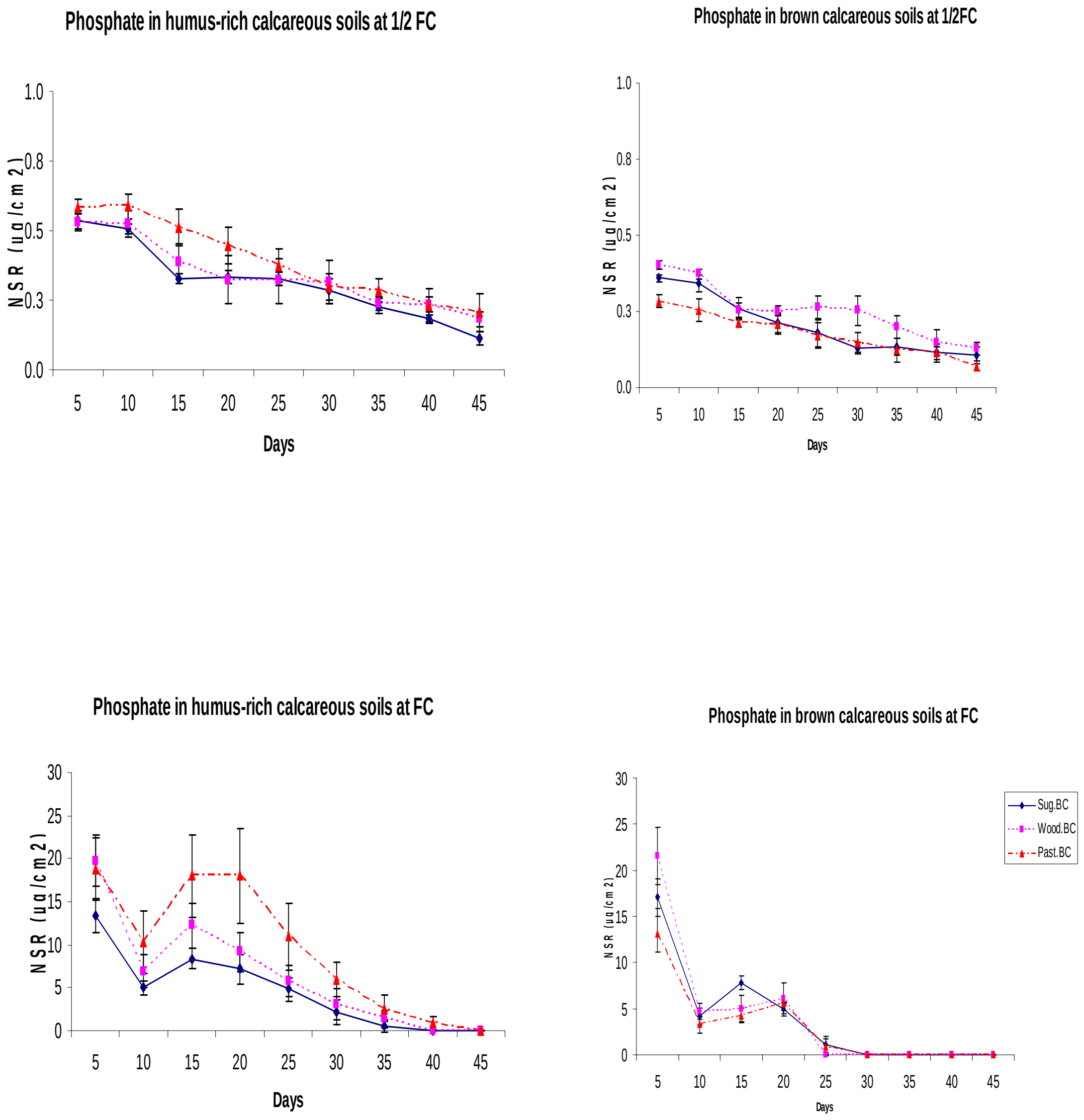


Figure 4. 12. Phosphate released in Cuban soils incubated at HFC and FC.

4.4.2. Calcium.

Calcium (Ca) availability is high in these limestone soils under both moisture levels (HFC and FC). In Mexican soils (Table 4.1), Ca availability was significantly lower at FC than at HFC for both soil groups from milpa and forest land uses. In homegardens the differences between moisture levels were not significant. In milpas, the reduction of Ca availability in red soils was almost double the reduction in the black group. However, in forests the reduction of Ca levels was twice as large in the black soils as in the red group (Table 4.1). T-tests showed significant differences between red and black soils only for milpas at FC and for forests and homegardens at HFC. Weisbach et al. (2002) measured the availability of the three main cations in Yucatecan soils using ion exchange membranes. During a 6-week field experiment in Yucatecan soils, they buried the resins in the soil at 5 cm depth. The membranes were changed weekly. But, soil moisture was not manipulated in this research, so; they did not find significant differences in Ca availability between red and black soils.

Misra and Tyler (1999) studied nutrient availability in a limestone soil. They reported that Ca solubility decreased when soil moisture is above 50% WHC. The diminution of the solubility was attributed to the possibility of precipitation processes. Under prolonged saturated conditions, soil water fills the microsites decreasing the gas exchange and causing an increase of carbon dioxide pressure, which promote calcium sedimentation. The role of secondary anaerobes in these processes is important, because calcium precipitated by photoautotroph microorganisms is dissolved by primary organic-acid-forming anaerobes, to be once again precipitated by secondary acid-decomposing anaerobes (Zavarzin, 2002).

