CALCIUM, MAGNESIUM, AND POTASSIUM STATUS IN SOME SOILS OF THE EASTERN PLAINS OF COLOMBIA

A Thesis

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ABSTRACT

The soils in the Eastern Plains of Colombia south of the Meta River ("altillanura plana") are mostly Oxisols, containing large amounts of quartz, kaolinite, intergradient-type minerals, and only traces of mica-vermiculite and feldspars. They are low in exchangeable bases, high in exchangeable Al, and very acid in nature. However, growth of some native and introduced species is remarkably good considering the generally impoverished nature of the soils.

To explain the good growth of plants it was hypothesized that there could be release of Ca, Mg, and K from nonexchangeable to plant available forms. This hypothesis was examined by measuring the exchangeable and total Ca, Mg, and K in 18 soil samples taken from the area described above. The total Fe was also determined. In addition, changes in exchangeable Ca, Mg, and K were measured during incubations following several chemical treatments which included addition of $CaCO_3$ and leaching of the soil with 10^{-3}M HCl.

The analyses showed mean contents of exchangeable Ca, Mg, and K below 0.1, 0.05 and 0.1 meq/100 g, respectively. The total Ca content was extremely low (<100 ppm) and up to 50% or more was in exchangeable form. The total Mg was between 400 and 1000 ppm, and the total K between 700 and 5000 ppm although most of the samples had around 1500-2000 ppm of K. Less than 2% of the total Mg or K was in exchangeable form. The total Fe content was below 3.5%.

Analyses of the clay and silt fractions of some soils showed that most of the total K, Mg, and Fe were in the clay fraction. Almost all the Fe was present as free iron oxides extractable with citrate-bicarbonate-dithionite.

In most of the cases the incubation experiment showed only slight fluctuations in the exchangeable Ca, Mg, and K after wetting and drying the soils for 2, 5, and 11 cycles (1 cycle = 26 days). However, in the soils that received $CaCO_3$, the exchangeable Mg decreased significantly, and not all the Ca added was recovered. The available evidence suggests that these soils may exhibit specific adsorption of Ca and Mg when a liming material is added.

Diluted HCl (10^{-3}M) was as effective as N NH_4OAc for the extraction of exchangeable Ca and Mg, but the latter extracted more K.

An additional incubation experiment, in the absence of added $CaCO_3$, indicated that some of these soils may fix small amounts of Mg ($<$25 ppm) or K ($<$20 ppm) when up to 240 ppm of Mg (as $MgSO$) or up to 195 ppm of K (as KCl) were added.

BIOGRAPHY

The author was born on June 7, 1945, in Medellín, Colombia, South America. In the same city he attended the Faculty of Agricultural Sciences of the National University and obtained the Degree of Ingeniero Agrónomo in February 1969. He worked for 3 years in the Soils Program of the International Center of Tropical Agriculture (CIAT), most of which he spent working at the Carimagua Station in the Eastern Plains of Colombia.

He went to Cornell University in January 1972, where he is currently enrolled for a M.S. - Ph.D. program in Soil Science.

DEDICATION

To my father, my late mother, and my brother and sisters.

To all those who have been patient with my questions.

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1 INTRODUCTION

The exchangeable Mg in the soils of the Eastern Plains of Colombia is very low, especially in the soils of the "altillanura plana" south of the Meta River. The analyses show exchangeable Mg levels below the values considered critical for plant production and for grazing cattle without grass tetany (Hypomagnesemia). However, clear or recognizable Mg deficiency symptoms are not seen in the field. No information is available about the total Mg contents of these soils, although mineralogical analyses indicate the presence of small amounts of mica-vermiculite and large amounts of intergradient 2:1-2:2 type minerals. It was speculated that there could be some release of nonexchangeable Mg from these minerals.

The initial plan was to incubate the soils for several wetting and drying cycles, in order to follow the changes in the exchangeable Mg. This experiment, analyses of total Mg, and a greenhouse or field experiment to test the response to Mg applications would provide a better understanding of the Mg status in these soils. This plan of study was changed after the incubation experiment began. It was decided to follow the effects of wetting and drying on the exchangeable Ca, Mg, and K and to determine the total Ca, Mg, and K in the soils and in some clay and silt fractions.

2 LITERATURE REVIEW

2.1 Calcium, magnesium, potassium, and iron bearing minerals.

Calcium (Ca) is found in feldspars, hornblende, calcite, and dolomite. Magnesium (Mg) is found in micas, hornblende, dolomite, and serpentine; also in secondary aluminum silicates, such as clays, specially montmorillonite, chlorite, and vermiculite. Potassium (K) is present in primary minerals such as feldspars and micas and in secondary aluminum silicates such as clays, specially illite. (Buckman and Brady, 1969). All 2:1 lattices may have Mg isomorphically substituted in the octahedral layers of the crystal lattice and chlorites and vermiculites also hold Mg in interlayer positions (Salmon, 1963a). The clay fraction is likely to contain about 2/3 of the total soil Mg (Salmon, 1963a). Ca in silicates is easily weathered and the principal source of soil Ca, other than $CaCO_3$ is exchangeable Ca (Rich, 1968a); silicate clays do not have structural Ca (Black, 1968). Kaolinite does not contain appreciable amounts of either Mg or K (Black, 1968).

Iron (Fe) in soils is found as oxides, hydroxides and phosphates, and also in the lattice structure of primary silicate and clay minerals (Tisdale and Nelson, 1966). The most common product of the oxidation of ferrous compounds is ferric hydroxide, which may be deposited as goethite, $HFeO_2$, or as hematite, Fe_2O_3. (Mason and Berry, 1968).

2.2 Total Ca, Mg, K, and Fe, and exchangeable bases in highly weathered soils of the tropics

According to Buckman and Brady (1969), the ranges in percentages that ordinarily may be expected in temperate-region mineral surface soils are: 0.17 - 3.30 for K, 0.07 - 3.60 for Ca, and 0.12 - 1.50 for Mg. The normal range for Fe is 0.5 - 5.0%, with a suggested analysis of 2.5% for a representative surface soil. The same authors give the following percentages for representative analyses of a humid temperate-region soil : 1.70, 0.40, and 0.30 for K, Ca, and Mg, respectively.

The contents of total Ca, Mg, and K in Oxisols are lower than in other soil Orders, in general, because by definition they must have a very low content of weatherable primary minerals and 2:1 clay minerals. Loss of silica and exchangeable bases and accumulation of Fe and Al oxides are also salient features of Oxisols. Note however, that the above statements refer to the oxic horizon and not necessarily to the soil above it. On the other hand, not all the soils called lateritic or latosols can be placed in the Oxisol order; many of them are Alfisols, Ultisols and Inceptisols. (Buol et al, 1973). The same applies to the soils simply called "red" soils in the tropics. Another complicating factor for comparative purposes is the lack of equivalence between the different soil classification systems. So, the "sols ferrallitiques" in the French system include Oxisols, Ultisols, and Inceptisols (Aubert and Tavernier, 1972).

Table 1 summarizes some of the results reported in the literature in relation to the contents of total Fe and total and exchangeable bases in the highly weathered soils of the tropics. It was not possible to make a better compilation of results concerning Oxisols. The lack of equivalence between the terms Oxisol, laterite, latosol, etc. should be kept in mind when trying to compare the results. Wild (1971) studied 33 soils (0-15 cms) of the Savanna area of Nigeria, most of them Ferruginous Tropical or Ferrisols tending to Ferrallitic. He did not report the results for individual soils but grouped by parent material. The total K varied from 0.06 to 3.99%, with means of 2.15% in soils derived from the Basement Complex, and 0.08% in soils derived from sandstone. Most of the soils have had accession of loess.

Mokunye and Melsted (1972) studied the Mg forms in 20 soils from different regions of the world. The Mg content was influenced by the nature of the parent materials, climate, and age of the soil. The Mg content increased with increasing contents of 2:1 lattice clays. Oxisols that had very low levels of exchangeable Mg contained appreciable amounts of Mg in the form of Mg-Al silicates of reduced solubility.

Ekpete (1972a) found that the exchangeable K in soils of Eastern Nigeria ranged between 12 and 39 ppm, with a mean of 20 ppm in 9 Oxisols derived from sands and sandstones; in 4 Oxisols derived from sandstones and shales the range was 20-109, and the mean 62 ppm.

Table 1. Mean contents and ranges of total Fe and total and exchangeable bases in highly weathered soils of the tropics

Country and area	Soil class	Depth cm		Total (T) and exchangeable (E) element				Ref. (see foot-notes)
				Fe	Ca	Mg	K	
				-----%---	---------- ppm	----------		
Puerto Rico	Nipe clay (Oxisol)	0-20	T	27.0 11.0-36.0	2600 1200-6600	4100 2200-7100	1400 1100-2100	1)
		20-50	T	32.0 14.0-40.0	2200 800-4800	4600 1000-7400	1300 800-2500	
Cuba	Nipe clay (Oxisol)	0-66 66-102 102-396	T	44.1 48.6 49.8	858 tr 72	1980 2880 3840	498 664 166	2)
Puerto Rico	Nipe clay (Typic Acrorthox)	0-28 28-46 > 46	E		260 20 ---	168 --- ---	39 --- ---	3)
	Coto clay (Tropeptic haplorthox)	0-25 25-43 43-64	E		570 240 740	84 48 72	98 39 39	
Malaysia, Sarawak	red yellow podzolic	0-30 30-60	T	3.7 4.9	1720 1540	1800 1920	3070 4814	4)

Table 1 (cont'd.)

Country and area	Soil class	Depth cm		Total (T) and exchangeable (E) element				Ref. (see footnotes)
				Fe	Ca	Mg	K	
				-- % --	---------- ppm	----------		
Brazil	Amazonian latosols	surf.	E		58 40-80	20 6-36	68 35-113	5)
Brazil, Rio Grande do Sul	Oxisols	0-20	T				3310 1860-6800	6)
			E				73 32-150	
	Utisols	0-20	T				3650 1780-12000	
			E				106 37-173	
Hawaii	Lahaima (low humic latosol)		T	16.3	5434	3060	1660	7)
	Humic ferruginous latosol			24.6	2574	3240	14027	
	Akaka (hydrol humic latosol)			19.6	143	3720	747	
Hawaii	Ookala (humic latosol)		T				5644	8)
			E				78	
	Kapara (humic ferrug. latosol)		T				2324	
			E				35	

Table 1 (cont'd.)

Country and area	Soil class	Depth cm		Total (T) and exchangeable (E) element				Ref. (see foot-notes)
				Fe	Ca	Mg	K	
				----%---	----------ppm----------			
Sierra Leone	Oxisols	surf.	T			514 346-721		9)
			E			56 20-133		
South Africa	2 laterites	0-25	T	13.4-14.5	640-790	7700-8400	2800-6100	10)
	1 laterite	0-30	E		18	16	16	
	3 lateritic red earths	0-30	T	3.8 0.5-5.8	790 430-1290	5520 3480-7920	13950 910-39000	
	2 lateritic red earths	0-30	E		176-480	82-264	39-117	
	3 lateritic yellow earths	surf.	T	5.4 3.1-9.6	2430 2000-2720	3720 1920-6120	3040 1830-4150	
			E		79 20-168	88 22-184	94 27-214	
India (south)	lateritic	0-20	T	6.6 2.7-8.3	2970 1360-4720	3550 2220-5760	3490 1830-4980	11)
		20 up to 60		7.3 5.7-9.9	2700 1430-4360	2590 1920-3720	3890 2820-5400	

Table 1. (cont'd.)

Country and area	Soil class	Depth cm		Total (T) and exchangeable (E) element				Ref. (see foot-notes)
				Fe	Ca	Mg	K	
				----%----	----------ppm----------			
India (south)		0-20	E		550 280-1320	400 140-1220	28 0-39	
		20 up to 60			597 320-1280	400 220-610	28 0-39	

Footnotes (Table 1)

1) Adapted from Sivarajasingham (1961). The author gives data of 6 sites but data of only 4 (noneroded) sites was taken. The depths are rough averages. The underlying bedrock is commonly serpentinite.

2) Bennett and Allison (1928), cited by Sivarajasingham (1961). Bedrock is serpentinite.

3) Beinroth (1972). Exchangeable Al in the surface soil is 1.4 and 1.6 meq/100 g in Nipe and Coto clays, respectively. Underlying Coto clay are Miocene limestones. The bedrock in Nipe clay is serpentinite.

4) Adapted from Bailey (1966). The soil is typical of many residual hill soils of Sarawak.

5) Adapted from Fassbender, et al (1970). Exchangeable cations extracted with diluted HCl. Data is average of 5 soils; a red latosol with >13 meq bases/100 g was not included. The contents of exchangeable bases decreased with depth.

6) Adapted from Oliveira, et al (1971). Data is average of 8 Oxisols and 7 Ultisols.

7) Mikami and Kimura (1964). The Akaka soil is a Hydrandept; the other 2 soils could be Trophomults.

8) Adapted from Graham and Fox (1971). Data selected includes only latosols with a pH around 5.0 and without illite.

9) Adapted from MoKunye and Melsted (1972). Data is average of 5 Oxisols. The total Mg content showed slight or large increases with depth (up to 0.5-1.5 m), but the exchangeable Mg decreased by 50% or more.

10) Adapted from Van Der Merwe (1941). Only part of his data was taken. The laterite soils are derived from dolomitic limestone; the lateritic red earths are derived from acid to intermediate rocks; the lateritic yellow earths are derived from old granite or dolerite (mafic rock).

11) Adapted from GowaiKar and Datta (1971). The parent material is a granitic-gneissic complex. The data is average of 7 lateritic soils, all of which have very high base saturation (<0.5 meq of exch. acidity/ 100 g). The depths given are rough averages.

A few generalizations can be drawn from the preceding data in relation to the elemental contents in some of the highly weathered soils of the tropics. The total Fe may vary from a small percentage up to 50%. The total Ca varies from a few hundred ppm up to 0.5% and seems to be very influenced by the parent material and/or nearby limestone deposits. The total Mg is usually much greater than the total Ca, a feature opposite to what is observed in temperate-zone soils. The total Mg varies roughly between 0.05 and 0.8% but it is less variable than the total Ca and the modal value is around 0.3%. High Mg contents seem to be associated with parent materials (or bedrocks) rich in Mg such as serpentinite, dolomite, and mafic minerals. The total K also shows large variation but values between 0.1 and 0.4% are more common. In relation to the level of exchangeable bases, it may vary from less than 1 to several meq/100 g, although the exchangeable K is usually less than 0.2 meq/100 g.

2.3 Specific adsorption and fixation of cations

The ability of soils and silicate clay minerals to retain certain cations in such a way that they are not easily replaced by other cations has been widely recognized. Terms such as fixation, specific adsorption, and selective sorption have been used to describe this phenomenon (Van Olphen, 1963; Sawhney, 1972; Davis, et al, 1971; Hanway et al, 1957; Rich, 1968a; Rich and Lutz, 1965). Most of the work dealing with fixation of cations in soils refers to the fixation of K

and NH_4 by micas and 2:1 clay minerals. However, in the last ten years an increasing number of papers have been published dealing with the specific adsorption of cations such as Ca and Mg by oxide systems. Most of this work has been done by colloid chemists and its implications in soil science have not been developed. Although the colloid chemists do not agree on the definition of specific adsorption, the papers reviewed by the author indicate that no work has been done to study the ability of different cations to replace other specifically adsorbed cations on oxide surfaces, and there is no information either on the consequences of it on the cation uptake by plants.

2.3.1 Silicate clays

The fixation of K is due primarily to 2:1 minerals such as montmorillonite, vermiculite, and micas (Davies, 1972; Hanway, et al, 1957; Sawhney, 1972). Minerals of the 2:1 type seem to fix K and NH_4 by a similar mechanism and very little fixed NH_4 is nitrified even during prolonged incubation periods (Hanway, et al, 1957).

The fixation of cations by 2:1 minerals is related to their hydration energy. Cations with high hydration energy such as Ca, Mg, and Sr are not fixed because they produce interlayer expansion, whereas cations with low hydration energies (K, NH_4, Rb, Cs) cause interlayer dehydration and layer collapse and may be fixed. (Sawhney, 1972; Rich, 1968a). However, Ca and Mg can be fixed by 2:1 layer silicates when physical blocking due to collapse in the edges occur (Rich,

1968a). According to Davies, et al (1971) cations such as K, NH_4, and Ba, which have a radius similar to that of the hexagonal voids of the tetrahedral layer of 2:1 clay minerals, could be fixed when dehydrated, although vermiculite fixes K in wet systems.

2.3.2 oxide systems

According to Van Olphen (1963), the preferential adsorption of certain kinds of ions on the particle surface may be due to chemical bonds ("chemisorption"), hydrogen bonds or van der Waals attraction (physical adsorption). In most hydrophobic sols the particle charge is created by the preferential adsorption of specific ions on the particle surface. The Stern model of the electric double layer is a refinement of the Gouy model and it can take into account specific adsorption forces besides the pure electrostatic attraction.

Parks (1967) defines specific adsorption as the adsorption under the combined influence of ionic and non-ionic bonding. The ionic bonding is due to pure electrostatic attraction. In nonionic bondings he includes hydrogen bonding, coordinate bonding, and London-van der Waals bonding. Charge reversal must occur in response to specific adsorption alone. In oxide systems specific electrolyte adsorption can occur by ion exchange with structural cations, with H or OH of the surface hydroxide groups or with impurities.

Stumm and Morgan (1970) state that the sorption of

metal ions on hydrous oxides of Fe and Mn may properly be interpreted as surface complex formation or as ion exchange, although it is necessary to realize that there is a continuous transition between purely electrostatic ion exchange reactions and coordination by covalent bond. Hydrous oxides show a strong tendency to interact chemically with anions as well as cations. These chemical interactions may be explained as a complex formation, involving a ligand exchange in the case of anions, or a coordination with electron acceptors in the case of cations:

$$-\overset{|}{\underset{|}{Me}} - OH + HPO_4^{2-} = -\overset{|}{\underset{|}{Me}}-OPO_3H^{-} + OH^{-}$$

$$-\overset{|}{\underset{|}{Me}} - OH + Zn^{+2} = -\overset{|}{\underset{|}{Me}} - OZn^{+} + H^{+}$$

According to Hingston, et al (1972), the adsorption of cations by goethite, gibbsite and other oxide surfaces, which is not due to simple cation exchange could involve the first hydrolysis product of the cations through the following reaction

$$-\overset{|}{\underset{|}{Me}} - OH + Ca(OH)^{+} = -\overset{|}{\underset{|}{Me}} - OCa^{+} + H_2O$$

Huang and Stumm (1973) studied the specific adsorption of cations on Al_2O_3. They found that the adsorption of Ca and other alkaline earth cations on hydrous γ- Al_2C_3 increases with increasing pH and with increasing Ca concentration. Finite adsorption was observed at the point of zero charge (ZPC) and slightly below it. The extent of adsorption increased in the order Mg>Ca>Sr>Ba. The

The adsorption was described by the formation of a surface complex:

$$AlOH + M^{2+} = AlOM^{+} + H^{+}$$

Huang and Stumm also found that the surface charge of the oxide suspension could be reversed upon the specific adsorption of cations. The adsorption of Ca at pH 8.5 and in a 5.0×10^{-4}M Ca solution was about 2 meq/100 g. The Ca adsorption could also be interpreted in terms of a Langmuir isotherm, with an adsorption maximum of about 600 ppm at pH8 and 3200 ppm at pH 10. The authors emphasize that no hydrous oxide has a unique ZPC. The exact value depends on sample origin, history, purity, crystallinity, temperature, sorbability of electrolytes and degree of hydration.

In an excellent paper Breeuwsma (1973) describes the adsorption of ions on hematite. He found that hematite could strongly adsorb Ca and Mg ions, and may also specifically adsorb anions such as SO_4 and PO_4. He defines specific adsorption as the adsorption of ions in the "Stern layer", i.e. The layer between the surface and the "outer Helmhotz plane" (plane through centers of purely electrostatically adsorbed ions nearest to the surface). For ions to penetrate into the Stern layer there must be some specific chemical interaction with the surface phase. The adsorption of ions on hematite is characterized by a large variety of interactions with the surface. Factors such as preparation, pretreatment and type of electrolyte affect markedly the double layer properties of hematite. When dehydrated,

cations like Li and Mg fit in the octahedral holes of the hematite lattice and this could explain the stronger preferential adsorption of these ions as compared to other alkali or alkaline earth ions. In soils the most frequently occurring highly crystallyne iron oxides are hematite (α- Fe_2O_3) and goethite (α- FeOOH). Amorphous iron oxides with general composition $Fe_2O_3.n\ H_2O$ ($1<n<3$) are more active in adsorption and interaction phenomena because of their higher surface area.

Hunsaker and Pratt (1971) found that a Brazilian Oxisol, 2 Mexican volcanic ash soils, and a Californian soil (high in allophane and chlorite) all showed a strong Ca preference over Mg, apparently related with the mineral components of the soil. Montmorillonite showed only a slight preference for Ca, but montmorillonite with hydroxy-Al coatings showed a strong Ca preference over Mg. However no data is given by the authors in relation to possible changes in the CEC or the completeness of recovery of the added Ca and Mg.

2.3.3 Organic matter

Van Dijk (1971) studied the capacity of humic acids to bind metal ions and he found no large differences in bond strength for the divalent ions Ba, Ca, Mg, Mn, Co, Ni and Fe (in this order only slightly increasing). He found also very small differences between soil humic acids as to the mechanism and the strength of the cation binding. According to Hunsaker and Pratt (1971), a slight preference for Ca is associated with the organic matter in soils. The soil organic matter has a low selectivity for K (Rich and Black,

1963). Salmon (1963,a) states that some Mg may be held by organic matter in other than exchangeable form. Mokunye and Melsted (1972) found that only 0.05 to 2.8% of the total Mg, in soils from different regions of the world, was in organic-complexed forms and they consider that this contradicts the above statement by Salmon. However, their method for determining the organic-complex Mg is questioable (extraction with NH_4OAc before and after oxidation of the organic matter with H_2O_2).

2.4 Influence of several factors on the fixation and release of exchangeable bases.

2.4.1 Temperature, moisture, and drying.

Most of the work done in this respect refers only to the exchangeable K. The results have shown that temperature may increase the fixation of K (Black, 1968, Davies, et al, 1971), or, on the contrary, may lead to release of non-exchangeable K (Haapala and Miller, 1961, Ismail and Scott, 1972; Burns and Barber, 1961). In some cases it is not possible to separate the effects of temperature and drying. According to Rich (1966a), commonly there is a release of K on drying but the opposite can also occur depending on the K concentration. Ahmad and Davis (1971) did not find any simple relationship of K fixation or release with rate or intensity of drying in 6 West Indian soils of contrasting mineralogy.

In soils of the savanna area of Nigeria, wetting and drying 20 times (in 60 days) gave a marked recovery of the

exchangeable K after depletion by intensive cropping. Keeping the soils at field capacity for 60 days showed no increase in the exchangeable K. (Wild, 1971). Burns and Barber (1961) found that varying moisture from 60 to 100% of moisture equivalent had no effect on the release of non-exchangeable K in 3 Indiana soils. Salmon (1963,b) reported an increase in the exchangeable Mg by wetting and drying of some exhausted soils According to Rich (1968b) weathered micas and vermiculites fix K under moist as well as dry conditions.

2.4.2 Presence of other cations.

Hydrogen saturated clays spontaneously change into Al-saturated clays and if the lattice structure contains Mg there is also a release of nonexchangeable Mg Barshad and Foscolos (1970) found that the rate at which adsorbed H ions are replaced by Al and Mg ions in colloidal vermiculites, montmorillonites and illites is directly proportional to the CEC and to the H_2O content Haagsma and Miller (1963) reported that no release of nonexchangeable K occurred in a Gray-brown podzolic soil when a Na- or a Ca-saturated resin was used, but the release to a H-saturated resin was proportional to the degree of H saturation. The mechanism for the release of K was not understood.

According to Hanway, et al (1957) when a system contains only one fixable cation (e.g. K or NH_4) an equilibrium seems to exist between the fixed, exchangeable, and soluble forms of such cation The addition of other cation will lead to a different equilibrium and to release of the fixed cation

although such release is smaller when another fixable cation is added.

2.4.3 Al and Fe interlayers

The presence of hydroxy-Al and Fe interlayers or islands may inhibit the fixation of K and other cations by preventing the collapse of the silicate layers (Rich and Black, 1963; Rich and Lutz, 1965, Rich 1968b; Davies, 1972). On the other hand, such interlayers could slow down the exchange of K and other cations through a physical blocking effect (Weaver, 1972).

3 MATERIALS AND METHODS

3.1 Soils

3.1.1 Sampling and classification

The soil samples used in this study were taken by Hubert Zandstra and George Naderman, in 1968, 1969, and 1971, in several locations of the Llanos (plains) of Colombia. Some of these locations were sites of experimental trials conducted by the Colombian Institute of Agriculture (Instituto Colombiano Agropecuario, ICA) and two of them, La Libertad and Carimagua, are Experimental Stations of ICA. The soils at La Libertad Station are representative of those of the piedmont, and the soils at the Carimagua Station are representative of the soils found south of the Meta River in the nondissected, well drained plains.

With exception of soil samples MR-1, MR-7 (Carimagua), MR-15 (El Piñal), and Cl-18, Cl-19 (La Libertad), the samples were taken from the soil pits described by Guerrero (1971). Mineralogical analysis of some of them are given in the Appendix. All samples come from sites under native vegetation (pastures) that had not been limed nor fertilized.

The samples MR-1 and MR-7 were collected in 1971 in the agronomy field at the Carimagua Station, from the plot used by George Naderman for his rice experiment.

The samples Cl-18 and Cl-19 were taken in 1969 at La Libertad Station (high terrace), by Hubert Zandstra from

the plot used for his corn and rice experiments.

The samples MR-8-9 to MR-14 were collected in 1969 by Zandstra at the Carimagua Station, from the pit described and sampled later by Guerrero (1971). This pit was near the south fence of the agronomy field.

The sample MR-15 was taken for G. Naderman in 1968 by R. Hernández, near the corn plot in the first experimental field (agronomy) used by ICA at the El Piñal farm. The samples C2-6, C2-2, and C2-3 (El Piñal); C3-1 and C3-2 (Matapalito); and C4-1-2 and C4-3 (El Viento) were taken by Zandstra in 1969, from the pits sampled and described by Guerrero (1971). The exact location of those samples is as follows:

Samples C2-6, C2-2 and C2-3: from the pit between the air strip and the second experimental field of ICA at the El Piñal farm.

Samples C3-1, C3-2, and C3-3: from the pit at the Matapalito farm, about 2 Km north of the ranch house.

Samples C4-1-2 and C4-3: from the pit near the 1969A ICA field experiments at the El Viento farm.

Soil profile descriptions of the pits mentioned above (Carimagua, El Piñal, Matapalito, and El Viento) are given in Appendix Tables 1, 2, 3, and 4, respectively.

Before the experiments described in this study began, in July 1972, all the samples were air-dried, with the exception of samples C1-18, C1-19, and C4-2, which were moist. All the samples were air-dried for several days in the laboratory, then ground with a metallic mortar and pestle and passed through a 2.38-mm square holes sieve.

The laboratories where all the operations related with this study were conducted have a constant temperature of 25± 1° C and a relative humidity of 15-20%.

Given the fact that some analyses of the same samples were available at Cornell, and also the fact that chemical and mineralogical analyses of the samples simultaneously taken by Guerrero (1971) were available, it was not considered necessary to do preliminary chemical analyses to characterize the samples.

No mineralogical data was available for samples MR-15, Cl-18 Cl-19, MR-1, and MR-7. However, the samples MR-1 and MR-7 were taken at about 300 m from the Carimagua pit and all the information available to the author indicates that their chemical and mineralogical properties are expected to be very close to those of the samples from the Carimagua pit.

In the Appendix Table 10 are shown the mineralogical analyses of samples from La Libertad and El Piñal used by León (1967). His samples from La Libertad seem to correspond to the high terrace and the samples from El Piñal were taken 1-1½ Km east of the farm house and 300 m south of the Meta River.

One of the limitations encountered in this study was the limited amount of some of the samples. Besides, the most abundant samples, namely MR-1, Cl-18 and MR-15, corresponded to soils for which incomplete chemical and mineralogical analyses were available. The depths at which the 19 soil samples included in this study were taken appear in Table 4. These 18 samples represent 7 topsoils

(0 to 15-20 cm) and 12 subsoils (as used here, the word subsoil represents soil layers at any depth below the top 15-20 cm). Each of the 19 soil samples are designated hereafter as simply soils.

Chemical and physical characteristics of the samples from the Carimagua, El Piñal, Matapalito and El Viento pits are presented in Appendix Tables 5 and 6.

Selected chemical properties of samples C1-18, C1-19, MR-15, MR-1, and MR-7 are presented in Appendix Table 7.

Mineralogical analyses are presented in Appendix Tables 8, 9, and 10.

Curves of pH vs. surface charge, in soils MR-1, C1-18, and MR-15 are presented in Appendix Figure 1.

Moisture retention data is presented in Appendix Table 11.

Both Guerrero (1971) and León (1967) found that in these soils the sand fraction is composed mainly of quartz with negligible contents of weatherable minerals. Following the criteria presented in the Soil Taxonomy of the U.S. Department of Agriculture, Guerrero (1971) found that the subsoils horizons of 7 profiles observed (soils near the piedmont not included) meet the requirements for oxic horizons. The soils were classified as follows:

Soil profile at the Carimagua pit (samples MR-8 to MR-14), as well as other soil profile north of the Carimagua Lake, and a soil profile at El Viento: clayey, kaolinitic, isohyperthermic, Typic Haplustox.

Soil profile at the El Piñal pit (samples C2-6, C2-2,

and C2-3) and soil profile at the Tabarís farm (see Appendix Table 8): fine loamy or fine silty Ultic Haplustox.

Soil profiles at the Matapalito (samples C3-1 to C3-3) and El Viento (samples C4-1-2, C4-3) pits: clayey, kaolinitic, isohyperthermic, Typic Umbraquox.

According to León (1967), the soils from La Libertad and El Piñal that he studied were members of the families clay loamy Umbric Tropept and loamy Typic Udox, respectively.

3.1.2 General Characteristics of the area:

Mean annual temperature about 28°C (82°F), with little variation throughout the year.

Average relative humidity 80% during the rainy season and 50-60% during the dry period.

Average annual rainfall: about 4000 mm in La Libertad, dropping to 1200 mm in Puerto Carre ño, on the Orinoco River. The mean annual precipitation near Carimagua, El Piñal, Matapalito and El Viento is about 1800-2000 mm. The dry season lasts from December to March.

Elevation above sea level: 550 m at La Libertad; 150-300 m in the other localities sampled.

With exception of La Libertad, located in the piedmont, east of the Andes, the rest of the samples came from a well-drained, nondissected strip of savanna that extends roughly from Puerto Gaitán to the Orinoco River and 50 Km south of the Meta River, with an estimated area of 2-3 million ha. and known as the "altillanure plana".

Although the piedmont area is presently dedicated to rather intensive agricultural and livestock enterprises, the

altillanura is used mostly for very extensive livestock exploitations, with a minimum of agriculture. The main subsistence crops grown are plantains, rice, cassava, some corn, and fruit trees such as mango and citrus.

The parent materials are mixed alluvial sediments, probably deposited during the Pleistocene. All surface sediments in the Llanos Orientales came from the Eastern Cordillera. The materials deposited are highly deficient in nutrients, partly as a result of the nature of the geological formations from which they derive. Inceptisols predominate in the piedmont, Ultisols in the low alluvial terraces, and Oxisols in the high level plains south of the Meta River. (FAO, 1965).

3.2 Methods

3.2.1 Exchangeable Ca, K, and Mg

Ten grams of air-dry soil received 20 ml of N NH_4OAc, pH7, in 125-ml erlenmeyer flasks. The flasks were shaken intermittently for half an hour, by hand, and then allowed to stand overnight. The suspensions were then filtered in 4.25-cm Pyrex buchner funnels, using Whatman filter paper #42. An additional 80 ml of N NH_4OAc was added in small portions. The suction applied ranged between 6 and 10 cm of Hg.

The extracts were received in 250-ml erlenmeyer flasks and evaporated to dryness on a hot plate. The organic matter present in the extracts was variable and apparently related to the percent of organic matter in the soil. To destroy the organic matter, 30% hydrogen peroxide was used.

The flasks received 10 ml of H_2O_2: H_2O (1:1) and were then heated and evaporated to dryness again. To dissolve any carbonate formed, the flasks received 20 ml of HCl:H_2O (2:8) and were evaporated to dryness once more. This HCl:H_2O addition was done rinsing the container walls.

The samples were sent to the Analytical Service Laboratory of the Agronomy Department where they were analyzed for Ca, Mg, and K by atomic absorption spectrophotometry. The dry residues were dissolved in 10 ml of N HCl solution with 5% lanthanum to reduce interferences. These extractions are designated simply as "exchangeable bases" or as "set 9112 . The extractions were duplicated in most cases.

3.2.2 Total Ca, Mg, K, and Fe

These determinations were made with soil samples and with a few clay and silt fractions, always in duplicate.

The silt and clay samples were kindly supplied by R. Weaver. The original separation of the soil samples into sand, silt, and clay fractions was done after the removal of organic matter with NaOCl and the removal of free iron and Al oxides with citrate-bicarbonate-dithionite (CBD) (Weaver, 1972).

The clay fractions were in saturated NaCl suspensions. To remove the NaCl, 25-ml aliquots of the suspensions received 6 ml of 0.4 N $(NH_4)_2CO_3$ and after shaking were centrifuged at 1200 rpm for 15 minutes. These operations were repeated 3 times. The samples were then oven dried at 110°C for 3 days.

The soil samples were finely ground with a mullite mortar and pestle. For the digestions the samples were first oven dried at 110°C for 2 hours and then 0.5 g (in the case of soil and silt samples) or 0.2 g (in the case of clay samples) were weighed into 50-ml Teflon beakers.

HF-H_2SO_4 digestion procedure: The samples were wetted with 1 ml of distilled water and then received 10 ml of 48% HF plus 0.5 ml of H_2SO_4 and were evaporated to dryness in a sand bath at 200°C. The HF-H_2SO_4 treatment was repeated and after evaporation to dryness the samples were allowed to cool. Then 5 ml of 6 N HCl and 15 ml of H_2O were added and the samples were heated for one hour at about 90°C. The solutions were then filtered into 100-ml volumetric flasks, using Whatman filter paper #42. After cooling the volume was completed to 100 ml with distilled water.