Table 4. 1. Total available calcium (sum of the 5-day extracts) in Mexican soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**Ca^{2+} (µg cm^{-2})**	**SD**
Milpa	Red	550	±42
	Black	546	±39
Forest	Red	515	±24
	Black	560	±22
Homegarden	Red	501	±34
	Black	537	±31

FPLSD	Red	ns	
	Black	ns	

FC

Land use	**Soil**	**Ca^{2+} (µg cm^{-2})**	**SD**
Milpa	Red	473	±40
	Black	506	±30
Forest	Red	484	±39
	Black	492	±27
Homegarden	Red	507	±61
	Black	525	±67

FPLSD	Red	ns	
	Black	33	

Significant interactions	**P**
Land use x Water content	0.000
Land use x Soil x Water content	0.040

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

In Cuban ecosystems, Ca availability (Table 4.2) was affected by land use, soil properties and soil moisture effects. Within the humus-rich calcareous group, no significant differences were found among land uses. However, within brown calcareous soil, the pasture area showed significant differences to the sugarcane and the woodland areas. Brown calcareous soils presented less Ca availability compared to the humus-rich calcareous soils. At HFC humus-rich calcareous soils released 34% more Ca than the brown calcareous soils. Under saturated conditions, the difference between both soils was reduced to 24%. These results reflected the mineralogical properties of both soils. Humus-rich calcareous soils are developed over limestone, which is found at 45-50 cm depth (Marin et al., 1994). Also, these soils contain primary minerals throughout the soil profile and are forming from clay-marl (Cairo and Fundora, 1994). Consequently, these soils presented high Ca levels.

In contrast, brown calcareous soils developed in the central region of the Cuban island tend to present residual carbonates, differing from the others developed in dryer eastern areas of the country, which present secondary carbonates. Another important aspect is the influence of serpentine minerals in the Santa Clara valley, which is surrounded by serpentinitic low hills. Serpentine minerals cause a non-typical cation imbalance in these brown calcareous soil which favor Mg levels and diminish the concentrations of Ca, especially in the woodland of the Botanical Garden, which is near to a transition from brown calcareous to serpentine soils (Fundora, 1979; Cairo and Fundora, 1994; and Torrecilla, 2005). Serpentine minerals are rich in iron and magnesium, but with less content of calcium (Bonifacio and Barberis, 1999; Koide and Mooney, 1987).

Table 4. 2. Total available calcium (sum of the 5-day extracts) in Cuban soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**Ca^{2+} (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	604	±47
	Brown calcareous	428	±44
Pasture	Humus-rich calcareous	625	±43
	Brown calcareous	523	±32
Woodland	Humus-rich calcareous	611	±66
	Brown calcareous	268	±17

FPLSD	Humus-rich calcareous	ns	
	Brown calcareous	31	

FC

Land use	**Soil**	**Ca^{2+} (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	516	±35
	Brown calcareous	472	±30
Pasture	Humus-rich calcareous	522	±33
	Brown calcareous	471	±36
Woodland	Humus-rich calcareous	513	±66
	Brown calcareous	238	±31

FPLSD	Humus-rich calcareous	ns	
	Brown calcareous	30	

Significant interactions	**P**
Land use x Soil	0.000
Land use x Water content	0.011
Soil x Water content	0.000

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

4.4.3. Magnesium

The magnesium (Mg) concentrations (Table 4.3) were affected by land use, soil type and moisture. In general, the availability of Mg was higher in homegardens and forests. At HFC and within the red group, Mg availability differed among land uses, whereas at FC no significant differences were found between homegarden and forest uses. Black soils from homegardens and forests did not present differences in available Mg, but both are significantly different from the Mg concentrations in black soils from the milpas. In general, Mg concentrations were higher in red soils than in the black ones, but these differences were not significant when data were analyzed by T-test.

Weisbach et al. (2002) did not reported significant differences in resin-Mg between red and black soils in areas used for shifting cultivation. In the Yucatan conditions, shifting cultivation can be defined as milpa farming, which alternates areas with the secondary forests. In homegardens, the inputs of manure and plant residues are mineralized and release ions to the soil solution in available forms. Although manure has much more potassium than calcium and magnesium (Johnson and Eckert, 1995), it appears that the constant inputs through the years enhanced Mg availability in homegardens compared to the other land uses.

At half moisture, Mg captured by the resin was near 30% more than Mg at full moisture for both black and red soils. These results agree with Misra and Tyler (1999), who observed that Mg concentrations decrease above 50%WHC.

Table 4. 3. Total available magnesium (sum of the 5-day extracts) in Mexican soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**Mg^{2+} (µg cm^{-2})**	**SD**
Milpa	Red	32	±4
	Black	33	±3
Forest	Red	42	±5
	Black	38	±6
Homegarden	Red	51	±10
	Black	40	±10
FPLSD	Red	5	
	Black	5	

FC

Land use	**Soil**	**Mg^{2+} (µg cm^{-2})**	**SD**
Milpa	Red	20	±5
	Black	21	±4
Forest	Red	30	±6
	Black	29	±9
Homegarden	Red	33	±8
	Black	29	±11
FPLSD	Red	5	
	Black	6	

Significant interactions	**P**
Land use x Soil	0.016

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

Table 4. 4. Total available magnesium (sum of the 5-day extracts) in Cuban soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**Mg^{2+} (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	11	±1
	Brown calcareous	52	±5
Pasture	Humus-rich calcareous	20	±4
	Brown calcareous	33	±2
Woodland	Humus-rich calcareous	16	±2
	Brown calcareous	185	±26
FPLSD	Humus-rich calcareous	3	
	Brown calcareous	14	

FC

Land use	**Soil**	**Mg^{2+} (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	5	±1
	Brown calcareous	35	±4
Pasture	Humus-rich calcareous	11	±3
	Brown calcareous	22	±4
Woodland	Humus-rich calcareous	10	±3
	Brown calcareous	141	±23
FPLSD	Humus-rich calcareous	2	
	Brown calcareous	13	

Significant interactions	**P**
Land use x Soil	0.000
Land use x Water content	0.002
Soil x Water content	0.000
Land use x Soil x Water content	0.001

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

The soils from Cuba presented notable differences in Mg availability (Table 4.4). Higher concentrations of Mg were found in the woodlands from both soils and in the pasture area from the humus-rich calcareous soil, probably due to the inputs of litter in the woodlands, which improve Mg recycling within the ecosystems. As well, manure amendments throughout the years may improve Mg availability in the pasture area from the humus-rich calcareous soil. Brown calcareous soils presented higher Mg concentrations in the soil solution due to mineralogical characteristics of this group compared to humus-rich calcareous soils. The influences of serpentine rocks in the brown calcareous soils from the Santa Clara valley explain and the higher Mg levels in these soils (Cairo and Fundora, 1994; Fundora, 1979). Also, the presence of dolomite in these soils could enhance Mg levels in these soils (de Vries, 2000). The extreme values of Mg in the woodland from the brown calcareous soil derived from a fersialitic deposit in the area (Fundora, 1979; Torrecilla, 2005). Mg availability in both soils was lower at FC than in the HFC, with an average reduction of 27% for the brown calcareous soils. In the humus-rich calcareous soils these differences were about 44%.

4.4.4. Potassium

Land use and soil type affected K availability in Mexican soils (Table 4.5). Soil moisture effect was not significant. Within the same soil group, homegardens had more K than milpa and forest ecosystems independently of the moisture level used in the incubation. On average, the differences between red and black soils were 30% at HFC and 22% at FC. In homegardens, at both levels of soil moisture, red soils released 34% less potassium that black soils.

Homegardens are intensive agricultural ecosystems where soil fertility is maintained through the addition of household garbage, animal manure and litterfall, which is burned in different areas of the homegarden (Benjamin, 2000). Commercial fertilizers, rich soil from the secondary forest, and resources in form of residues from the milpa are all brought to the homegarden enriching soil nutrients (Andrist, 2003) and allowing the maximum exploitation of the available growing space in these silvicultural ecosystems.

Table 4. 5. Total available potassium (sum of the 5-day extracts) in Mexican soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**K^+ (µg cm^{-2})**	**SD**
Milpa	Red	3.1	±1.2
	Black	4.2	±1.2
Forest	Red	2.3	±0.9
	Black	2.9	±0.8
Homegarden	Red	10.0	±3.5
	Black	14.9	±9.6
FPLSD	Red	1.6	
	Black	4.1	

FC

Land use	**Soil**	**K^+ (µg cm^{-2})**	**SD**
Milpa	Red	3.1	±1.2
	Black	3.3	±1.6
Forest	Red	2.9	±1.1
	Black	2.4	±0.7
Homegarden	Red	7.9	±2.8
	Black	11.9	±11.1
FPLSD	Red	1.4	
	Black	4.8	

Significant interactions	**P**
Land use x Soil	0.015

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

There was no significant interaction with water content in the Mexican soils. However, in Cuban soils (Table 4.6), water content influenced K release in humus-rich calcareous soils. At FC, the availability of K was 31% lower in this soil group than at HFC. Soil moisture affects soil potassium (K) availability and its diffusive flux, as well as K uptake. Misra and Tyler (1999) studied the availability of five major nutrients in a calcareous soil reporting that the optimum moisture range for K concentration in the soil solution is between 50-70%WHC. However, brown calcareous soil did not responded significantly to the two levels of moisture used in the incubation experiment.

The land use and soil type affected K availability in Cuban ecosystem. Pasture areas presented the highest availability of K. At HFC, humus-rich calcareous soil had 53% more K than the brown calcareous. At FC the differences between both soils were 38%. The grassland in the humus-rich soil is a stable ecosystem, which have been used extensively for more that 35 years. The amount of nutrients available in manure fertilizers varies with the type and size of animal, but in general, manure is considered as a good source of potassium and phosphorus. Losses of these both nutrients are usually negligible, nearly 100 percent of total phosphorus and potassium from manure application are considered available the first growing season (Johnson and Eckert, 1995; Jahns, 2005). However, the artificial pasture in the brown calcareous soil was used almost 30 years under intensive agricultural systems for diverse purposes. The degradation of the land, reflected in yield depletions, forced to change the land use from minor crops to the actual pasture area, formed by graminea and legumes, but this was only two years before the sampling. So, many years of continued manure application explain the differences between both grasslands.

Table 4. 6. Total available potassium (sum of the 5-day extracts) in Cuban soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**K^+ (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	2.3	±0.2
	Brown calcareous	2.4	±0.3
Pasture	Humus-rich calcareous	8.4	±6.1
	Brown calcareous	2.5	±0.2
Woodland	Humus-rich calcareous	3.9	±1.3
	Brown calcareous	2.1	±0.2
FPLSD	Humus-rich calcareous	3.3	
	Brown calcareous	0.2	

FC

Land use	**Soil**	**K^+ (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	2.3	±0.1
	Brown calcareous	1.7	±0.2
Pasture	Humus-rich calcareous	5.4	±3.8
	Brown calcareous	2.9	±0.3
Woodland	Humus-rich calcareous	2.6	±1.3
	Brown calcareous	1.6	±0.2
FPLSD	Humus-rich calcareous	2.1	
	Brown calcareous	0.2	

Significant interactions	**P**
Land use x Soil	0.000

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

For both Mexican and Cuban soils, the low values of available potassium likely result from the competition among the three cations (Ca, Mg, and K). High levels of available calcium may suppress Mg and K uptake by plants. It has been reported that when calcium availability exceeds 80%, the proportion of available magnesium is low (less than 4%), and also potassium decrease due to the competition among the cations (Hagin and Tucker, 1982, and Marschner, 1995 in Imas, 2000).

4.4.5. Nitrate

Mexican soils presented significant differences in nitrate (NO_3^-) availability (Table 4.7). Among land uses, forest presented the highest levels of nitrate. At HFC no significant differences were found between forest and homegardens. In both ecosystems the presence of perennial plants may have enhanced the levels of organic matter in the soil (Zech et al., 1997), therefore affect nitrate concentrations. On average, black soils presented 33% more nitrate than red soils under both moisture levels. Nitrate availability was 26% less at FC compared to HFC in both soil groups.