The solutions were sent to the Analytical Service Laboratory and were analyzed for Ca, Mg, K, and Fe by atomic absorption, using a HCl-La solution to reduce interferences.

After the digestion and analysis of the first set of samples, a very low content of total Ca was found. So to make sure that this was not due to sulfate interference (Pawluck, 1967), the soils were also digested with HF-HCl, as described next (Pawluck, 1967).

HF-HCl digestion procedure: 0.5 g of oven-dry soil, in Pyrex beakers, were put in the muffle furnace at 480°C for 6 hours to destroy the organic matter. After cooling, they were transferred to 50-ml Teflon beakers and 10 ml of HCl:H_2O (1:1) were added.

The samples were warmed on the steam plate at about 80°C for 1 hour and 5 ml of distilled water were added. The suspensions were stirred and when the solids had settled out, they were decanted to 100 ml volumetric flasks. Ten ml of distilled water were added and, after mixing and settling, the suspensions were decanted again. The samples received then 5 ml of 48% HF and 5 ml of concentrated HCl and were evaporated to dryness on the hot plate. After cooling, the HF-HCl treatment was repeated and after evaporation to dryness and cooling, 10 ml of concentrated HCl was added and the samples were evaporated to dryness once more. The residues were dissolved in 10 ml of HCl: H_2O (1:9) and transferred quantitatively to the original volumetric flasks. The volume was then completed to 100 ml with distilled water. As before, the solutions were sent to the Analytical Service Laboratory for analysis by atomic absorption.

3.2.3 Incubation Experiment

To study the possible release of Ca, Mg, and K from nonexchangeable to exchangeable forms, the soils were incubated for several wetting and drying cycles, including untreated (check) soil, soil leached with 10^{-3}M HCl, and soil plus $CaCO_3$.

3.2.3.1 Leaching of the soil with 10^{-3}M HCl

Ten-gram samples of 18 topsoils and subsoils were leached with 100 ml of 10^{-3}M HCl (pH 3.02) and the extracts were collected in 250-ml erlenmeyer flasks. Additional 10-g samples of the soils MR-1, MR-15 and Cl-18 were also extracted with 200 ml of 10^{-3}M HCl. Immediately after the HCl extraction

the same 10-g samples were extracted with 100 ml of N NH_4OAc, pH 7, but the extracts were collected separately of those with HCl. Both the HCl and the NH_4OAc extractions were made by adding small portions of solution to the soils. The extraction was made in 4.25-cm Pyrex buchner funnels, using Whatman filter paper #42 and a suction of 5-10 cm of Hg.

The HCl extracts were evaporated to dryness on the hot plate and sent to the Analytical Service Laboratory. They are designated hereafter as "set 9122". The NH_4OAc extracts were done in duplicate in most cases.

The objective of the HCl and NH_4OAc extractions was to estimate the effect of the acid treatment on the levels of exchangeable bases. The next step was the leaching of the soil samples that were going to be incubated.

For the leaching of the samples for incubation, from 45 to 75 g of each soil were leached with 100 ml of 10^{-3}M HCl (pH 3.02) per 10 g of soil, excepting the soils C3-1 and C2-2 of which only 22 g were available. The leaching was done in 7-cm Pyrex buchner funnels. After extraction, the volume was completed with 10^{-3}M HCl to the initial volume before extraction, to compensate for the HCl retained in the soil. Then, 100-ml aliquots were evaporated to dryness and sent to the Service Laboratory for analysis of Ca, Mg, and K as before. This set of extractions is designated hereafter as "set 9111". Included in this set are additional separate extractions of the soils MR-1, C1-18, and MR-15 with 200 ml of 10^{-3}M HCl per 10 g of soil.

After leaching the soils with HCl (set 9111), the samples were air-dried in the laboratory for 2 days.

3.2.3.2 Incubation of the soil samples

The experiment included 3 basic soil "pretreatments" (check soil, i.e., soil with no chemical treatment; soil plus $CaCO_3$, and soil leached with 10^{-3}M HCl) and 3 sets of wetting and drying (W-D) cycles. One W-D cycle was 26 days. Due to limitations in the amount of soil available, not all the 9 treatment combinations for all the samples were possible. These 9 basic treatments are presented in Table 2 and all of them included successive wetting and drying of the samples. Details of wetting and drying are described later.

The treatments 4, 5, and 6 received an amount of $CaCO_3$ equivalent to twice the exchangeable Al. The leaching of the soil with HCl was explained previously.

Table 2. Basic treatments in the incubation experiment

No	Soil pretreatment	W-D cycles	Incubation time days
1	check soil	2	52
2		5	130
3		11	286
4	soil + $CaCO_3$ (2:1)	2	52
5		5	130
6		11	286
7	soil leached with 10^{-3}M HCl	2	52
8	(100 ml / 10 g of soil)	5	130
9		11	286

To get more information about the conditions that might influence the release of Ca, Mg, and K, and taking advantage of the fact that larger amounts of soil were available of the samples MR-1, Cl-18 and MR-15, and considering that these 3 soils tend to represent rather different kinds of soils within all the samples under study, a set of 11 extra treatments were applied to these 3 soils, as shown in Table 3.

Table 3. Extra treatments in the incubation experiment

Nº	Soil pretreatment	W-D cycles	Incubation time days
10	soil + $CaCO_3$ (1:1)	2	52
11		5	130
12		11	286
13	soil leached with 10^{-3} M HCl	always wet	130
14	(100 ml/10 g of soil)	always wet	286
15	soil leached with 10^{-3}M HCl	5	130
16	(200 ml/10 g of soil)	11	286
17	soil leached with 10^{-3}M HCl	always dry	130
18	(100 ml/10 g of soil)	5 (35°C)	130
19	check soil	always dry	130
20		5 (35°C)	130

Treatments 10, 11, and 12 received an amount of $CaCO_3$ equivalent to the exchangeable Al. In the treatments 13 and 14 the soils received 10 ml of distilled water and were kept

always wet, with a water layer of 2-10 mm above the surface.

In the treatments 17 and 19 the soils were never re-wetted but kept dry.

In the treatments 18 and 20 the soils received 3 ml of distilled water every 26 days (as in the basic treatments) and were allowed to dry in the laboratory, covered with cheese cloth, for 21 days, but for the last 5 days of each W-D cycle they were put in the oven at 35° C

Both the basic treatments (1 to 9) and the extra treatments (11 to 20) were applied in one completely randomized design (CRD) with 2 replications. For each treatment, 10-g soil samples were put in 125-ml erlenmeyer flasks and kept in the laboratory, covered with 2 layers of cheese cloth. With exception of the treatments 13, 14, 17, and 19, all the treatments received 3.5 ml of distilled water at the beginning of the incubation experiment on August 21, 1972. 15-20 days after the addition of water the soils were fairly dry. Every 26 days the soils received 3 ml of distilled water. In the treatments 13 and 14 it was necessary to apply water more frequently to keep the soils always wet.

To account for any possible contamination from the reagents, water added during the incubation, and/or dust, special blanks were set up for the different treatments:

a) one group of blanks received only water, in the same way as the soil samples.

b) one group of blanks received 30.0 mg of $CaCO_3$ and water.

This amount of $CaCO_3$ is a rough average of the $CaCO_3$ applied in the treatments 4, 5, and 6.

c) one group of blanks received 4 ml of 10^{-3}M HCl and water. (The HCl retained in the soil after leaching with 10^{-3}M HCl was between 2.6 and 4.5 ml/10 g of soil).

d) a group of blanks received nothing during the incubation.

The $CaCO_3$ used in the experiment was analytical grade, Mallinckrodt brand, and had a certified maximum Mg content of 0.02%. Assuming a Mg content of 0.02%, 30 mg of $CaCO_3$/10 g of soil would supply a maximum of 0.005 meq of Mg/100 g of soil, i.e. 0.6 ppm of Mg. It was found that the actual Mg content in the $CaCO_3$ was less than 0.01%. Its K content was less than 0.03%. With this K content, 30 mg of $CaCO_3$ per 10 g of soil would supply a maximum of 0.0023 meq of K/100 g of soil, i.e. 0.9 ppm of K.

To calculate the amounts of $CaCO_3$ to be applied to the soils, the levels of exchangeable Al in the soils were not directly determined, but taken from analyses done previously in the Cornell Agronomy Department or from Guerrero (1971). In some samples the exchangeable Al was unknown and was guessed by considering pH and/or Al levels of neighbor plots (soils).

Table 4 gives the soils incubated, the levels of exchangeable Al, the $CaCO_3$ applied in treatments 4, 5, and 6, and the basic treatments applied to each soil.

In order to determine the effect of the incubation (wetting and drying) on the pH and the exchangeable Al of the check soils, 10-g samples of the soils MR-1, Cl-18, and MR-15 were incubated in the same way as treatments 1, 2, and 3. This was done in duplicate for both Al and pH.

Table 4. Soil samples used in the incubation experiment

Locality	Sample	Depth cm	Exch.Al meq/100g	$CaCO_3$ mg/10g of soil	Treatments 1	2	3	4	5	6	7	8	9
Carimagua	MR-1	0-15	3.3[b]	33.0	+	+	+	+	+	+	+	+	+
	MR-7	33-50	2.0[b]	20.0	+	+	+	+	+	+	+	+	+
La Libertad	Cl-18	0-20	3.23	32.3	+	+	+	+	+	+	+	+	+
	Cl-19	20-40	2.38	23.8	+	+	+	+	+	+	+	+	+
Carimagua (pit)	MR-8-9	0-20	4.0[a]	40.0		+	+	+	+	+	+	+	+
	MR-10	20-38	2.5[a]	25.0	+	+	+	+	+	+	+	+	+
	MR-11	38-94	1.3	13.0		+	+		+	+	+	+	+
	MR-12	94-114				+	+				+	+	+
	MR-13	114-137				+	+				+	+	+
	MR-14	152				+					+	+	+
El Piñal	MR-15	0-15	2.1[b]	21.0	+	+	+		+	+	+	+	+
Matapalito (pit)	C3-1	0-16	3.4[a]	34.0			+			+			+
	C3-2	16-42	2.9[a]	29.0		+	+		+	+	+	+	+
El Piñal (pit)	C2-6	0-16	2.5[a]	25.0		+	+		+	+		+	+
	C2-2	18-30	2.2[a]	22.0			+			+			+
	C2-3	30-80				+	+				+	+	+
El Viento (pit)	C4-1-2	0-19	3.7[a]	37.0		+	+		+	+	+	+	+
	C4-3	19-31	2.8[a]	28.0		+	+		+	+	+	+	+

a: value includes exchangeable H
b: assumed value
c: added only in treatments 4, 5, and 6

3.2.3.3 Exchangeable Ca, Mg, and K after 2, 5, and 11 wetting and drying cycles.

After 2, 5, and 11 W-D cycles were completed (52, 130, and 286 days, respectively, after the beginning of the incubation), each of the corresponding sets of samples were extracted with N NH_4OAc, pH 7, to determine the levels of exchangeable Ca, Mg, and K, following the same procedure described before. The only difference was that in the sets corresponding to 2 and 5 W-D cycles, only 4 ml of HCl: H_2O (1:1) were added before the final evaporation to dryness.

All the analyses were done by the Analytical Service Laboratory, with the atomic absorption spectrophotometer.

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Note: The first sets of analyses of exchangeable cations done in connection in this study gave inconsistent results. It was found that one of the possible causes, although not always acting, was contamination from the rubber stoppers used at several steps during the handling of the NH_4OAc or HCl extracts.

It was speculated that another possible cause might be incomplete recovery of the extracts, following the destruction of the organic matter with H_2O_2. Some bits of solution could be splashed to the container walls and then a careful washing of the walls would be required to get a complete recovery of the sample. These factors and others were analyzed in a separate experiment (see Appendix Table 12 for a complete description).

Of all the analyses already described, the contamination from rubber stoppers, if any, could be present only in the

set of samples incubated for 2 W-D cycles. In all the other cases either the rubber stoppers were not used or the analyses were repeated.

3.2.3.4 Exchangeable Al and pH

After 2, 5, and 11 W-D cycles, the pH and the exchangeable Al were determined in the samples incubated for these purposes. (Note: in the set corresponding to 5 W-D cycles, the soils were very dry at the end of the 5th W-D cycle, i.e. 130 days. The flasks were then stoppered but the pH and Al determinations were made 43 days later).

The pH was measured with a Leeds & Northrup potentiometer, using a soil: water ratio of 1:1 (10 g of soil). The suspension was stirred intermittently for ½ hour and, after ½ hour more of equilibrium, the pH was measured putting the calomel electrode in the sediment.

The exchangeable Al was extracted with N KCl, using the following procedure: Ten-gram samples of dry soil were placed in 250-ml plastic centrifuge bottles and 40-ml N KCl was added. The samples were shaken by hand twice and after 15 minutes were centrifuged in an international centrifuge at 500 rpm for 5 minutes. The supernatant was poured through a filter into a 250-ml volumetric flask. The soil was extracted with five additional 40-ml aliquots of KCl and the extracts were combined and diluted to 250 ml. The Al was determined by titration using the procedure described by McLean (1965, pp. 992-993).

3.2.3.5 Recovery of $CaCO_3$

After the analyses of the sets of samples incubated for

2 and 5 W-D cycles, it was found that the recovery of added Ca was low in the blanks and in some soil samples. To check the calcium content in the $CaCO_3$ and some possible causes of the low recovery of added Ca, it was decided to extract $CaCO_3$ (from the same bottle used in the incubation experiment) with N NH_4OAc pH 7, and with 0.1 N HCl. Two 30.0-mg samples of $CaCO_3$ were put in 125-ml erlenmeyer flasks and equilibrated with 20 ml of NH_4OAc; two other samples were equilibrated with 20 ml of HCl. After 1 hour, the samples were filtered, using additional 80 ml of NH_4OAc and HCl, respectively. The extracts were handled following the same procedure described for the sets of samples incubated for 5 W-D cycles. Parallel blank samples were run for both the NH_4OAc and the HCl extracts.

3.2.3.6 Recovery of Ca, Mg, and K from the standard solutions

Using a standard solution (labelled A-4) supplied by the Analytical Service Laboratory, several solutions were prepared to cover roughly the ranges of exchangeable Ca, Mg, and K in the (check) soils under study. The composition of this standard solution was: Ca: 60, Mg: 26.6, and K: 78.6 γ/ml. This composition was based on analyses against the standard solutions used by that time in the Analytical Service Laboratory.

Eighteen ml of the solution A-4 were diluted to 450 ml with distilled water and 50- and 150-ml aliquots were transferred, in duplicate, to 250-ml erlenmeyer flasks. After partial evaporation to dryness, the flasks received

100 ml of N NH_4OAc, pH 7, and were then handled as the NH_4OAc extracts of the sets of samples incubated for 5 W-D cycles. Parallel blanks were run with the samples.

As the recovery of Ca, Mg, and K was not as expected in the samples prepared with the solution A-4, a new standard solution (labelled S-9) was obtained from the Analytical Service Laboratory. The composition of this standard solution was: Ca: 60, Mg : 20, and K : 80 γ/ml. Twenty-five ml of the solution S-9 was diluted to 500 ml, with distilled water, and 40- and 120-ml aliquots were transferred, in duplicate, to 250-ml erlenmeyer flasks. Then, 100 ml of N NH_4OAc were added and the samples were handled as in the experiment above. About two weeks later, a new portion of solution S-9 was obtained although from a different stock bottle. The same procedure just described was followed and then both sets of samples (from solutions S-9) were sent to the Analytical Service Laboratory, where they were analyzed on the same date.

As significant differences in the recoveries of Ca, Mg, and K were still present, 3 weeks later a new portion of standard solution S-9 was obtained from the Analytical Service Laboratory. Fifty ml of this solution were diluted to 500 ml with distilled water. Two sets of 20- and 60-ml aliquots were then transferred to 250-ml erlenmeyer flasks, in duplicate, and 100 ml of N NH_4OAc were added. The solutions were then handled as in the previous case, with two modifications: a) after evaporation to dryness of the H_2O_2: H_2O, the flasks received 10 ml of HCl: H_2O (1:4) added rinsing the container walls. b) 1 set of solutions

received 10 ml of distilled water, again rinsing the walls, immediately after the addition of the HCl: H_2O (1:4). When analyzed in the Analytical Service Laboratory, these 2 sets of samples were diluted to 10 ml using only a N HCl solution, without La, as usual, because the stand solution S-9 already contained La. As in previous cases, parallel blank samples were also run. (Note: The standard solution A-4 was in 2N HNO_3, with no La). The results are presented in Appendix Table 20.

3.2.4 Additional incubation experiment

In order to find out if the soils under study could fix significant amounts of K or Mg, especially within the ranges that these two elements are likely to be applied under practical conditions, a new and smaller incubation experiment was conducted using only 3 soils: MR-1, Cl-18, and MR-15. The soils were incubated for 2 W-D cycles, for a total of 52 days. The experiment was conducted as a CRD, with 2 replications, and had 6 treatments, described in Table 5.

Table 5. Treatments in the additional incubation experiment

No	Soil pretreatment	W-D cycles
1	check soil	always dry (not incubated)
2	check soil	2
3	soil + 0.25 meq of K/100 g	2
4	soil + 0.50 meq of K/100 g	2
5	soil + 1 meq of Mg/100 g	2
6	soil + 2 meq of Mg/100 g	2

This incubation was carried out in 125-ml erlenmeyer flasks using 10-g soil samples. Appropriate blank samples were also run at both levels of Mg and K.