Table 4. 7. Total available nitrate (sum of the 5-day extracts) in Mexican soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	Soil	NO_3^{-}–N (µg cm^{-2})	SD
Milpa	Red	83	±18
	Black	119	±15
Forest	Red	97	±16
	Black	147	±20
Homegarden	Red	92	±15
	Black	141	±14

FPLSD	Red	12	
	Black	12	

FC

Land use	Soil	NO_3^{-}–N (µg cm^{-2})	SD
Milpa	Red	58	±7
	Black	88	±12
Forest	Red	77	±9
	Black	116	±20
Homegarden	Red	67	±18
	Black	92	±24

FPLSD	Red	9	
	Black	14	

Factors and its interactions	P
Soil x Water content	0.006

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.
FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level
HFC: half of the water needed to reached field capacity
FC: Field capacity

In Cuban ecosystems, the highest nitrate availabilities (Table 4.8) were found in the woodland from the brown calcareous soil and the pasture from the humus-rich calcareous soils. The woodland from the brown calcareous soil was identified as the oldest of all Cuban ecosystems in this research, with more than 50 years under this land use. The pasture from the humus-rich soil has been 35 years under this land use. It has been reported that grass turnover may replace litterfall return as the predominant mechanism of nutrient recycling (Markewitz et al. 2004). In general, the ecosystems from the humus-rich areas (excepting the woodland) had more nitrate than the same ones from the brown calcareous areas. Soil properties may explain the differences in nitrate availability between both Cuban soils. At HFC, humus-rich calcareous soil presented 30% more nitrate than the brown calcareous. This difference was less at FC (24%), but it was still significant. The differences between soils under the same moisture conditions may be attributed to their differences in soil organic matter content. Humus-rich soils have double the amounts of organic matter compared to the brown calcareous (Cairo and Fundora, 1994).

The influence of the water content was important for both soils. Nitrate availability was affected by soil moisture under all land uses. Within the same soil group nitrate availability was 31% lower at FC than at HFC for the humus-rich calcareous soil, whereas the difference for the brown calcareous soils was around 25%.

Nitrate availability depends on microbial activity, net mineralization, soil moisture and other factors. Full water content may not be suitable for determine nitrogen availability in these soils if ammonium concentrations in the soil solution are not considered in the research. Pampolino and Hatano (2000) did an incubation experiment for studying soil moisture effect on phosphorus, nitrogen, and potassium, comparing the availability of these nutrients in two soils under saturated and unsaturated conditions. Their results reported that total nitrogen was higher under saturated compared to the unsaturated conditions, but nitrate ions dominated the nitrogen availability under unsaturated soils, whereas ammonium was the predominant when soils were saturated, suggesting that the availability and form of nitrogen varied with the moisture content.

Table 4. 8. Total available nitrate (sum of the 5-day extracts) in Cuban soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**NO_3^-N (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	75	±11
	Brown calcareous	41	±3
Pasture	Humus-rich calcareous	112	±10
	Brown calcareous	27	±4
Woodland	Humus-rich calcareous	86	±13
	Brown calcareous	124	±15
FPLSD	Humus-rich calcareous	10	
	Brown calcareous	8	

FC

Land use	**Soil**	**NO_3^-N (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	51	±4
	Brown calcareous	30	±4
Pasture	Humus-rich calcareous	87	±13
	Brown calcareous	12	±3
Woodland	Humus-rich calcareous	51	±7
	Brown calcareous	102	±6
FPLSD	Humus-rich calcareous	8	
	Brown calcareous	4	

Significant interactions	**P**
Land use x Soil	0.000
Land use x Water content	0.017
Soil x Water content	0.000

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

Also, Fierer and Schimel (2002) studied the effects of moisture and drying and rewetting cycles on soil carbon and nitrogen transformations in two soils with a Mediterranean climate considered 50% WHC as unstressed treatment, which was used as control for comparisons with stressed samples (35% WHC). For both soils at both moisture levels, this authors reported very low soil extractable NH_4^+, accounting for less than 5% of total extractable inorganic nitrogen.

The dominance of nitrate under unsaturated conditions may be explained by the soil water effect on the mineralization processes. Nitrogen mineralization may proceed most rapidly at low soil moisture due to a lack of oxygen for nitrification under high moisture conditions. Under drier conditions, ammonium is usually quickly oxidized to nitrate, whilst ammonium is accumulated when soil is saturated. Together with high temperatures and soil properties, excessive moisture is another condition that might adversely affect the biological process of nitrification of ammonium. (Kleinhenz et al., 1997).

Microbial processes in a soil are adversely affected by both high and low water contents. Inadequate aeration affects reaction rates at high water contents. At low water content, nitrate mineralization is affected by diminished rates of substrate diffusion, physical protection of bacteria from predation by protozoan grazers and low water potential, whereas nitrate resulting from mineralization and nitrification under aerobic conditions may subsequently be denitrified if anaerobic conditions develop, especially when water-filled pore space (WFPS) is above 80% (Drury et al., 2003) because the oxidation state of the soil declined progressively over time when soil is saturated (Kay et al., 1999).

In forest and woodland ecosystems, the litterfall production is higher than in the other land uses enhancing soil organic matter content of the soil that is highly related with carbon and nitrogen status in soils. It has been reported that the conversion of forest to pasture causes a decrease in soil organic matter (i.e. in an oxisol Costa Rican forest converted to pasture soil organic matter decreased 23%) and also, elevated losses of important limiting elements through leaching (Cleveland et al., 2003). However, it is also important the constant input of manure in the old pasture area because, only about one-third of the organic nitrogen in animal manure is available to crops during the year it is applied, and the remaining two-third, residual organic nitrogen, becomes part of the soil organic matter, which is mineralized or becomes available at the rate of about 5 percent a year (Johnson and Eckert, 1995).

4.4.6. Phosphate

In Mexican ecosystems (Table 4.9), phosphate extraction by the resin membrane was significantly higher in homegardens, than in the other land uses which presented similar values of available phosphate. Homegarden is a traditional production system, which is frequently enriched by additions of different crop and organic residues, such as kitchen wastes, litterfall, ashes and manure, which increase nutrient availability (Benjamin, 2000; Andrist, 2003).

The differences between red and black soils at FC and HFC conditions were significant. On average, black soils had 28% and 21% more phosphate at FC and HFC, respectively, than the red ones. These differences were greater in soils under milpa use at FC, where the differences were around 48%. Weisbach et al. (2002) found that in red soils available Pi was 64% lower than in the black group. However, they explain that farmers preferred red soils, which are considered more productive.

Table 4. 9. Total available phosphate (sum of the 5-day extracts) in Mexican soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**PO_4^{2-} P (µg cm^{-2})**	**SD**
Milpa	Red	1.0	±0.1
	Black	1.2	±0.2
Forest	Red	1.4	±0.3
	Black	1.5	±0.3
Homegarden	Red	6.7	±1.5
	Black	8.8	±2.0
FPLSD	Red	0.6	
	Black	0.9	

FC

Land use	**Soil**	**PO_4^{2-} P (µg cm^{-2})**	**SD**
Milpa	Red	17.3	±3.6
	Black	33.1	±8.0
Forest	Red	17.4	±2.8
	Black	23.6	±5.8
Homegarden	Red	156.5	±93.2
	Black	207.7	±46.4
FPLSD	Red	40	
	Black	20	

Significant interactions	**P**
Land use x Water content	0.000
Soil x Water content	0.010

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

In Cuban ecosystems (Table 4.10), phosphate availability was influenced by the effects of land use, soil properties and soil water content. Phosphate was higher in the pasture from the humus rich calcareous soil, following by the forest in the same soil type. In general, phosphate content was higher in the humus rich soil demonstrating the influence of soil properties on phosphorus availability (Cross and Schlesinger, 2001, Stewart and Tiessen, 1987, and Tiessen at al., 1994). However, at HFC the differences between soil types were not significant neither for Mexican nor Cuban soils, which suggests that soil moisture had a main role in determining phosphate availability in the incubation experiment.

For all Cuban and Mexican ecosystems, the concentrations of phosphate were around 95% higher at FC than at HFC, suggesting that available soil phosphate is strongly dependent on soil moisture. Phosphorus uptake by plants is greatly influenced by soil moisture, being largely controlled by diffusion, and P depletion in the rhizosphere (Gahoonia et al., 1994 in Misra and Tyler, 1999). Because phosphorus diffusion occurs in water-filled pore spaces within the soil, the volumetric soil water content is an important factor controlling diffusive flux (Kovar and Claassen, 2005), so the diffusive flux of phosphorus increase significantly as the soil moisture increases. Misra and Tyler (1999) reported that phosphate concentrations increased with soil moisture, but most of this increase occurred above 70%WHC. At low soil water content, the diffusion path is impeded, which make phosphorus less available to plants. Pampolino and Hatano (2000) also reported a large increase (about 80%) in phosphate availability in saturated soils compared with the same soils under unsaturated conditions. They explain that the lower content of phosphate in resins at a low soil moisture content indicate that P diffusion decreased due to increased tortuosity.

Table 4. 10. Phosphate availability (sum of the 5-day extracts) in Cuban soils captured in the incubation experiment using ion exchange membranes.

HFC

Land use	**Soil**	**PO_4^{2-}—P (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	1.8	±0.1
	Brown calcareous	1.2	±0.1
Pasture	Humus-rich calcareous	2.3	±0.3
	Brown calcareous	1.0	±0.0
Woodland	Humus-rich calcareous	2.0	±0.4
	Brown calcareous	1.5	±0.0
FPLSD	Humus-rich calcareous	0.3	
	Brown calcareous	0.2	

FC

Land use	**Soil**	**PO_4^{2-}—P (µg cm^{-2})**	**SD**
Sugarcane	Humus-rich calcareous	26.7	±3.6
	Brown calcareous	22.6	±2.6
Pasture	Humus-rich calcareous	55.0	±20.9
	Brown calcareous	17.4	±3.0
Woodland	Humus-rich calcareous	37.5	±12.2
	Brown calcareous	24.0	±3.2
FPLSD	Humus-rich calcareous	13.0	
	Brown calcareous	2.7	

Significant interactions	**P**
Land use x Soil	0.000
Land use x Water content	0.003
Soil x Water content	0.000
Land use x Soil x Water content	0.000

Within the same soil type at the same moisture, differences are significant when greater than FPLSD.

FPLSD value correspond to the one-way ANOVA analyses for the single factor land use within the same soil type at the same moisture level

HFC: half of the water needed to reached field capacity

FC: Field capacity

4.5. CONCLUSIONS

Soil moisture influences nutrient availability in calcareous soils. Although not always statistically significant for cations, it was observed that at HFC, the resin adsorption of Ca, Mg and K, as well as nitrate was higher compared to FC, while at full moisture phosphate adsorption by the resin was significantly higher than at half water content. Under most soil conditions, phosphorus is both the least mobile and the least available of the major nutrients (Kovar and Claassen, 2005). In calcareous soils, P is often the limiting factor for plant growth (Leytem and Mikkelsen, 2005) due to its reaction with lime forming insoluble precipitates.Soil management is also an important factor affecting nutrient availability. Homegardens, recognized as an intensive agroforestry system, appear as the most sustainable Mayan agricultural practices with the highest nutrient availability. However, this richness depends on the constant inputs of organic residues from diverse sources and the cultural practices of farmers and families on the area. In Cuba, woodlands can be identified as the most stable ecosystems; while old pasture areas with constant input of manure and balanced nutrient recycling also represent a sustainable management of these calcareous soils.