The source of K was KCl (Mallinckrodt brand) analytical grade. The KCl was put in the oven at 110°C for 24 hours. After cooling in the dessicator, 0.9320 g of KCl were diluted to 1 liter. A 500-ml aliquot of this solution was diluted to 1 liter.

The source of Mg was $MgSO_4 \cdot 7H_2O$ (B & A, reagent in crystals, ACS code 1924), with a certified minimum content of 99.5% of $MgSO_4.7H_2O$. From the reagent, 6.1626 g were weighed and dissolved to 1 liter. A 500-ml aliquot of this solution was diluted to 1 liter.

The K and Mg levels were applied by adding 4.0 ml of the prepared solutions to the corresponding 10-g soil samples and blanks. In treatment 1 the soils received 4.0 ml of distilled water. After 26 days all the samples received 3 ml of distilled water. The flasks were kept covered with 2 layers of cheese cloth. After 52 days of total incubation period, the exchangeable Ca, Mg, and K were determined by extraction with N NH_4OAc, following the procedure described before (under 3.2.1.)

Immediately after the NH_4OAc extraction, the erlenmeyer flasks used in the incubation and the buchner funnels used in the filtration were rinsed with 100 ml of 10^{-3}M HCl. The HCl was then analyzed for Ca, Mg, and K.

4 RESULTS AND DISCUSSION

4.1 Statistical Considerations

In the planning and course of the incubation experiments and also in other analyses carried out for this investigation one factor was overlooked: the possibility of significant differences between analyses done on different dates. This effect will be designated hereafter as "time effect" and it reflects or involves all changes or differences that might occur when the same soil sample or solution is analyzed on different dates : operator variability, systematic errors in measurement or sampling, differences in standard solutions or in the setting of the equipment, etc. This time effect is not to be confused with the effect of one or more factors operating in time and affecting the samples themselves between analysis, i.e. the effect of wetting and drying cycles (incubation) is not included in the time effect. However, spontaneous changes (if any) occurring in solutions kept in glass or plastic containers would be included in that time effect.

As the experiments went on, the importance of this time effect started to become evident. However, due to the size of the experiments, especially in the case of the main incubation experiment it was not feasible to make corrections in order to eliminate such time effect. To evaluate the magnitude of the time effect several kinds of samples were analyzed on different occasions.

Details about the estimation of the time effect in the analyses of total K, Mg, and Fe, as well as in other sets of analyses related with the main incubation experiment are presented in Appendix Tables 17, 18, and 19.

The recovery of Ca, Mg, and K from the standard solutions is presented in Appendix Table 20. These analyses also indicated the presence of the time effect.

Table 6-11 summarizes the estimates of the among times and within times errors (variances) calculated with the different sets of data and also includes the within times error in the main incubation experiment. It does not include the errors in the analyses of total elements.

By looking at Table 6-11 it is clear that the variation among times was consistently and statistically significantly higher than the variation within times. It failed to be statistically significant only in the case of K in the NH_4OAc extracts and this can be attributed to the rather high within times variation observed in this set of data.

The best available estimate of the within times error comes from the main incubation experiment. The best available estimate of the among times error comes from the NH_4OAc extracts (Appendix Table 18) because even though it has few degrees of freedom, it may be assumed to include the same types of errors and variability affecting the results of the incubation experiment (from the weighing of the soil samples up to the final analytical determination). The F ratios of the corresponding mean squares are significant at $a = 0.1\%$ for Ca, Mg, and K.

Table 6-11 Variation within times (between duplicates) and among times of analysis in several sets of data (ppm)

Set of data	Cation	among times			within times			$F = \frac{S_1^2}{S_2^2}$	$F_{.95}$
		S_1^2	d.f.	S_1	S_2^2	d.f.	S_2		
HCl extracts (see Appendix Table 19)	Ca	1.253	6	1.119	0.341	6	0.584		
	Mg	0.199	6	0.446	0.021	6	0.145		
	K	1.305	6	1.142	0.043	6	0.207		
NH_4OAc extracts (see Appendix Table 18)	Ca	3.336	10	1.826	0.535	8	0.731	6.24**	3.35
	Mg	0.388	10	0.623	0.061 a)	7	0.247	6.36*	3.64
	K	3.176	10	1.782	1.536	8	1.239	2.07	3.35
Main incubation experiment	Ca	----			0.460	97	0.678		
	Mg	----			0.036	144	0.190		
	K	----			0.423	143	0.650		

*,** : significant at the 5% and 1% level of significance, respectively.
a) two observations (4.9 and 7.9) were deleted for this calculations (due to the abnormally high variation).

Due to the significantly higher error associated with times of analysis as compared with the error associated with duplicates (usual experimental error), the true experimental error in the main incubation experiment is higher than the within times error. It can be said that the pooled experimental error in the incubation experiment is at least 0.7 ppm for Ca, 0.2 ppm for Mg, and 0.7 ppm for K. As an approximation, the pooled true experimental error in the incubation experiment will be considered to be 1.5 ppm for Ca, 0.4 ppm for Mg, and 1.5 ppm for K.

However, in relation to the main incubation experiment, it should be realized that a proper statistical analysis to evaluate the effect of wetting and drying cycles alone cannot be done because this effect is completely confounded with the time effect.

Another factor to take into account in relation to the statistical analyses that follow refers to the populations from which the data arise. The assumption of normality will always be made. Besides, the soil samples kept in jars in the laboratory (ground and well mixed) will be considered as the original populations from which the data arise and therefore any statistical inference would apply strictly only to the samples in the jars, and not to the soils in the field. This is due to the fact that in order to make inferences about soils in the field it would be required to have at least 2 separate samples of each soil and not to have just duplicate samples from the same jar (soil sample) when the determinations are performed.

4.2 Exchangeable Ca, Mg, and K

The levels of exchangeable Ca, Mg, and K are presented in Table 12 (means of duplicates) together with the total contents of the same elements. The results for both duplicates are shown in Appendix Tables 14, 15, and 16. The results (means of duplicates) are also plotted against several variables in Figures 1 and 4 (Ca), 2 and 5 (Mg), and 3 and 6 (K).

The levels of exchangeable basic cations are very low and are below the levels considered suitable for any but limited crop production. The mean contents of Ca, Mg, and K and the ranges (in parenthesis) were. 16.6 (7.4 - 31), 5.9 (3.3 - 9.7), and 27.3 (15.8-42.1) ppm, respectively, for the topsoils, and 5.6 (2.2-9.0), 3.0 (1.3-3.8), and 13.7 (6.4-18.8) ppm, respectively, for the subsoils. (Note: for short, the top soil sample of a given location will be referred to as topsoil, the next sample as subsoil and all other samples as deep subsoils). The sample MR-8-9 was not considered for the above figures because it shows rather high values of Ca, Mg, and K that do not reflect a real situation in the field. As noted by Guerrero (1971) this sample had some contamination. The largest contents of all three elements occurred in the topsoil from the Piedmont (C1-18) whereas the lowest in both topsoils and subsoils were found in samples from El Pinal pit, which correspond to the sandiest of all samples.

The contents of the 3 elements decreased with depth in the first 40-80 cm, with a sharp decrease going from the

TABLE 12. Total contents of Ca, Mg, K, and Fe (by digestion with $HF-H_2SO_4$), and exchangeable Ca, Mg, and K. (means of duplicate samples).

Locality	sample	depth (cm)	total content				exchangeable			exchangeable/total		
			%	ppm			ppm			%		
			Fe	Ca	Mg	K	Ca	Mg	K	Ca	Mg	K
Carimagua	MR-1	0-15	2.66	<100	850	2000	12.0	5.2	31.4	>12.0(16)[a]	0.61	1.57
	MR-7	33-50	3.04	<100	860	2200	8.3	3.2	9.5	> 8.3(28)	0.37	0.43
La Libertad	C1-18	0-20	2.02	<100	400	674	31.0	9.7	42.1	>31.0(53)	2.42	6.25
	C1-19	20-40	2.30	<100	460	732	3.4	3.1	18.8	> 3.4(11)	0.67	2.57
El Piñal	MR-15	0-15	1.64	<100	940	4920	15.8	5.4	29.0	>15.8(26)	0.57	0.59
El Viento	C4-1-2	0-19	3.10	<100	604	1370	13.3	5.4	26.0	>13.3	0.79	1.90
(pit)	C4-3	19-31	3.33	<100	667	1470	3.8	[illegible].4	15.0	> 3.8	0.51	1.02
El Piñal	C2-6	0-16	1.52	<100	484	1110	7.4	3.3	15.8	> 7.4	0.68	1.42
(pit)	C2-2	18-30	1.51	<100	470	1230	2.2	1.3	6.4	> 2.2	0.28	0.52
	C2-3	30-80	1.76	<100	462	1360	1.2	0.9	5.2	> 1.2	0.19	0.38
Matapalito	C3-1	0-16	1.98	<100	655	1600	19.8	6.2	19.3	>19.8	0.95	1.21
(pit)	C3-2	16-42	2.14	<100	730	1600	7.0	3.8	14.4	> 7.0	0.52	0.90
	C3-3	42-72	2.04	<100	540	1610	5.0	1.8	9.8	> 5.0	0.33	0.61
Carimagua	MR-8-9	0-20	2.53	136	820	1600	32.9	15.9	41.5	24.2	1.93	2.46
(pit)	MR-10	20-38	3.04	<100	850	1430	9.0	3.5	18.0	> 9.0	0.41	1.26
	MR-11	38-94	3.14	<100	830	1650	5.4	2.1	12.6	> 5.4	0.25	0.76
	MR-12	94-114	3.25	<100	865	2160	6.0	2.8	14.8	> 6.0	0.32	0.69
	MR-13	114-137	3.40	<100	800	2740	3.8	2.2	15.4	> 3.8	0.28	0.56
	MR-14	150	2.97	<100	815	2230	6.4	2.7	20.0	> 6.4	0.33	0.90
	mean		2.49	<100	694	1778	10.2	4.3	18.7	> 9.7	0.65	1.4

200 ppm Ca = 1 meq Ca/100 g; 120 ppm Mg = 1 meq Mg/100 g; 390 ppm K = 1 meq K/100 g
a : data in parenthesis are based on digestions with HF-HCl

topsoil to the subsoil, which could be related to the higher CEC expected in the topsoils due to the higher organic matter content. The fact that the decrease is consistently sharper in the case of Ca suggests that perhaps comparatively more Ca is associated with the organic matter than are Mg and K.

In relation to the Carimagua pit, it can be seen that the levels of all three elements do not show a definite trend to decrease or increase from 38 to 150 cm.

To measure the degree of correlation between the levels of exchangeable basic cations several regression lines were fitted to the means (excluding the sample MR-8-9). The regression of exchangeable Mg (ppm) on exchangeable Ca (ppm) give the equation $Y = 1.29 + 0.27 X$, with a standard error of estimate $s = 0.57$ and a correlation coefficient $r = 0.965$. The regression of exchangeable K (ppm) on exchangeable Ca (ppm) gave the equation $Y = 8.94 + 1.04 X$, with a standard error of estimate $s = 5.29$ and a correlation coefficient $r = 0.835$. The regression of exchangeable Mg (ppm) on exchangeable K (ppm) gave $Y = 0.04 + 0.20 X$, $s = 0.97$ and $r = 0.895$. It is clear that the closest association is that between the exchangeable Ca and Mg.

4.3 Total Ca, Mg, K, and Fe

4.3.1 Comparison of the HF-HCl and HF-H_2SO_4 procedures

The total contents of Ca, Mg, K, and Fe in the five soils analyzed by both digestion procedures are presented in Table 13.

TABLE 13. Comparison of two methods for the determination of total Ca, Mg, K, and Fe in five soils

Soil Sample	Ca (ppm)		Mg (ppm)		K (%)		Fe (%)	
	A[a]	B[b]	A	B	A	B	A	B
MR-1	60	<100	750	860	0.220	0.200	2.34	2.61
	88	<100	750	840	0.220	0.200	2.34	2.70
	74	<100	750	850	0.220	0.200	2.34	2.66
MR-7	30	<100	780	860	0.230	0.220	2.60	3.04
	30	<100	780	860	0.230	0.220	2.60	3.04
	30	<100	780	860	0.230	0.220	2.60	3.04
C1-18	30	<100	360	400	0.070	0.067	1.89	2.04
	88	<100	360	400	0.080	0.068	1.89	2.00
	59	<100	360	400	0.075	0.068	1.89	2.02
C1-19	30	<100	380	460	0.080	0.072	2.12	2.30
	30	<100	380	460	0.080	0.074	2.08	2.30
	30	<100	380	460	0.080	0.073	2.10	2.30
MR-15	60	<100	840	900	0.470	0.484	1.50	1.64
	60	<100	840	980	0.460	0.500	1.46	1.64
	60	<100	840	940	0.465	0.492	1.48	1.64

a. digestion with HF-HCl (analysis done on 3/11/73
b. digestion with HF-H_2SO_4 (analysis done on 2/12/73)

4.3.1.1 Statistical analysis

One alternative would be to analyze the experiment using the model (1)

$$X_{ijk} = U + R_i + S_j + (RS)_{ij} + E_{ijk} \quad (1)$$

Where R_i is the method effect and S_j is the soil effect. However, the analyses were not done at the same time but with one month of difference between both methods. Therefore, it is likely that a "time effect" could be present (see Appendix Table 17). If so, the method effect and the time effect are completely confounded.

If the presence of the time effect had been known initially, two approaches could or should have been followed in this context " a) to carry out parallel analyses of control (master) samples, b) to perform analyses by both methods at the same time and in 2 or more occasions in order to evaluate the time effect. In the latter case, the model to be used would be

$$X_{ijkl} = U + R_i + S_j + T_k + (RS)_{ij} + (RT)_{ik} + (ST)_{jk} + (RST)_{ijk} + E_{ijkl}$$

where R_i and S_j have the same meaning as before and T_k is the time effect. In the model it is assumed that the time effect is additive, i.e. it is going to add the <u>same</u> quantity to each soil or to each method. It is possible however, that the time effect could be multiplicative rather than additive.

In the second model, if it were necessary to cut down the number of analyses, it could be assumed that the following interactions are absent : method x time, soil x time,

and the triple interaction. Then, it would not be necessary to replicate and the pooled interactions could be used as an estimate of the experimental error.

If the time effect is assumed or known to be present but the experimental setting is according to model (1), then R_i comprises the method and the time effects and their interaction. The interactions soil x time and soil x time x methods are also somehow confounded under R_i and S_j. Assuming that these 3 interactions are absent, the complete confounding of the method and time effects still occurs. Keeping in mind the last restriction, an analysis of variance was performed (according to model (1)) with the data in Table 13. The analysis showed a highly significant method-and-time effect for Mg and Fe (at a = 1%) but not significant for K (at a = 5%). The differences among soils were highly significant (a = 1%) for all 3 elements, as expected. The interaction method x soil was not significant (a = 5%) for Mg, but it was highly significant (a = 1%) for K and Fe.

4.3.1.2 Comments.

Looking at the ratios method A/method B it was found that the means were 0.88 for Mg, 1.07 for K, and 0.90 for Fe. These mean ratios are larger than those reported in App. Table 17 when the same solutions were analyzed on two dates. However, it is impossible to tell whether the differences are due a method effect, to a time effect or to a mixture of both. It is interesting to note that the ratios are not consistently above or below unity for all 3 elements. This suggests that a systematic error when weighing the

soil samples or when taking aliquots for analysis was not the main factor involved in the differences observed.

A direct implication of the foregoing discussion is that the analyses of total elements reported in this work should be regarded not as absolute, true values, but as approximations. If we consider that the means of both methods of analysis (Table 13) and the means of analyses performed by the same method but on different dates (Appendix Table 17) are good estimates of the true values, then we may consider that the values reported here for total Ca, Mg, K, and Fe (and based on duplicate analysis by a single method and on a single date) give the true values with a relative error of 1 up to 10% and with a mean relative error of 5%.

It should be noted that the total Ca contents by the $HF-H_2SO_4$ method were reported as <100 ppm in most cases and exact values were not given because the readings in the spectrophotometer were made with a different sensitivity setting as compared to the readings for the HF-HCl digestion. Besides, at such a low concentrations, the accuracy in the determinations was low and so exact readings were not justified (this applies to the Ca analyses by both digestion procedures).

The major reason for comparing both digestion procedures was to examine the hypothesis that the $HF-H_2SO_4$ method underestimated Ca. The results indicate that this is not the case; the HF-HCl did not give higher Ca values than the $HF-H_2SO_4$ method.

4.3.2 Analysis of the results with the $HF-H_2SO_4$ digestion

The results are presented in Table 12. The total contents of Ca, Mg, K, and Fe are low or very low. In the case of Ca, the results clearly indicate that the soils are almost completely depleted of this element. There are however, some reserves of Mg and especially K. Considering the nature of the soils, the Fe content is also rather low. The sample MR-15 showed the highest contents of Mg and K, with a K level that is much higher than that in the other soils. This could be related to the dust blown up from the Meta River beaches during the dry season. However, this influence was not shown in samples from the El Piñal pit, which were taken in the same farm and less than 3 Km apart from sample MR-15.