Black soils from Mexico always presented higher nutrient availability than the red group, although the differences are significant only for anions (nitrate and phosphate). The possible explanation could be the important role of the soil organic matter in the cycle of these nutrients, and, of course, the microbial activity. Weisbach et al. (2002) has reported a much greater accretion of soil organic matter in black soils, about twice that seen in red soils, even when both soils were under similar plant residue inputs. The authors attributed this to delayed decomposition of plant residues or to their concentration in the thin soil layer of the black soils. Both things can prevent nutrient losses and the high organic matter levels accumulated may release nutrients to plant and microbes when water availability is sufficient.

Cuban soils are influenced by their mineralogical properties. The presence of serpentine minerals, rich in magnesium and iron, and secondary or residual carbonates in the formation of brown calcareous soils determine the differences in nutrient availability, especially in Mg, of this soil type to that of humus rich calcareous soil. Also, the exploitation under intensive agriculture systems (specifically sugarcane monoculture and minor crops) has degraded the natural fertility of this soil.

CHAPTER 5: MAIN RESULTS AND GENERAL CONCLUSIONS.

In the previous chapters, various soil quality and nutrient supply indicators of four calcareous tropical soils from Mexico and Cuba under contrasting land uses have been presented. Soil test related to SOM and the availability of five main nutrients were conducted with this purpose. Furthermore, the effect of soil moisture on the availability of the nutrient-ions was included considering the relevance of water availability in the semiarid areas. Integrating all the results we can concluded that:

- In general, within the Mexican group, black soils had more nutrients than the red ones. On average, they presented twice OC, IC and total N content than red soils. Nitrate availability in black soils was near two fold more than in red soils. Total P content in black soils was near 1000 mg kg^{-1} in forest and milpa areas, and more than double that in homegardens (3659 mg kg^{-1}). Under this land use, red soils also contained more than red or black soils under the other two land uses (2690 mg kg^{-1}). The differences between both soils group were not so pronounced for the exchangeable cations, but black soils still had more Ca and K than the red soils. The incubation experiment evidenced that black soils had a better nutritional status. However, farmers prefer red soil for cropping. Black soils presented some hydrophobic properties and had a shallow thickness and high rockiness compared to red soils.

- Within the Cuban group, humus-rich calcareous soils had higher Ca and K and lower Mg availabilities than brown calcareous soils. The presence of serpentine minerals in the Santa Clara valley is the main reason for the extreme difference found in Mg levels. The high Mg levels in the brown calcareous soils resulted in an imbalance in the main base cations in these calcareous soils. P content was significantly higher in humus-rich calcareous soils, although only a small portion is within the labile pools. In the incubation experiment phosphate availability was also higher in the humus-rich calcareous soil than in the brown calcareous soil. In general, Cuban soils did not presented total P content as high as the Mexican soils, being between 500-800 mg kg^{-1}.

- Soil C and N stocks in the Yucatecan soil were higher than those in Cuban soils, and higher than in most other tropical soils. SOC and total N were higher in the Yucatecan secondary forests and Cuban woodlands; although the pasture area in the humus-rich calcareous soil also presented high SOC and total N contents. These results confirmed the influence of land use on SOM and total N stocks, because disturbance and management practices affect SOM dynamics.

- Exchangeable cations are dominated by Ca ions. This imbalance among cations may cause some K deficiencies in plants. We realized that Ca and Mg availability is lower at FC than at HFC, but even at FC the levels of Ca were much higher than the other nutrients. This suggests that an excess of water does not avoid that plants may suffer nutrient deficiencies and may cause some problems by Ca toxicity. It has reported that when excess Ca is present in the rhizosphere some toxicity problems may appear in the plants, and it has also been observed that germination of the seeds and plant growth is reduced.

- K is deficient in these tropical calcareous soils. Water availability did not show a conclusive relationship with its availability. The effect of soil moisture only was ascertained in the humus-rich calcareous soils from Cuba, but not in the Mexican group. However, K was influenced by land use in both Mexican and Cuban groups. The enrichment in K in soils under homegarden and pasture land uses was likely caused by inputs of manure and other residues throughout the years.

- P is by far the most limiting nutrient for plant growth in these soils. Even when Pt content ranged within and above the world average values, most of P was not readily available to plants. Po accounted only for a small portion of total P. However, because most of P is comprised in recalcitrant pools, Po should play an important role in the release of P through mineralization. Phosphate availability was strongly influenced by land use and soil moisture. In Mexican soils, the continuous inputs of manure, plant and household residues determined the high availability of P in soil under homegarden use. Similar results were seen for the pasture area from the humus-rich calcareous soil in Cuba. The excrements from animals in this area during more than 30 years have increased P content and also the lability of this nutrient. P availability responded to soil moisture effect, being the only nutrient-ion that presented higher availability at FC than at HFC conditions.

- It was not suitable to measure N availability at FC due to the effect of prolonged saturation on mineralization and nitrification. Nitrate was lower at FC than at half HFC, although we suppose that this result was due to a shift of available N towards the ammonium form. So, it will be necessary to account for the concentrations of ammonium in the soil solution if the aim is determine labile N.

- Soil fertility in these ecosystems is limited by low P and K levels, and limited water availability. The incubation experiment showed nutrient release with time varied for each. At 25 days, phosphate availability declined in all sites (except homegardens), whereas K availability declined at 30 days. However, Ca availability was more or less constant throughout the time of the incubation and Mg declined and dropped to zero at 40-45 days. Nitrate availability showed a marked depletion at 10 days, but although low, the concentrations were constant until 40 days. This variability with time suggests that phosphate and K will be deficient for plant before any other nutrients.