Comparing topsoils and their respective subsoils it was found that the average Mg contents were 648 and 672 ppm, with ranges of 400-820 and 460-850 ppm, respectively. For K the means were 1407 ppm fcr the topsoils and 1444 ppm for the subsoils, with ranges of 674-2000 and 732-2200 ppm, respectively. In the case of Fe, the means were 2.30 and 2.56%, and the ranges 1.52-3.10 and 1.51-3.33%, for topsoils and subsoils, respectively.

The Mg content tended to stay about the same with depth whereas K and specially Fe tended to increase with depth. Looking at Table 13, it seems that Ca tends to decrease with depth. It is possible that the decrease of total Ca with depth could be related to the corresponding decrease of organic matter (a soil with 3% of organic

matter and 0.2% of Ca in the organic matter would have 60 ppm of Ca accounted for in this way). The reserves of Mg and K are mainly in the mineral fraction.

Table 12 also shows the percentages of total elements exchangeable with N NH_4OAc, pH 7. A high proportion of the total Ca is exchangeable with N NH_4OAc. Taking the figures of Table 13, the percentages are 16, 28, 53, 11, and 26% for soils MR-1, MR-7, Cl-18, Cl-19, and MR-15, respectively. The proportions of total Mg and K exchangeable with N NH_4OAc are greater in the topsoils than in the subsoils (1.23 vs o.43% for Mg and 2.47 vs 1.12% for K, on the average).

Scatter diagrams (not included) showed no correlation between total Mg and total Fe, or between total K and total Fe, but a good correlation seemed to exist between total Mg and total K (not including sample MR-15). A regression of total K on total Mg (means) gave a correlation coefficient of r = 0.95** for 6 topsoils, and r = 0.81 for the corresponding subsoils. A test of the equality of the slopes showed them to be equal and a single regression line was then fitted to the 12 points giving the equation Y = -121.18 + 2.34 X, with a standard error S = 225 and a correlation coefficient r = 0.88**, where Y = predicted total K and X = total Mg (both in ppm). Note that neither sample MR-15, nor deep subsoils were considered in the above regressions because they did not follow the same trend of the other samples.

4.3.3 Analysis of the silt and clay fractions

The total contents of Ca, Mg, K, and Fe in the silt and clay fractions analyzed and in the whole soils from which

the silt and clay were derived are shown in Tables 14 and 15. It was necessary to make several assumptions to express the elemental contents in the silt and clay fractions on a whole soil basis (Table 15). Firstly, using data of Guerrero, (1971) a curve of the distribution of organic carbon at several depths was drawn. From it, interpolations were made to find the organic carbon content in the soil samples (MR-8-9 to MR-14). The organic matter content was calculated multiplying the percentage of organic carbon by a factor of 2. Then, the percentages of sand, silt, and clay, and of iron-and aluminum oxides reported by Weaver were corrected (he did not include the percentages of organic matter in the calculations). These corrected values are shown in Appendix Table 13. It was assumed that the clay and silt contents in sample MR-8 were as those of MR-9 and then a weighted average was found for sample MR-8-9 (0-20 cm).

Excepting the sample MR-11, the other 3 samples analyzed had a content of total Ca less than 100 ppm. The form in which the results were reported did not permit calculation of which portions of the total Ca were present in the silt and clay fractions. In the sample MR-11 the total Ca in the silt fraction was 140 ppm; this soil had 51% of silt, and the whole soil contained <100 ppm Ca; then, at least 71% of the total Ca of this sample was present in the silt fraction. This was not surprising, however, because the Ca content is very low anyhow and, besides, according to Guerrero's results (see Appendix Table 8), the small amounts or traces of feldspars or vermiculite present could account

TABLE 14. Total content of Ca, Mg, K, and Fe in the clay and silt fractions of soil samples of the Carimagua pit.

Sample	Depth cm	Clay[a] <2μ %	Silt[a] 2-50μ %	Ca Clay	Ca Silt	Mg Clay	Mg Silt	K Clay	K Silt	Fe Clay	Fe Silt	Element in clay / Element in silt Mg	Element in clay / Element in silt K
				ppm						%			
MR-9	8-20	28.5	52.5	<100	<100	1865	336	4900	1360	1.39	0.13		
				<100	<100	1865	312	4900	1140	1.49	0.12		
				<100	<100	1865	324	4900	1250	1.44	0.12	5.76	3.92
MR-11	38-94	31.6	50.9	<100	140	1975	252	4900	1040	1.39	0.11		
				<100	140	1975	252	4900	1140	1.49	0.11		
				<100	140	1975	252	4900	1090	1.44	0.11	7.84	4.50
MR-12	94-114	33.4	50.6	<100	<100	1865	232	6000	1320	1.69	0.10		
				<100	<100	1865	208	6250	1180	1.69	0.10		
				<100	<100	1865	220	6125	1250	1.69	0.10	8.48	4.90
MR-13	114-137	39.7	44.2	<100	<100	1450	180	6250	760	1.39	0.10		
				<100	<100	1450	172	6450	760	1.39	0.09		
				<100	<100	1450	176	6350	760	1.39	0.10	8.24	8.36

a. Adapted from Weaver (1972)

for it. For instance, if the silt fraction had just 0.1% of pure anorthite (with 14% of Ca), the silt would have 140 ppm of Ca from this source.

These results are not all comparable with those reported by FAO (1965) for the clays from the oxic horizons of 2 soils of the Llanos:

series	depth cm	Ca	K	Fe
		----------	%----------	
Horizontes	35-66	0.26	0.20	5.8
Sáliva	26-80	0.09	0.20	5.0

As can be seen by comparison with the analyses in Table 14, the Ca content in the clay fractions used by FAO are at least one order of magnitude greater than those found in this study.

Analysis of the data in Table 14 shows that the percentages of Mg in the silt fraction in the Carimagua pit samples decreased with depth. The percentages of Mg in the clay fraction did not show the same consistent trend but was also lower in the 114-137 cm sample The percentages of K in the silt fraction showed some fluctuation in the first 3 samples and the smallest occurred in the 114-137 cm sample. The trend of K in the clay fraction was completely different: its percentage increased consistently with depth. The percentage of Fe stayed about the same with depth in both the silt and the clay fractions.

As expected, most of the total K and Mg are found in

the clay fraction. The ratio of the percentages of total element in clay to total element in silt ranges from 5.76 to 8.24 for Mg, from 3.92 to 8.36 for K, and from 12.0 to 16.9 for Fe. The ratio increased consistently with depth for Mg and K and tended to increase with depth in the case of Fe. The clay fraction is comparatively richer in Mg than in K with respect to the silt fraction, although, in absolute terms, the clay fraction contained from 2.62 to 4.20 times more K than Mg. Almost all the Fe is found as free iron oxides extractable with CDB.

The changes with depth in the total content of a given element are, nevertheless, difficult to analyze due to the confounding effect of losses and gains in other elements. The gains and losses of the various elements can be better interpreted when an element that can be regarded as stable or immobile is taken as reference. Usually Ti or Zr is used for this purpose. (Sivarajasingham, 1961).

The increase with depth of the ratio of total element in clay to total element in silt, for both K and Mg could have some significance in relation to the pedogenic processes occuring in the soil, but at this moment its meaning is not clear. In general one would expect an increase in the Mg and K content with depth because of the more active weathering and leaching in the topsoil. The lower contents of Mg and K in the silt fraction of the 114-137 cm sample do not agree with this and two factors could be suggested to explain it.

a) the influence of wind-blown materials during the

dry season. Guerrero (1971) did not find evidence that the soils are mineralogically influenced by wind-blown material from the Meta River flood plain. However, given the low contents of Mg and K in these soils, it takes only a small amount of silt-size dust of less weathered materials to account for the differences found. Biological activity by earthworms, termites and ants could explain the incorporation of the dust below the soil surface.

b) the water table in this site is at about 2 m in the dry season. The 114-137 cm soil sample would then be wetter for a longer time during the year than the soil above it. This would favor a more active weathering in that portion of the soil and it would explain the lower contents of Mg in the silt and clay fractions and of K in the silt fraction. However, the increase with depth of K in the clay fraction remains unexplained.

It may be speculated that the soils of the Llanos have received or receive aeolian additions of relatively unweathered minerals brought by the trade winds and originated from the Sahara Desert. Syers, et al (1972) found micaceous minerals, quartz, chlorite, feldspars, kaolinite, vermiculite, montmorrillonite and talc in aerosolic dust at Barbados and which had originated from North Africa ("Sahara Desert - Caribbean dust circulation system"). The authors are referring to the trade winds as an air circulation system which may carry dust. These winds, coming from the Sahara Desert, cover not only the Caribbean but also the Llanos of Colombia and Venezuela.

The results shown in Table 14 are shown again in Table 15 but now expressed on a whole soil basis, i.e. the total contents of Mg, K, and Fe in the soil samples are partitioned into the portions present in the clay and silt fractions. The trends discussed above in relation to the changes occurring with depth are maintained in general, although some variations occur as a consequence of the increase in percentage of clay and the decrease of the percentage of silt with depth (see Table 14).

Table 15 shows that the sum of element in clay plus element in silt is not equal to the total element content in a given sample. The sums were lower in the case of Mg, higher for K, and higher for Fe. The ratio of Mg in clay + silt to Mg in soil was between 0.82 and 0.90. For K, the ratio was between 1.04 and 1.27, and between 1.29 and 1.38 in the case of Fe. Two factors could account for this difference:

a) the "time effect" mentioned before: all the analyses shown in Table 14 were performed at the same time, but the analyses of the (whole) soil samples were done on a different date. The fact that the ratio is not consistently above or below unity for all 3 elements in a given sample is consistent with the time effect influence, and so is the fact that the ratios are closer to unity in the case of Mg because the time effect variation was observed to be smaller for Mg than for K.

b) The fact that the percentages of silt and clay were not directly determined for the present study but

TABLE 15. Total content of Mg, K, and Fe, expressed on whole soil basis, in the clay and silt fractions.

Element		Sample → Depth(cm)	MR-8-9 0-20	MR-9 8-20	MR-11 38-94	MR-12 94-114	MR-13 114-137
Mg (ppm)		Soil	820	n.d.	830	865	800
		Clay	526	532	624	623	576
		Silt	168	170	128	111	78
	Mg in clay/Mg in silt		3.13	3.12	4.88	5.61	7.38
	Mg in clay + Mg in silt		694	702	752	734	654
	(Mg in clay + Mg in silt) / Mg in soil		0.85		0.90	0.85	0.82
K (ppm)		Soil	1690	n.d.	1650	2160	2740
		Clay	1382	1396	1548	2046	2521
		Silt	649	656	555	632	336
	K in clay/K in silt		2.13	2.12	2.79	3.23	7.50
	K in clay + K in silt		2031	2052	2103	2678	2857
	(K in clay + K in silt) / K in soil		1.20		1.27	1.23	1.04
Fe (%)		Soil	2.53	n.d.	3.14	3.25	3.40
		Clay (1)	0.41	0.41	0.46	0.56	0.55
		Silt (2)	0.06	0.06	0.06	0.05	0.04
	Tamm extractable (3)		0.21	0.20	n.d.	n.d.	0.12
	CBD extractable (4)		2.59	2.52	3.22	3.36	3.57
	(1) + (2) + (3) + (4)		3.27	3.19	4.07	4.35	4.70
	((1) + (2) + (3) + (4)) / Fe in soil		1.29		1.30	1.34	1.38

Tamm extractable and CBD extractable Fe adapted from Weaver (1972)

taken from another source, and the corrections that were introduced in relation to the organic matter content can explain also part of the differences found. In the case of Fe the ratios are higher than for Mg and K, because it was necessary to take into account too, from another source, the Tamm and CBD extractable Fe.

4.4 Incubation Experiment

To analyze the results of the several extractions made with both 10^{-3}M HCl and N NH_4OAc, the "time effect" mentioned earlier should be considered. Strictly speaking the time effect is confounded with any potential difference between two sets of extractions analyzed on different dates. As discussed earlier, the experimental error in the incubation experiment is at least 0.7, 0.2, and 0.7 ppm for Ca, Mg, and K, respectively. Considering the estimates of the "among times" error, and in order to make the following discussion more meaningful without introducing a personal bias, it seems reasonable to approximate the true experimental error in all these sets of analyses as being 1.5, 0.4, and 1.5 ppm for Ca, Mg, and K, respectively. As can be seen in Appendix Tables 14, 15, and 16, the differences between 2 sets of analyses are, in most cases, a few ppm or <1 ppm. By using the above estimates of the true experimental error and the least significant difference (LSD) concept, an <u>approximate</u> statistical criterion is available to compare the results of different sets of analyses. In those cases in which

the differences are a few ppm, the agronomic significance of such differences is very small. In the cases in which the differences are very pronounced, the agronomic significance will agree with the statistical significance.

Clearly, for comparisons within a given set of analyses, the 'among times' error, i.e. the time effect is irrelevant and the experimental error is 0.7 (97), 0.2 (144), and 0.7 (143) ppm for Ca, Mg, and K respectively (the figures in parenthesis are the d. f.).

As an auxiliary technique for the analysis of the results, the simple linear regression (LR) approach was used repeatedly. However, several points should be kept in mind. The LR model assumes that the independent variable X is not a random variable and that the several values of it are measured without error. In this study there is as much variation involved in the measurement of the independent variable X as in the dependent variable Y. The time effect is going to have an effect in the coefficients and it will vary with the type of time effect (systematic or random). For these reasons, no attempt will be made to carefully discuss the significance of the different intercept and regression coefficients, which, otherwise, could have very specific meanings. The main purposes of the regression lines (calculated using only the means of duplicates) was to provide an indication of the trends present, and to give an objective basis of evaluation of the differences found between sets of analyses, through the examination

of the scatter of points around the regression line.

The scatter diagrams and the regression lines, showed that the sample MR-1 on the one hand, and the samples MR-11 to MR-14 on the other hand, behaved quite differently from the others in many sets of analyses. Regarding the sample MR-1, it has already been said that this sample suffered some kind of contamination because its levels of exchangeable Ca, Mg, and K do not represent the real situation of the soil in the field. In relation to the samples MR-11 to MR-14, the cations (Ca, Mg, and K) extracted with 10^{-3}M HCl were consistently lower than the extractions with N NH_4OAc, specially in the case of K. This could be related either to the lower content of organic matter or to some other significant difference in the chemical characteristics of these samples as compared to the samples above them. For the regressions reported here, the sample MR-8-9 was deleted for all Mg regressions and in most of the regressions involving HCl extractions. The samples MR-11 to MR-14 were also excluded for those regressions related to HCl extractions (alone).

In general, no emphasis will be put on the results obtained on a given soil but to trends or similarities between groups of soils.

4.4.1 Leaching of the soils with HCl

The cations (Ca, Mg, and K) extracted with 10^{-3}M HCl (set 9122) and the results of the extractions with N NH_4OAc (set 9124) following the HCl extractions are shown in Appendix Tables 14, 15 and 16. Included in these tables

are also the results of the leaching of the samples with 10^{-3}M HCl for the incubation (set 9111). The data is plotted (means of duplicates) against the exchangeable Ca, Mg, and K in Figures 1, 2, and 3, respectively.

The purpose of the leaching with 10^{-3}M HCl was to remove part of the exchangeable bases and to increase the percentage of H saturation in the soils, because, according to the literature, this increases the release of Mg from non-exchangeable forms. In order to distinguish between an immediate solubilization of basic cations due to the acid treatment and a slow release of cations with incubation, the soils were extracted with N NH_4OAc just after the extraction with HCl. The sums of cations extracted in both cases were compared to the initially exchangeable cations.

4.4.1.1 Extraction with HCl, set 9122.

a) Ca: The HCl extracted about all the exchangeable Ca present in the soils. As can be seen in Figure 1, the points are well scattered around the regression line. The mean exchangeable Ca was 11.9 ppm whereas the mean Ca extracted with HCl was 12.0 ppm. The differences between means of duplicates are statistically within the magnitude of the experimental error. The LSD (1%) is 3.9 ppm.

b) Mg: As in the case of Ca, the HCl extracted about all the exchangeable Mg. The means were 4.2 ppm in both cases. As shown in Figure 2 (and in Appendix Table 15), the differences between individual means are small and within the LSD (1.0 ppm, at 1% level of significance).

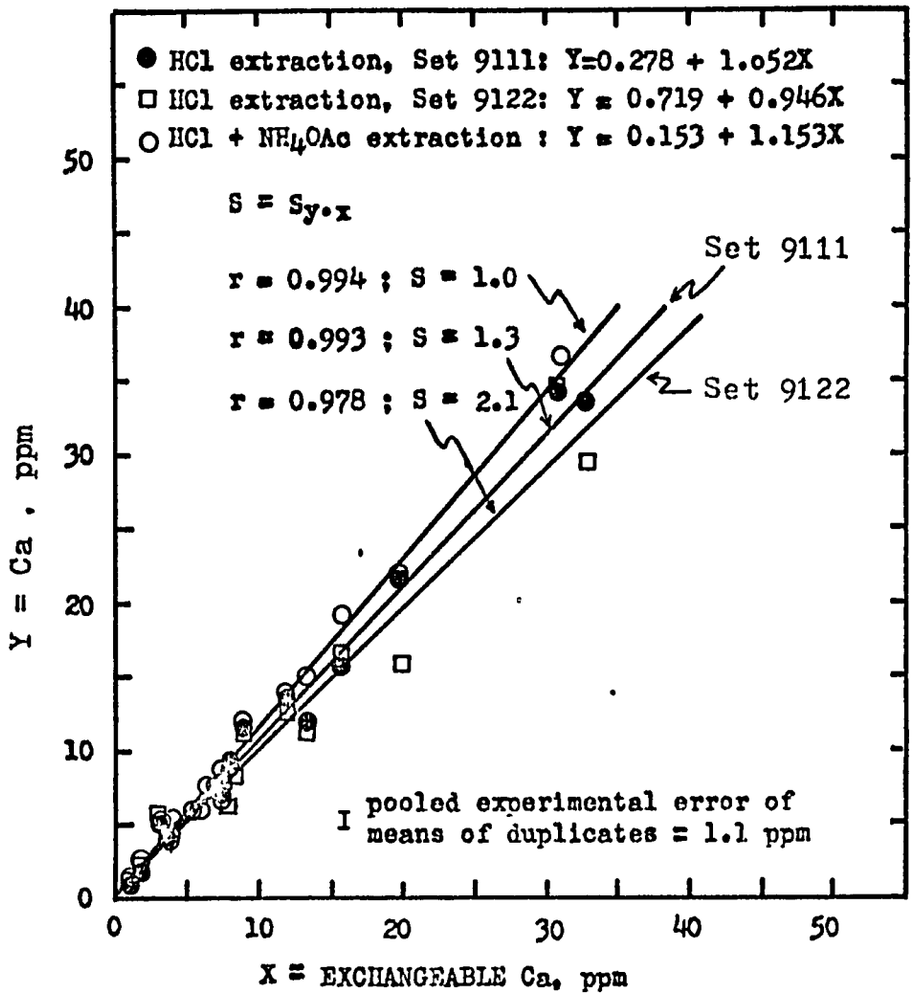

FIGURE 1. Ca EXCHANGEABLE WITH N NH_4OAc (pH 7) vs Ca EXTRACTED WITH 10^{-3} M HCl, AND vs TOTAL Ca EXTRACTED WITH 10^{-3} M HCl FOLLOWED BY EXTRACTION WITH N NH_4OAc (MEANS OF DUPLICATES).

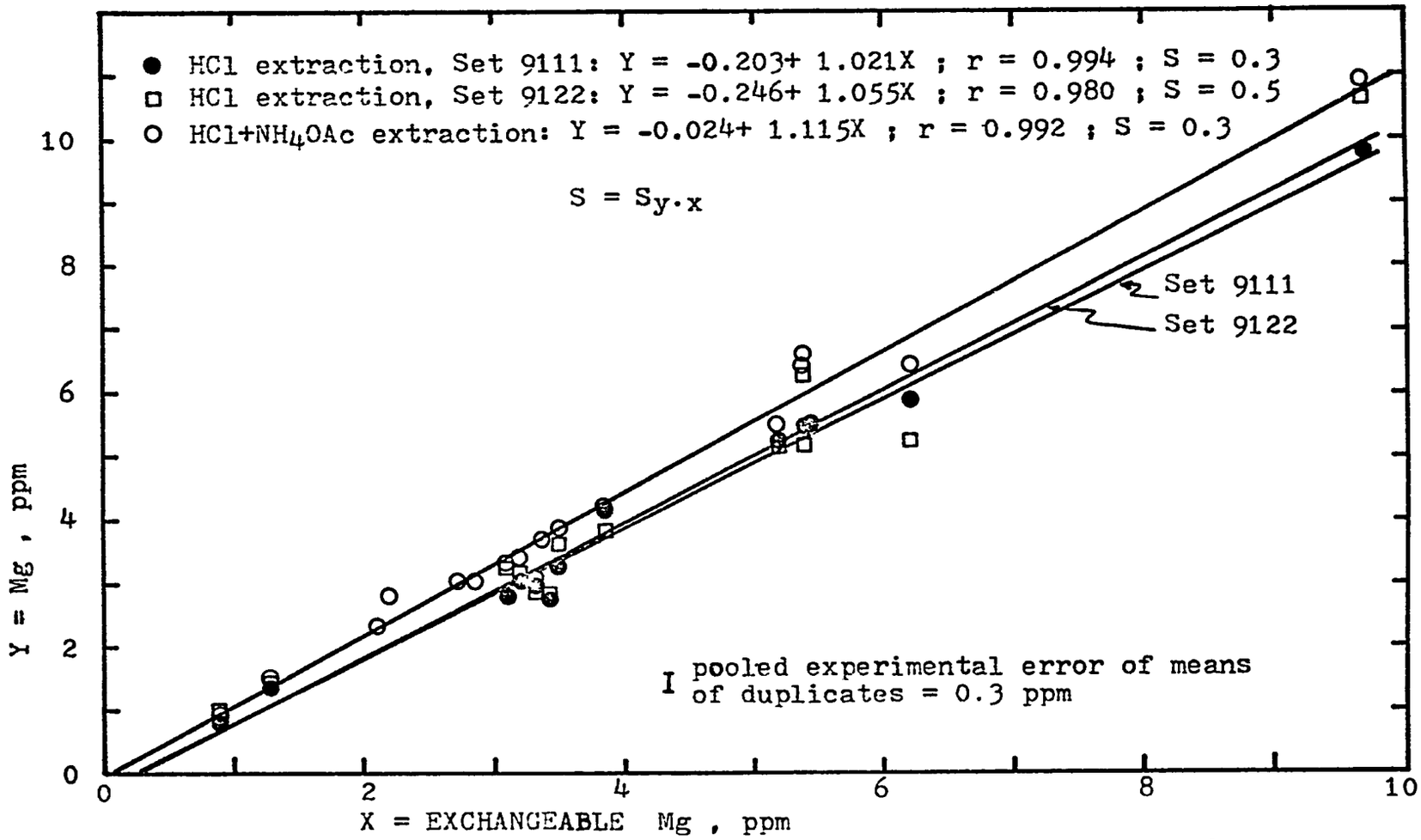

FIGURE 2. Mg EXCHANGEABLE WITH N NH_4OAc (pH 7) vs Mg EXTRACTED WITH 10^{-3} M HCl, AND vs TOTAL Mg EXTRACTED WITH 10^{-3} M HCl FOLLOWED BY EXTRACTION WITH N NH_4OAc (MEANS OF DUPLICATES).

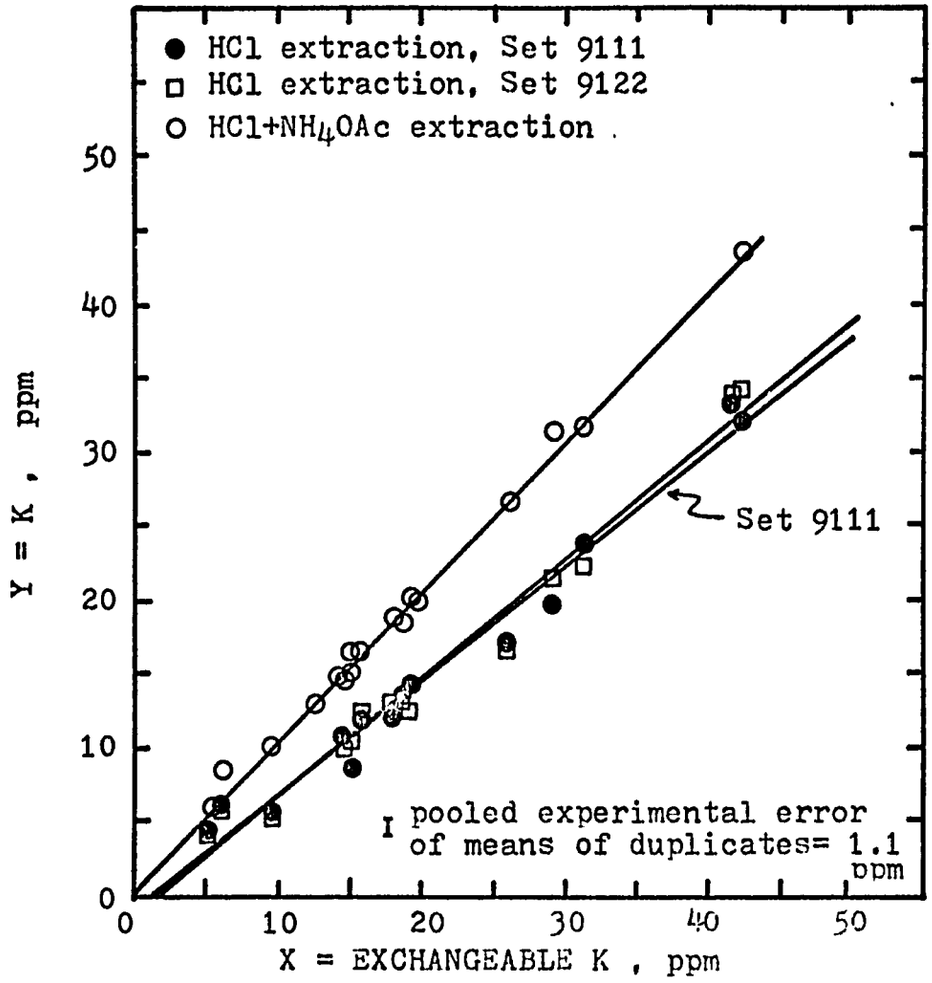

FIGURE 3. K EXCHANGEABLE WITH N NH_4OAc (pH 7) vs K EXTRACTED WITH 10^{-3} M HCl, AND vs TOTAL K EXTRACTED WITH 10^{-3} M HCl FOLLOWED BY EXTRACTION WITH N NH_4OAc (MEANS OF DUPLICATES).

Set 9111: $Y = -1.033 + 0.780X$; $r = 0.989$; $S_{y \cdot x} = 1.4$

Set 9122: $Y = -1.633 + 0.815X$; $r = 0.988$; $S_{y \cdot x} = 1.6$

HCl + NH_4OAc extraction:

$Y = 0.363 + 1.020X$; $r = 0.997$; $S_{y \cdot x} = 0.8$

c) K: The HCl extracted significantly and consistently smaller amounts of K than those exchangeable in the soils (Figure 3; Appendix Table 16). The mean exchangeable K was 20.9 ppm and the mean K extracted with HCl was 15.4 ppm. Given the magnitude of the differences and the almost identical results obtained in the other set of HCl extractions (set 9111), it is most unlikely that it could be explained just in terms of a time effect. The LSD (1%) is 3.4 ppm, and it is smaller than all the differences within samples, excepting the samples from the El Piñal pit. Thus, the K extracted with HCl was below the average in the samples below 38 cm in the Carimagua pit and in the sample MR-7 (33-50 cm), whereas it was well above the average and very close to the exchangeable K in the sandiest samples used in this study (those from El Piñal pit. See Appendix Table 6). It seems that the HCl extracted less K as the percentage of clay increased and/or the percentage of organic carbon decreased (see Appendix Table 5). By close comparison of different sites and of topsoils vs subsoils it seems that the main factor is the percentage of clay content.

Generally speaking, one would expect that the proportion of K extracted with another monovalent cation would be larger than those of divalent cations. Thus, the results reported here are somewhat unusual. No mechanism was found to explain it in terms of a pH effect or of a physical blocking effect. As shown in Figure 1, the K extracted with HCl plus the K extracted immediately after

with NH_4OAc was equal to the exchangeable K. Maybe the explanation resides in a stronger ability of NH_4^+ ions to replace K in certain particular sites of the mica-vermiculite and intergradient type minerals present in these soils. If this is true, the K extracted with NH_4OAc is not all equally available to plants.

The literature in relation to the ability of H and NH_4 ions to replace K is contradictory. Ekpete (1972,a) found that 6N H_2SO_4 extracted equal amounts of K as N NH_4OAc in soils of Eastern Nigeria, including 13 Oxisols. Ekpete (1972,b) also found that, in the same soils, N NH_4OAc extracted less K than 0.5 or 0.7N HCl with extraction periods of 1 hour and a ratio 1:20 (soil : solution); however, when the extraction was only for 2 minutes and with a ratio 1:3, the HCl extracted slightly less K than NH_4OAc. In a fersiallitic soil of Western Nigeria, N NH_4OAc extracted about 4 times more K than 0.5 or 0.1N HCl (Unamba-Oparah, 1972).

Rich and Black (1963) found that NH_4OAc and $MgCl_2$ removed more K from 14 acid soils than did Mg $(OAc)_2$. They suggested that K is not uniformly distributed over the exchange material but part of it is in wedge-shaped interlayer spaces of micas and 2:1 clays. Only small ions such as NH_4 or H can exchange K rapidly in such positions. The Mg Cl_2 may cause hydrolysis of Al and so increase the H ion concentration. According to their figures, NH_4OAc extracted an average of 8% more K than $MgCl_2$, although in

some soils it extracted up to 25% more K. According to Sawhney (1972), K is not replaced effectively by cations such as NH_4 which produce interlayer collapse in minerals. Tincknell and López (1962) reported that N NH_4OAc extracted much less K than N HNO_3 in 2 very poor red latosols of Venezuela; however, when 100 ppm of K were added and the soils were subjected to wetting and drying the HNO_3 extracted significantly less K than NH_4OAc. In soils of Sao Paulo, Brazil, 0.05 N HNO_3 extracts the same amount of K as NH_4OAc (De Freitas, et al, 1966).

4.4.1.2 Extraction with NH_4OAc (set 9124) after the HCl extraction

The results are shown in Appendix Tables 14, 15, and 16. The Ca and Mg extracted with NH_4OAc following the extraction with HCl were very low. The Ca ranged from 0 to 6 ppm, with an average of 1.6 ppm. The average for Mg was 0.6 ppm and the range 0-1.4 ppm. Not considered in these figures were the values obtained in sample MR-8-9. In the case of K, the mean was 6.8 ppm and the range 2.0-10.1 ppm. On the average, not considering individual cases, only the data for K have some agronomic importance.

4.4.1.3 Comparison with the exchangeable cations

For comparing the exchangeable cations with the sums of cations extracted with HCl plus cations extracted with NH_4OAc immediately afterwards, the LSD's are bigger because each comparison for a given sample now involves three means. The correlation coefficients between cation extracted with NH_4OAc after HCl and cation extracted with HCl were 0.46,

0.26, and 0.81 for Ca, Mg, and K, respectively. The LSD's (1%) were found to be 5.5, 1.4 and 6.0 ppm for Ca, Mg, and K, respectively. (For this type of comparisons, the variance of the difference is given by $S_D^2 = S^2(3+2r)/n$, where S^2 = population variance, r = correlation coefficient mentioned above, and n = 2. The values found for S_D were 2.1, 0.5, and 2.3 for Ca, Mg, and K.

The sum of Ca extracted with HCl plus Ca extracted with NH_4OAc after the HCl extraction ("HCl + NH_4OAc" -Ca, for short), was slightly higher than the exchangeable Ca in most cases (Figure 1; Appendix Table 14) but generally the difference was much smaller than the LSD (5.5 ppm). Only in the samples MR-8-9 and Cl-18 the difference is greater than the LSD.

In the case of Mg (figure 2; Appendix Table 15) the results were very similar to those obtained for Ca: the "HCl + NH_4OAc" -Mg was slightly higher than the exchangeable Mg, but only in the sample MR-8-9 the difference was significant. In the sample Cl-18 the difference was very close to the LSD = 1.4 ppm.

The differences between "HCl + NH_4OAc" -K and exchangeable K were comparatively smaller than for Ca and Mg ıd, excepting sample MR-8-9, were always much less than the LSD = 6.0 ppm (Figure 3; Appendix Table 16)

4.4.1.4 Comparison of the extractions with 100 and 200 ml of 10^{-3}M HCl.

The results are presented in Table 16. The LSD's

TABLE 16. Ca, Mg, and K extracted in 3 soils with 100 and 200 ml of 10^{-3}M HCl per 10 g of soil.

Cation	Sample	Exch. Cation	Cation extracted with 10^{-3}M HCl set 9122		Cation extracted with NH_4OAc after HCl		HCl extraction plus NH_4OAc extraction		Exchang. cation after HCl extraction	
			100 ml	200 ml	100 ml	200 ml	100 ml	200 ml	100 ml	200 ml
		ppm								
Ca	MR-1	12.1	12.5	14.4	1.5	0.6	14.6	15.0	0.3	0
		11.9	12.2	14.4	1.5	1.0	13.7	15.4	0.0	0
		12.0	12.4	14.4	1.5	0.8	13.9	15.2	0.2	0
	C1-18	30.1	34.7	36.7	1.8	1.5	36.5	38.2	1.0	3.1
		32.0	34.7	34.7	2.0	0.4	36.7	35.1	3.0	---
		31.0	34.7	35.7	1.9	1.0	36.6	36.6	2.0	3.1
	MR-15	15.2	16.6	17.7	2.6	2.3	19.2	20.0	3.5	3.5
		16.5	16.6	17.0	2.6	2.0	19.2	19.0	3.5	---
		15.8	16.6	17.4	2.6	2.2	19.2	19.5	3.5	3.5
Mg	MR-1	5.2	5.2	5.2	0.4	0.2	5.6	5.4	0.4	0.5
		5.2	5.0	5.2	0.4	0.2	5.4	5.4	0.1	0.5
		5.2	5.1	5.2	0.4	0.2	5.5	5.4	0.2	0.5
	C1-18	9.5	10.6	10.6	0.3	0.2	10.9	10.8	1.0	0.6
		9.9	10.6	10.6	0.3	0.2	10.9	10.8	1.3	---
		9.7	10.6	10.6	0.3	0.2	10.9	10.8	1.2	0.6
	MR-15	5.2	6.3	6.3	0.3	0.3	6.6	6.6	1.2	0.8
		5.7	6.1	6.3	0.4	0.2	6.5	6.5	1.2	---
		5.4	6.2	6.3	0.4	0.2	6.6	6.6	1.2	0.8

(cont'd.)