- We ascertained that the nutrient status of Yucatecan soils was much higher than that one in the Cuban soils. On average, Yucatecan soils had four fold more OC and N stocks compared to Cuban soils. In the Mexican soils, the OC and total N stocks ranged from 55 to 124 g kg^{-1} and from 5.1 to 16.0 g kg^{-1}, respectively. Cuban soils presented OC and total N contents ranging from 13 to 32 g kg^{-1} and from 1.8 to 4.4 g kg^{-1}, respectively. P content was about twice larger in Mexican soils. Specifically, black soils presented more than 1000 mg kg^{-1} in forest and milpa areas, being more than double in homegardens (3659 mg kg^{-1}). Under this land use, red soils (2690 mg kg^{-1}) also reached more than the red and black soils under the other two ecosystems. Cuban soils presented total P levels within the usual range of 500-800 mg kg^{-1}. However, in both Yucatecan- and Cuban-soil groups most of P was comprised of unavailable forms. The labile pools in Yucatecan soils raged from 79 to 739 mg kg^{-1}, being especially high in black and red soils from homegardens (593 and 739 mg kg^{-1}, respectively). Cuban soils did not present values as high as homegarden areas. The labile pools in Cuban soils ranged from 46 to 106 mg kg^{-1}, being 74% lower than the labile P of the Mexican soils. The readily available nutrients measured in the incubation experiment with ion exchange membranes also demonstrated that phosphate availability was higher in Yucatecan soils, specifically black soils and homegarden ecosystem, compared to Cuban soils. Nitrate availability was also higher than in the Cuban soils. However, the exchangeable cations and the results obtained in the incubation with the resins showed only small differences. In the extraction to obtain the exchangeable cations as well as in the incubation, the highest concentrations of exchangeable Ca were found in the humus rich soil from Cuba. Also, Mg was higher in the brown calcareous soil from Cuba and K did not show strong differences among the four soils, but was higher in the Mexican group.

Our results may contribute to a better understanding of nutrient cycling in these calcareous soils from semiarid areas. According to them, fertility problems of Yucatecan and Cuban soils will start as P and K deficiencies in crops. Maize and pulses are the main crops of the milpa system in Yucatan, whereas sugarcane has been cropped for centuries in the central region of Cuba. These crops demand high levels of potassium and less, but also important levels of phosphorus. For this reasons, the estimation of nutrient availability for crops is very important to evaluate fertility in these soils. The total stocks of nutrients are not useful indicators of sufficiency due to only a small part of these stocks becomes readily available for plants. For instance, the total P amounts in these soils are high in these soils, but available P represent only a small portion of the total stock and may not satisfy plant needs. According to the results of the resin experiment, phosphate availability declined first than the other four nutrient ions. So, it should be deficient for crops, whereas Ca may be in excess.

Similar could happen with K availability. Exchangeable K is low, probably deplete by cation competition and imbalances. The resin experiment ascertained that its availability declined just after phosphate dropped to zero. This imply that K and P deficiencies may determine the beginning of nutrient depletion in these soils considering that are highly demanded by the main crops in these areas.

It is also important the effect of soil moisture on nutrient availability. The process of nutrient uptake by plants involves a phenomenon of ion exchange. Ion movement in soils is dependent of their concentration in soil solution, how strongly they are absorbed by clays and organic matter, and how fast they can move. The diffusion patterns of some nutrients from the incubation with resin may be over-ridden by mass flow. Nutrients weakly retained, e.g. nitrate and magnesium or those which have a high concentration in soil solution, e.g. calcium, may be uptake through this mechanism when soil moisture increase. However, P and K are immobile ions, so they should maintain the diffusion patterns from the resin experiment. So, the management of soil moisture also affects nutrient balance. An excess of water may favor those nutrients that mainly move by mass flow, even when the concentration of less mobile nutrients also increases.

In situ monitoring of the bioavailability of soil nutrients may provide useful information for fertilization considering soil moisture, land use and soil properties influences. This could provide an advantage over traditional fertilizer practices because it could avoid excessive applications. At the same time, the understanding of these processes contributes to optimize the efficiency of applied fertilizers and soil fertility restoration.

SUMMARY.

Calcareous soils are common in the semiarid tropics, but little is known about the influence of land use changes on their fertility. In these soils, the presence of free carbonates may cause some nutritional problems such as deficiencies in P and cation imbalances.

Four tropical calcareous soils from Yucatan, Mexico, and Villa Clara, Cuba were assessed in this research. In Mexico, the selected soils were redish brown redzinas and black lithosols. In Cuba; they were brown calcareous (Orthic-Calcaric Cambisol) and humus-rich calcareous (Hyper-Calcaric Phaeozem) soils. Three main land uses were considered for each country. In the Yucatecan group were chose three main land uses: milpa, forest, and homegardens. At the Cuba sites: sugarcane monoculture, pasture and woodland (isolated patches of secondary vegetation) were the selected land uses.

The aim of this study was characterize the main indicators of soil fertility for these calcareous soils. With this purpose, the amounts of SOC and total N were determined as basic indicators of soil quality. Also, the exchangeable Ca, Mg and K were measured, in order to identify imbalance problems among them. P distribution based on its bioavailability was assessed considering that P is the most limiting nutrient in semiarid ecosystems. As well, the effect of soil moisture on nutrient availability was another aim of the research. To this end, an incubation experiment using ion exchange membranes was done. In this thesis, the different topics above mentioned were grouped in three experimental chapters (Chapter 2 to Chapter 4) and the major findings were highlighted in the conclusion chapter (Chapter 5).

Within the Mexican group, black soils were richer than the red soils. Black soils doubled red soils in SOC and total N. As well, P content was threefold in black soils compared to the red group. In general, black soils presented more Pt than most tropical soils. Black soils also had more exchangeable Ca than red soils, but the differences between soils were not significant for exchangeable Mg and K. Comparing land uses, homegardens showed higher amounts of

available and total P, and also, more exchangeable K. Forests had more exchangeable Mg and more SOC and total N than the other ecosystems.