TABLE 16. Ca, Mg, and K extracted in 3 soils with 100 and 200 ml of 10^{-3}M HCl per 10 g of soil.

Cation	Sample	Exch. Cation	Cation extracted with 10^{-3} M HCl set 9122		Cation extracted with NH_4OAc after HCl		HCl extraction plus NH_4OAc extraction		Exchang. cation after HCl extraction	
			100 ml	200 ml	100 ml	200 ml	100 ml	200 ml	100 ml	200 ml
		ppm								
K	MR-1	31.2	22.8	26.0	9.4	6.6	32.2	32.6	8.1	7.4
		31.5	22.4	26.0	9.1	6.6	31.5	32.6	7.7	7.4
		31.4	22.6	26.0	9.2	6.6	31.8	32.6	7.9	7.4
	C1-18	42.1	34.3	37.0	9.4	6.8	43.7	43.8	11.8	7.5
		42.1	34.3	36.5	9.6	6.1	43.9	42.6	11.8	---
		42.1	34.3	36.8	9.5	6.4	43.8	43.2	11.8	7.5
	MR-15	30.0	21.4	24.2	9.7	6.3	31.1	30.5	11.5	6.9
		27.9	21.4	24.2	10.4	6.8	31.8	31.0	11.7	---
		29.0	21.4	24.2	10.0	6.6	31.4	30.8	11.6	6.9

(1%) for these comparisons are again 3.9, 1.0, and 3.9 ppm for Ca, Mg, and K, respectively. In general, the 200-ml extractions gave slightly higher values of Ca, Mg, and K than the 100-ml extractions, but the differences were much lower than the LSD's. Correspondingly, the cations extracted with NH_4OAc after the HCl extraction were slightly lower in the samples extracted with 200 ml of HCl than in those with 100 ml. Again, the differences were below the LSD's.

The"HCl + NH_4OAc" -Ca was practically the same in the 100- and 200-ml extractions. The same happened with Mg and K.

4.4.1.5 Extraction with HCl, set 9111.

The results are plotted in Figures 1, 2, and 3. The cations extracted in the samples leached with 10^{-3}M HCl for the actual incubation experiment (set 9111) were about the same as those extracted with the other HCl extraction discussed before (set 9122). The differences were always smaller than the LSD's (the same as those cited in the above paragraph) excepting the samples MR-8-9 and C3-1. In the latter sample only one observation was available. The differences were even smaller than the experimental error (1.5, 0.4 and 1.5 ppm for Ca, Mg, and K, respectively) in the great majority of cases (the data is presented in detail in Appendix Tables 14, 15, and 16).

4.4.1.6 Summary

Similar although less amounts of Ca and Mg were extracted with 100 ml of 10^{-3}M HCl as compared with

extractions with 100 ml of N NH_4OAc, pH 7. However, the HCl extracted significantly less K than the NH_4OAc. Although the interlayers of hydroxy-Al and -Fe present in these soils could be responsible for this difference, no clear mechanism was found to explain it and it is suggested that it is due to a better ability of NH_4 ions to replace K ions. The exchangeable K not extracted with HCl was recovered with a NH_4OAc extraction following the HCl extraction. The HCl extraction followed by the NH_4OAc extraction gave slightly higher amounts of Ca and Mg than those initially exchangeable with NH_4OAc; such differences were generally attributed to the experimental error. No significant differences were found between extractions with 100 and 200 ml of 10^{-3}M HCl/ 10 g of soil.

4.4.2 Exchangeable cations after incubation

4.4.2.1 Effect of the W-D cycles on the exchangeable cations.

4.4.2.1.1 Basic treatments.

In order to analyze the effect of the incubation in the exchangeable Ca, Mg, and K, the 'exchangeable cation' is compared with the 'exchangeable cation after incubation' in the treatments 1 to 6 (except in the case of Ca in which the treatments that received $CaCO_3$ are analyzed separately). In the treatments 7, 8, and 9, the 'exchangeable cation after HCl extraction' is compared to the 'exchangeable cation after incubation.'

The exchangeable Ca, Mg, and K after 2, 5, and 11 W-D cycles are presented in Tables 17, 18, and 19, respectively.

The comparison of the means associated with the different treatments and effects is not an easy task given the complications introduced by the "time effect," the many treatment combinations missing, and the fact of having only one replicate in some cells. Besides, the variation between duplicates was small in some cases and large in others. Hence, to use a pooled experimental error is not necessarily the best alternative for looking at the results of a given individual soil sample. However, the many samples and extractions involved in this experiment make it necessary to analyze the results in general terms, i.e. looking at general trends or very pronounced differences. The reader interested in the results obtained in a given soil should look at them using his own criterion and having in mind the limitations imposed by the "time effect," etc.

It should be mentioned that the level of exchangeable cations in a given soil or soils may be expected to show at least some small fluctuations upon wetting and drying, given the nature and characteristics of the exchange reactions, specially in soils in which silicate minerals, oxide minerals, and organic matter (including the biomass) interact dynamically Changes in the specific nature of exchange sites or exchangeable cations may occur as a consequence of partial drying, which may change the degree of cation hydration as well as the relative warping of silicate layers (Rich, 1968a). Drying the soil involves changes in the basal spacing and hydration status of minerals and side reactions such as blocking of the exchange sites may occur (Ismail and Scott,

1972). Microbial activity, mineralization of the organic matter and nitrification may alter the ionic equilibrium and lead also to fluctuations in the level of exchangeable cations. Tincknell and López (1962) found small fluctuations up and down in the K exchangeable with NH_4OAc in 2 latosols after wetting and drying them from 1 to 5 cycles, as well as in other mature soils.

Besides the small fluctuations mentioned above, the soils may exhibit other characteristics conducive to a net fixation or release of a given cation, or both. However, by conventional techniques one can only measure a net overall effect and the interpretation of the results may be made difficult by apparent inconsistencies.

Calcium

The results for Ca appear in Table 17. The incubation had little effect on the exchangeable Ca in most of the soils. There are some fluctuations up and down but the differences in general are very small and few of them would be statistically significant. Even if the differences are real and not a product of the experimental error, the quantities involved are generally so small that they are not agronomically very important.

In Figure 4 the exchangeable Ca was plotted against the Ca exchangeable after 11 W-D cycles. The respective regression line and equation are also shown.

The experimental error was 1.5 ppm. The LSD (1%) for looking at the effect of treatments 1, 2, and 3 is 3.9, whereas the LSD (1%) for treatments 7, 8, and 9 is approximately

TABLE 17. Exchangeable Ca after incubation.

Sample	Exch. Ca	Exch. Ca after HCl extract.	Exchangeable Ca after incubation								
			Treatment								
			1	2	3	4	5	6	7	8	9
			Check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-1	12.1	0.3	11.0	12.4	14.6	1070	1370	1140	4.8	3.8	4.0
	11.9	0.0	11.3	12.4	13.4	1070	1280	1170	3.1	5.6	4.2
	12.0	0.2	11.2	12.4	14.0	1070	1325	1155	4.0	4.7	4.1
MR-7	8.0	0	10.6	9.4	11.6	640	700	670	2.1	1.4	2.0
	8.6	---	12.5	10.0	11.2	640	740	725	---	2.2	2.0
	8.3	0	11.6	9.7	11.4	640	720	698	2.1	1.8	2.0
C1-18	30.1	1.0	36.0	29.4	32.2	1140	1330	1170	3.7	2.6	3.6
	32.0	3.0	36.0	32.4	32.2	1140	1280	1200	---	3.1	3.6
	31.0	2.0	36.0	30.9	32.2	1140	1305	1185	3.7	2.8	3.6
C1-19	3.2	0.1	5.6	6.4	4.6	800	900	840	1.5	1.0	1.3
	3.5	---	4.6	5.3	4.8	800	860	810	1.8	---	0.9
	3.4	0.1	5.1	5.8	4.7	800	880	825	1.6	1.0	1.1
C4-1-2	12.1	3.0		12.4	17.6		1280	1240	6.4	8.2	9.2
	14.5	---		12.4	18.0		1240	1240	7.0	8.2	8.6
	13.3	3.0		12.4	17.8		1260	1240	6.7	8.2	8.9
C4-3	3.4	1.4			4.8		1070	960	3.5	1.2	2.7
	4.2	---			4.8		980	990	3.4	3.6	2.2
	3.8	1.4			4.8		1025	975	3.4	2.4	2.4

(cont'd.)TABLE 17. Exchangeable Ca after incubation.

Sample	Exch. Ca	Exch. Ca after HCl extract.	Exchangeable Ca after incubation								
			Treatment								
			1	2	3	4	5	6	7	8	9
			Check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-15	15.2	3.5	18.0	---	20.6		820	810	---	6.7	6.1
	16.5	3.5	20.0	17.4	20.6		820	780	6.1	5.9	5.9
	15.8	3.5	19.0	17.4	20.6		820	795	6.1	6.3	6.0
C2-6	7.4	0.7		7.1	7.6		860	900		3.0	3.7
	---	---		8.1	---		860	870		3.2	4.0
	7.4	0.7		7.6	7.6		860	885		3.1	3.8
C2-2	2.2	0.3			2.0			780			1.6
	---	---			2.0			780			1.9
	2.2	0.3			2.0			780			1.8
C2-3	1.5	0.7		1.6	2.0				1.4	1.0	0.4
	0.8	---		1.0	2.0				0.0	1.6	0.7
	1.2	0.7		1.3	2.0				0.7	1.3	0.6
C3-1	19.6	0			20.6			1170			8.9
	20.0	---			20.6			1170			8.9
	19.8	0			20.6			1170			8.9
C3-2	7.0	1.3		---	6.6		1070	1050	3.4	1.8	2.5
	---	---		8.0	7.0		1150	1080	---	3.0	2.5
	7.0	1.3		8.0	6.8		1110	1055	3.4	2.4	2.5

(cont'd)TABLE 17. Exchangeable Ca after incubation.

Sample	Exch. Ca	Exch. Ca after HCl extract.	Exchangeable Ca after incubation								
			Treatment								
			1	2	3	4	5	6	7	8	9
			Check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-8-9	32.0	7.4		32.4	34.6	1300	1370	1430	10.0	10.0	11.2
	33.8	---		29.4	32.2	1300	1470	1390	8.2	10.0	11.2
	32.9	7.4		30.9	33.4	1300	1420	1410	9.1	10.0	11.2
MR-10	9.0	0.9	11.9	10.4	12.4	810	940	900	4.0		3.4
	9.0	---	---	10.4	11.6	810	900	840	4.1		3.1
	9.0	0.9	11.9	10.4	12.0	810	920	885	4.0		3.2
MR-11	5.4	0.3		4.7	4.8		460	450	2.8	2.2	1.3
	---	---		5.6	5.0		460	475	3.0	---	1.3
	5.4	0.3		5.2	4.9		460	462	2.9	2.2	1.3
MR-12	6.4	2.2		5.0	5.2				2.7	2.4	3.4
	5.5	---		4.5	5.2				---	2.8	3.0
	6.0	2.2		4.8	5.2				2.7	2.6	3.2
MR-13	3.9	2.3		4.8	4.4					2.6	3.3
	3.7	---		3.8	4.6					3.4	3.0
	3.8	2.3		4.3	4.5					3.0	3.2
MR-14	6.4	2.7		4.7						3.3	2.0
	---	---		5.0						2.6	2.3
	6.4	2.7		4.8						3.0	2.2

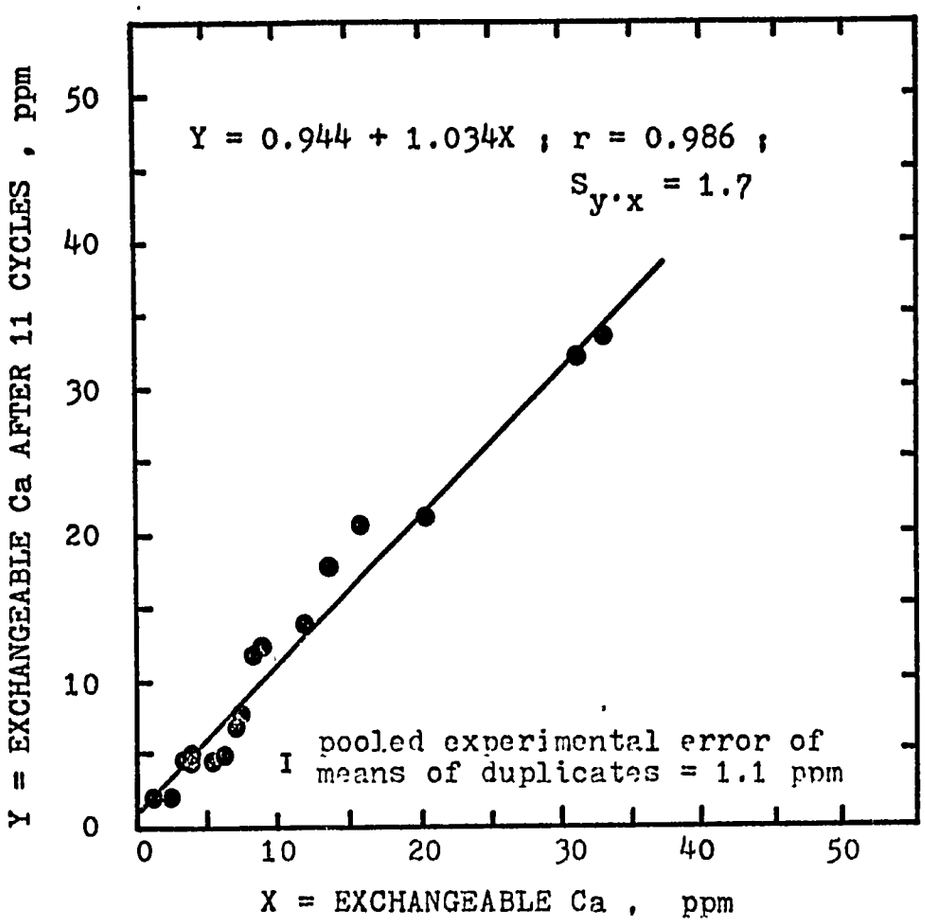

FIGURE 4. INITIAL EXCHANGEABLE Ca vs EXCHANGEABLE Ca AFTER 11 WETTING AND DRYING CYCLES. CHECK SOILS. (MEANS OF DUPLICATES)

4.7 ppm (The LSD's given are for comparing individual sample means, i.e. means of duplicates).

The effect of the incubation on the level of exchangeable Ca was statistically significant in the samples C4-1-2 and MR-15 (in the check soil), and in the samples C4-1-2 and C3-1 (in the soil leached with HCl). The differences were not significant but larger than the experimental error in the samples MR-7, C1-19 and MR-10 (in the check soil), and in the samples MR-1, MR-7, MR-15, C2-6, MR-8-9, MR-10, and MR-11 (in the soil leached with HCl). There were no significant reductions in the exchangeable Ca after incubation.

There is no definite trend associated with the increase in the number of W-D cycles.

Magnesium

The exchangeable Mg changed little upon incubation in the check soils and in the soils leached with HCl. The soils that received $CaCO_3$ showed a marked decrease in the exchangeable Mg (see Table 18). The experimental error was 0.4 ppm. The LSD (1%) for comparing sample means is 1.0 for treatments 1 to 6, and 1.3 for treatments 7, 8, and 9.

Figure 5 shows the exchangeable Mg after 11 W-D cycles plotted against the initial exchangeable Mg. The regression equations and lines are also shown.

In the check soils the exchangeable Mg did not increase significantly (LSD at 1%) in any of the samples, whereas the sample MR-8-9 showed a significant decrease of 1.1 ppm upon incubation. The sample C4-1-2 showed an increase

TABLE 18. Exchangeable Mg after incubation.

Sample	Exch. Mg	Exch. Mg after HCl extract.	Exchangeable Mg after incubation								
			Treatment								
			1	2	3	4	5	6	7	8	9
			check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-1	5.2	0.4	4.8	5.2	5.4	2.2	3.4	3.5	0.8	0.8	0.9
	5.2	0.1	5.0	5.4	5.4	2.3	2.9	3.7	0.8	0.9	0.9
	5.2	0.2	4.9	5.3	5.4	2.2	3.2	3.6	0.8	0.8	0.9
MR-7	3.3	0.4	3.5	3.2	3.1	1.3	1.1	1.5	0.3	0.3	0.5
	3.2	---	3.0	3.2	3.2	1.2	1.2	1.4	0.4	0.4	0.4
	3.2	0.4	3.2	3.2	3.2	1.2	1.2	1.4	0.4	0.4	0.4
C1-18	9.5	1.0	10.4	9.2	9.6	2.6	2.7	2.9	0.7	0.7	0.7
	9.9	1.3	9.0	9.4	9.6	2.6	2.9	3.3	0.8	0.7	0.7
	9.7	1.2	9.7	9.3	9.6	2.6	2.8	3.1	0.8	0.7	0.7
C1-19	3.0	0.5	3.0	3.0	2.8	0.1	0.1	0.2	0.4	0.3	0.4
	3.2	---	2.8	3.0	2.8	0.1	0.1	0.1	0.3	0.3	0.3
	3.1	0.5	2.9	3.0	2.8	0.1	0.1	0.2	0.4	0.3	0.4
C-4-1-2	5.2	1.0		6.4	6.1		1.8	2.5	1.5	1.6	1.8
	5.7	---		5.9	6.1		1.8	2.5	1.5	1.6	1.7
	5.4	1.0		6.2	6.1		1.8	2.5	1.5	1.6	1.8
C4-3	3.3	0.9		3.4	3.4		0.8	1.0	0.5	0.5	0.7
	3.5	---		3.7	3.4		0.8	1.2	0.6	0.8	0.6
	3.4	0.9		3.6	3.4		0.8	1.1	0.6	0.6	0.6

(cont'd.)