In the Cuban soils, the highest SOC and total N levels were influenced by land use. Specifically, the time under the same land use was decisive in the SOC and total N contents. Both woodland areas and the pasture area in the humus-rich calcareous soil showed highest levels of SOC and total N. These areas are the oldest and more stable ecosystems. Cuban soils presented P levels between 500-800 mg kg^{-1}, the usual range for most soils of the world. Humus-rich calcareous soils showed around 1.5 more available P and Pt than the brown calcareous. On average, humus-rich calcareous soils had more exchangeable Ca and less exchangeable Mg than the brown calcareous soils. Exchangeable K was not significant different between both soils.

In general, Yucatecan soils were richer in SOC, total N, P and K that the Cuban soils. Mexican soils had fourfold SOC and total N stocks that Cuban ones. P content was several folds higher in the Mexican group than in Cuban soils. However, in both cases most of P (around 60%) was comprised in unavailable forms. In both cases, Mexican and Cuban soils, the organic fraction comprised only a small portion of Pt. Even when small, Po seemed to be an important plant-P source in these calcareous soils.

Accounting for the characteristics of the semiarid tropics, we studied the effect of soil moisture on nutrient release in these soils. With this aim, it was conducted an incubation experiment in laboratory conditions. Two moisture levels were used: FC and HFC. The availability of five nutrients ions (Ca, Mg, K, nitrate and phosphate) were measured at both moisture conditions. The availability of all nutrients, except phosphate, was lower at FC than at HFC in both soil types. The depletion in Ca and Mg concentrations may be attributed to the possibility of precipitation processes. K availability did not respond to the water treatments, excepting for the humus-rich calcareous soil from Cuba. At HFC, K availability was 31% more than at FC for this soil group. Nitrate availability was around 30% less at FC compared to HFC, suggesting a shift toward ammonium forms. In contrast with the other nutrients, phosphate availability was around 95% more at FC than at HFC. This suggests that

available soil phosphate is strongly dependent of soil moisture. P uptake by plants is greatly influenced by soil moisture, because at low soil moisture P diffusion decrease due to increased tortuosity. Also in this incubation experiment, we found that Yucatecan soils are richer than Cuban soils.

The effect of land use changes on soil fertility was ascertained in our results. The particular management of each land use and ecosystems is reflected in the availability of the soil nutrients. Forests and woodlands presented higher SOC, total N and exchangeable Mg than the other ecosystems. As well, manure applications seem to increase phosphate availability and K levels in homegardens and pasture areas.

Soil properties also exert an influence on nutrient availability. The presence of free carbonates plays an important role in these semiarid soils, stabilizing soil aggregation. Black soils had double carbonates content compared to the red ones, which may delay mineralization in this soil group. This fact, together with the difficult for moistening, may exacerbate limiting nutrient availabilities. Both reasons may explain why local farmers prefer red soils for cropping. In the Cuban group, it was significant the particular influence of serpentine soils in the brown calcareous soils from the Santa Clara valley. This is the main reason for the atypical cation imbalance found in brown calcareous soils.

We may conclude that, in both Mexican and Cuban soil groups, soil fertility problems may be caused mainly by low levels of phosphate and potassium. In the case of phosphate is important the interaction between soil moisture and its availability. The interaction between potassium availability and soil moisture need to be analyzed in further studies.

Finally, the effectiveness of “*in situ*” ion exchange membranes contributes to understand the soil processes considering the influences of soil moisture, land use and soil properties. This could provide an advantage over traditional fertilizer practices and contribute to the understanding of the tropical ecosystems functioning.

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ACKNOWLEDGEMENTS

I would like to thanks to my main supervisor, Prof. Dr. Holm Tiessen, for his guidance, advices and support throughout this work. His help and ideas were decisive for the experimental part of this research and also, for the writing of the thesis. Also, my gratitude for my other two co-referees: Dr. Pedro Cairo Cairo, from Universidad Central de Las Villas, in Cuba; and Dr. Juan J. Jimenez Osornio, from Universidad de Yucatan, in Mexico. Thanks for all their help during my field work, and also for their comments and suggestions.

I want to thank to the Universidad Central de Las Villas, my university in Cuba. My especial gratitude to the Faculty of Agricultural Sciences in this university for allowed me this opportunity and supported my field work in Cuba. To my colleagues in the Agronomy Department, I know that they have been pendent of me all this time. I could not forget to the members of the Research Group of Soil Sciences in my university in Cuba. They help me a lot during my field work in my home country.

During my stay in Protropics, at the Yucatan University, I received a lot of help of the researchers, technicians, and field guides. I wish to thanks to Don Alfonso, who was the most important person for me there. His knowledge and guidance in the field was a decisive help for my job. Thanks also for Martina and Imme for carried my samples from Mexico to Germany.

Come to Germany was a challenge for me. The IPAG program gave me the opportunity to be here. I could not mention this without thanks to Dr. Heinzemann by all his help and support.

Thanks too for the German Academic Exchange Service (DAAD) that sponsored my scholarship.

I want to express my endless gratitude for all the members of the Section of Agronomy in the Tropics. I wish to thank Ute Ronsöhr for his help in the laboratory. There are so many samples that she measured for me! Also for Ester who helped Ute in the AAS; to Dr. Ronald Kühne, for his statistical advices; to Thomas, my thanks for helping so many times. Dr. Worbes, Dr. Frau Maass, Birgit and Frau Friedrich, thanks a lot for be nice with me and help when I need you.

I thank to all my friends by their emotional support everywhere they are: in Cuba, in Germany or back in their home countries. I do not give names because I can forget one and this will be a terrible mistake.

My deepest gratitude to my family, they support me at every second of my life. When the things were wrong, they were my best refuge. To my mother and my father, my unconditional love. You encouraged in me the passion for knowledge since I was a little child. You deserve the credits more than me.

Last but not least, my sincere thankfulness to a special friend for supporting me every day in spite of the distance. This time apart could not change anything in me.