TABLE 18. Exchangeable Mg after incubation.

Sample	Exch. Mg	Exch. Mg after HCl extract.	Exchangeable Mg after incubation								
			Treatment								
			1	2	3	4	5	6	7	8	9
			check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-15	5.2	1.2	5.3	5.2	6.0		3.7	4.0	0.6	0.8	0.7
	5.7	1.2	5.3	5.2	6.6		3.7	4.2	0.6	0.7	0.8
	5.4	1.2	5.3	5.2	6.3		3.7	4.1	0.6	0.8	0.8
C2-6	3.3	0.3		3.0	2.4		0.3	0.3		0.4	0.6
	---	---		2.8	---		0.3	0.4		0.7	0.6
	3.3	0.3		2.9	2.4		0.3	0.4		0.6	0.6
C2-2	1.3	0.2			1.3			0.0			0.4
	---	---			1.2			0.0			0.4
	1.3	0.2			1.2			0.0			0.4
C2-3	1.0	0.2		0.9	0.9				0.1	0.3	0.2
	0.8	---		0.6	0.8				0.1	0.1	0.2
	0.9	0.2		0.8	0.8				0.1	0.2	0.2
C3-1	6.1	0.5			5.7			3.2			1.3
	6.4	---			5.7			3.2			1.3
	6.2	0.5			5.7			3.2			1.3
C3-2	3.8	0.0		4.1	3.6		0.8	0.9	0.2	0.2	0.3
	---	---		4.1	3.8		0.8	1.1	0.2	0.2	0.3
	3.8	0.0		4.1	3.7		0.8	1.0	0.2	0.2	0.3

(cont'd.)

TABLE 18 . Exchangeable Mg after incubation.

Sample	Exch. Mg	Exch. Mg after HCl extract.	Exchangeable Mg after incubation								
			Treatment								
			1	2	3	4	5	6	7	8	9
			check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-8-9	16.1	0.8		14.7	15.8	12.2	12.3	14.7	2.8	2.6	2.6
	15.7	---		14.4	14.2	12.2	12.7	14.4	2.6	2.8	2.8
	15.9	0.8		14.6	15.0	12.2	12.5	14.6	2.7	2.7	2.7
MR-10	3.5	0.7	3.2	3.4	3.6	1.2	1.4	1.5	0.5	0.6	0.5
	3.5	---	3.4	3.4	3.4	1.3	1.4	1.5	0.4	0.6	0.5
	3.5	0.7	3.3	3.4	3.5	1.2	1.4	1.5	0.4	0.6	0.5
MR-11	2.1	0.0		2.2	2.0		0.8	1.2	0.7	0.6	0.4
	---	---		2.4	2.0		0.9	1.2	0.6	0.8	0.4
	2.1	0.0		2.3	2.0		0.8	1.2	0.6	0.7	0.4
MR-12	2.6	0.9		2.8	2.6				0.7	0.8	1.2
	2.9	---		2.4	2.6				0.8	1.0	1.1
	2.8	0.9		2.6	2.6				0.8	0.9	1.2
MR-13	2.3	1.4		2.6	2.6				1.5	1.4	1.7
	2.2	---		1.8	2.6				1.3	1.6	1.6
	2.2	1.4		2.2	2.6				1.4	1.5	1.6
MR-14	2.7	0.7		2.4					0.5	0.5	0.8
	---	---		2.6					---	0.7	0.8
	2.7	0.7		2.5					0.5	0.6	0.8

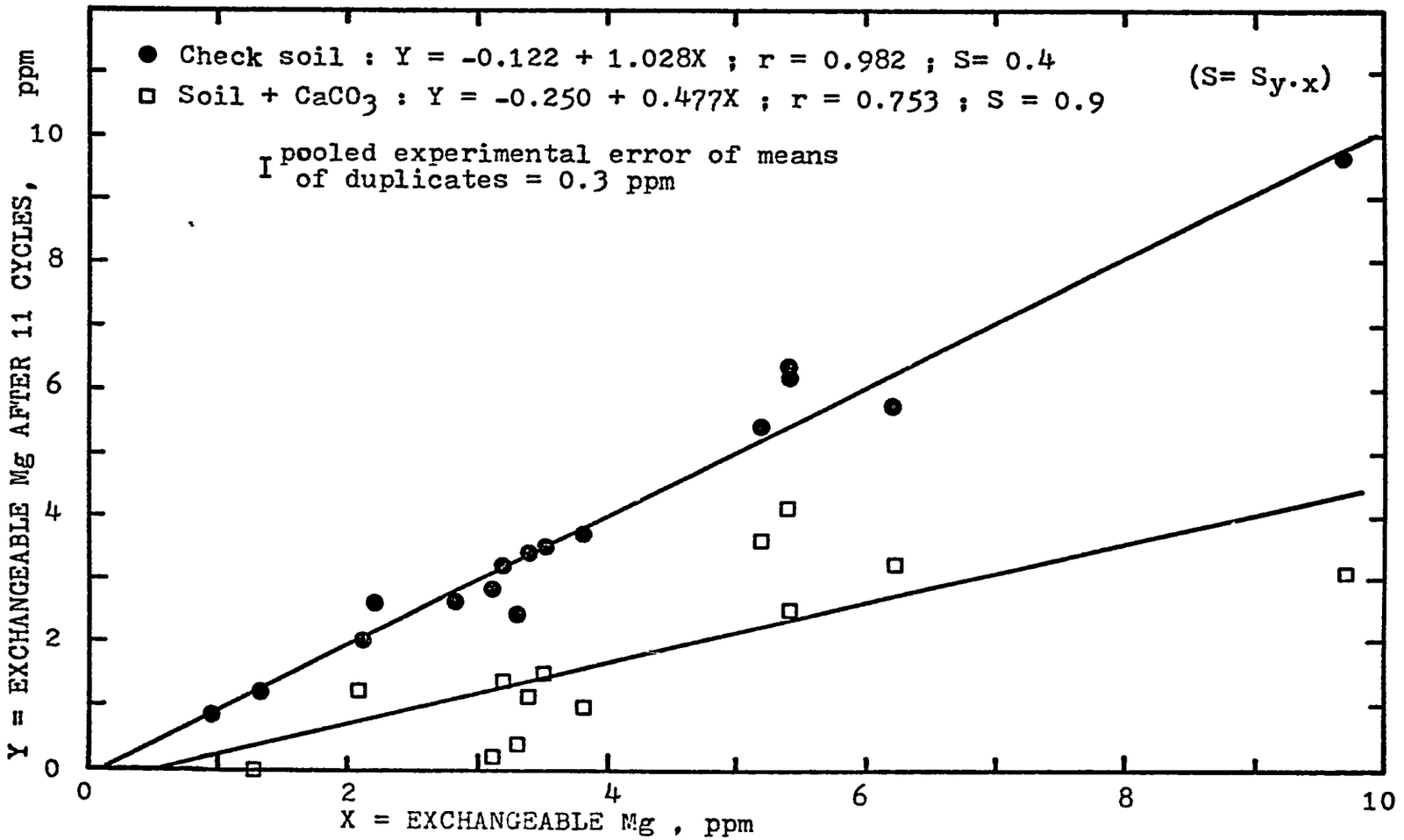

FIGURE 5. INITIAL EXCHANGEABLE Mg vs EXCHANGEABLE Mg AFTER 11 WETTING AND DRYING CYCLES (MEANS OF DUPLICATES).

larger than the experimental error, and the samples C2-6 and C3-1 showed a decrease larger than the experimental error.

In the soils leached with HCl the exchangeable Mg showed a statistically significant increase only in the sample MR-8-9 (by 1.9 ppm). Increases larger than the experimental error were found in the samples MR-1, C4-1-2, C3-1, and MR-11.

In the treatments that received $CaCO_3$ the exchangeable Mg showed a consistent and statistically significant decrease in all the W-D cycles and in all the soils. The decrease ranged from 1 ppm in the sample MR-11 to 7 ppm in the sample C1-18. The average decrease in 14 samples was 2.4 ppm after 11 W-D cycles.

The increase in the number of W-D cycles did not have an effect in the exchangeable Mg in the check and HCl-treated soils. In the treatments that received $CaCO_3$ the exchangeable Mg tended to increase with increasing number of W-D cycles, the difference between 2 and 11 W-D cycles being statistically significant only in the samples MR-1 and MR-8-9.

Another feature to be observed in Figure 5 is the poor fit of the regression line to the points corresponding to the treatment that received $CaCO_3$. This departs from what has been observed in all the regressions discussed up to this point and is reflected in the rather low correlation coefficient ($r = 0.75$) and the large standard error of estimate ($s = 0.9$.) This indicates that the decrease in

the exchangeable Mg in the samples incubated with $CaCO_3$ is related not only to the level of exchangeable Mg but also to other factor(s).

As will be discussed in the next section, the recovery of calcium added to the treatments that received $CaCO_3$ was significantly lower than expected. The recovery of exchangeable K in these treatments was below 100% but the difference was not statistically significant in most cases. The large differences observed between the recoveries of Ca and Mg on the one hand and K on the other hand, indicate that the low recoveries are not due to a physical loss of sample or to errors in weighing the samples or taking aliquots. The possibility of explaining the low recoveries of Mg in such samples in terms of a negative interference due to the high level of Ca relative to Mg was considered but rejected. If Ca interfered with the Mg determination by atomic absorption in the conditions considered, the interference would be expected to be positive, not negative (Thomas Greweling, personal communication, 1974). Thus, it seems that the low recoveries of Mg (and of added Ca) reflect some changes that occurred in the soils as a result of the $CaCO_3$ additions.

Plots (not included) of the data showed no correlation at all between the $CaCO_3$ added and the percentage of Mg not recovered, or between the ratio of $CaCO_3$ added to exchangeable Mg and the Mg not recovered (ppm), or between the ratio of Ca recovered (ppm) to exchangeable Mg and the Mg not

recovered (ppm). The correlation between the ratio of $CaCO_3$ added to exchangeable Mg and the percentage of Mg not recovered was also very poor.

Potassium

The exchangeable K changed slightly upon incubation in most cases (Table 19); the magnitude of the changes was usually about 2 ppm. As mentioned before, the experimental error for K was estimated as 1.5 ppm. The LSD (1%) is 3.9 ppm for sample means in treatments 1 to 6, and 4.7 ppm in treatments 7, 8, and 9.

Figure 6 shows the exchangeable K after 11 W-D cycles plotted against the exchangeable K. The fitting of the regression lines to the data is comparatively better than for Ca and Mg (Figures 4 and 5).

In the check soils the exchangeable K after incubation was always lower than before, except in soil MR-13 and in one analysis of sample MR-15. However, the only statistically significant differences occurred in the samples MR-8-9 and MR-15, in which the K decreased after incubation.

In the HCl treatments, there were some fluctuations in the exchangeable K, but none of the differences was statistically significant.

In the treatments that received $CaCO_3$ the exchangeable K after incubation was always lower than before, except in one analysis of the sample MR-8-9. The only statistically significant decreases occurred in the samples C1-18 and C4-1-2.

TABLE 19. Exchangeable K after incubation.

Sample	Exch. K	Exch. K after HCl extract.	Exchangeable K after incubation								
			Treatment								
			1	2	3	4	5	6	7	8	9
			check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-1	31.2	8.1	26.7	28.3	29.9	26.2	27.9	27.4	10.3	10.8	10.7
	31.5	7.7	28.2	29.9	29.9	24.7	28.2	28.4	10.2	10.7	11.0
	31.4	7.9	27.4	29.1	19.9	25.4	28.0	27.9	10.2	10.8	10.8
MR-7	9.5	4.6	8.4	7.8	8.7	6.7	7.6	8.5	4.6	4.4	6.1
	9.5	---	7.4	7.8	9.1	7.0	8.1	8.8	5.0	4.7	5.4
	9.5	4.6	7.9	7.8	8.9	6.8	7.8	8.6	4.8	4.6	5.8
Cl-18	42.1	11.8	40.8	34.9	39.5	33.3	36.7	37.0	11.0	11.3	11.2
	42.1	11.8	37.0	35.6	39.1	33.9	37.2	37.3	11.6	11.1	11.3
	42.1	11.8	38.9	35.2	39.3	33.6	37.0	37.2	11.3	11.2	11.2
Cl-19	18.3	5.3	16.5	17.6	16.2	14.7	15.2	15.6	7.1	5.8	6.4
	19.3	---	16.2	17.3	16.4	14.7	14.6	15.6	6.5	6.1	6.5
	18.8	5.3	16.4	17.4	16.3	14.7	14.9	15.6	6.8	6.0	6.4
C4-1-2	25.7	9.4		24.0	24.3		21.4	21.8	11.2	12.0	11.6
	26.4	---		24.8	23.7		22.0	22.3	10.9	11.1	11.4
	26.0	9.4		24.4	24.0		21.7	22.0	11.0	11.6	11.5
C4-3	14.6	6.4		13.9	13.8		12.3	12.3	6.6	6.2	6.4
	15.4	---		14.6	13.8		11.6	12.6	6.8	6.3	6.2
	15.0	6.4		14.2	13.8		12.0	12.4	6.7	6.2	6.3

(cont'd.)

TABLE 19. Exchangeable K after incubation.

Sample	Exch. K	Exch. K after HCl extract.	Exchangeable K after incubation								
			1	2	3	4	5	6	7	8	9
			check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-15	30.0	11.5	24.2	24.0	28.9		26.2	28.4	11.0	11.7	12.3
	27.9	11.7	25.2	24.4	31.9		27.2	28.0	11.4	11.7	12.8
	29.0	11.6	24.7	24.2	30.4		26.7	28.2	11.2	11.7	12.6
C2-6	15.8	4.1		13.6	14.3		11.5	12.6		4.6	5.1
	---	---		13.3	---		11.5	12.6		4.7	5.1
	15.8	4.1		13.4	14.3		11.5	12.6		4.6	5.1
C2-2	6.4	2.6			5.2			4.4			3.3
	---	---			5.1			4.4			3.3
	6.4	2.6			5.2			4.4			3.3
C2-3	5.7	1.9		4.1	4.4				2.2	2.6	3.2
	4.8	---		3.1	4.4				2.3	2.9	2.0
	5.2	1.9		3.6	4.4				2.2	2.8	2.6
C3-1	19.0	6.0			17.0			17.6			8.3
	19.6	---			16.9			17.3			8.0
	19.3	6.0			17.0			17.4			8.2
C3-2	14.4	4.1		13.6	12.8		11.4	12.0	4.9	4.4	5.4
	---	---		13.3	13.3		11.9	13.2	4.6	4.6	5.4
	14.4	4.1		13.4	13.0		11.6	12.6	4.8	4.5	5.4

(cont'd.)

TABLE 19. Exchangeable K after incubation.

Sample	Exch K	Exch. K after HCl extract.	Exchangeable K after incubation								
			1	2	3	4	5	6	7	8	9
			check soil			soil + $CaCO_3$ (2:1)			soil leached with HCl		
			wetting and drying cycles								
			2	5	11	2	5	11	2	5	11
	ppm										
MR-8-9	41.5	14.5		37.2	---	38.7	40.0	44.0		14.8	15.6
	41.5	---		35.2	37.5	40.2	41.2	42.0		15.4	16.3
	41.5	14.5		36.2	37.5	39.4	40.6	43.0		15.1	16.0
MR-10	18.0	6.7	15.9	15.8	16.7	14.7	15.5	16.3	7.0	7.4	6.8
	18.0	---	15.9	16.6	16.9	15.4	15.2	16.3	6.8	7.4	6.6
	18.0	6.7	15.9	16.2	16.8	15.0	15.4	16.3	6.9	7.4	6.7
MR-11	12.6	5.1		11.6	11.9		10.2	11.3	7.4	6.2	5.9
	---	---		12.9	12.6		10.7	11.6	7.2	6.2	5.9
	12.6	5.1		12.2	12.2		10.4	11.4	7.3	6.2	5.9
MR-12	14.6	8.7		14.4	12.8				---	7.3	9.6
	15.1	---		---	12.6				7.6	8.5	8.0
	14.8	8.7		14.4	12.7				7.6	7.9	8.8
MR-13	14.8	10.9		16.6	15.9				10.6	10.3	11.9
	16.0	---		---	15.9				9.3	12.0	11.0
	15.4	10.9		16.6	15.9				10.0	11.2	11.4
MR-14	20.0	8.4		17.9					7.4	7.1	12.1
	---	---		20.2					---	10.4	10.2
	20.0	8.4		19.0					7.4	8.8	11.2

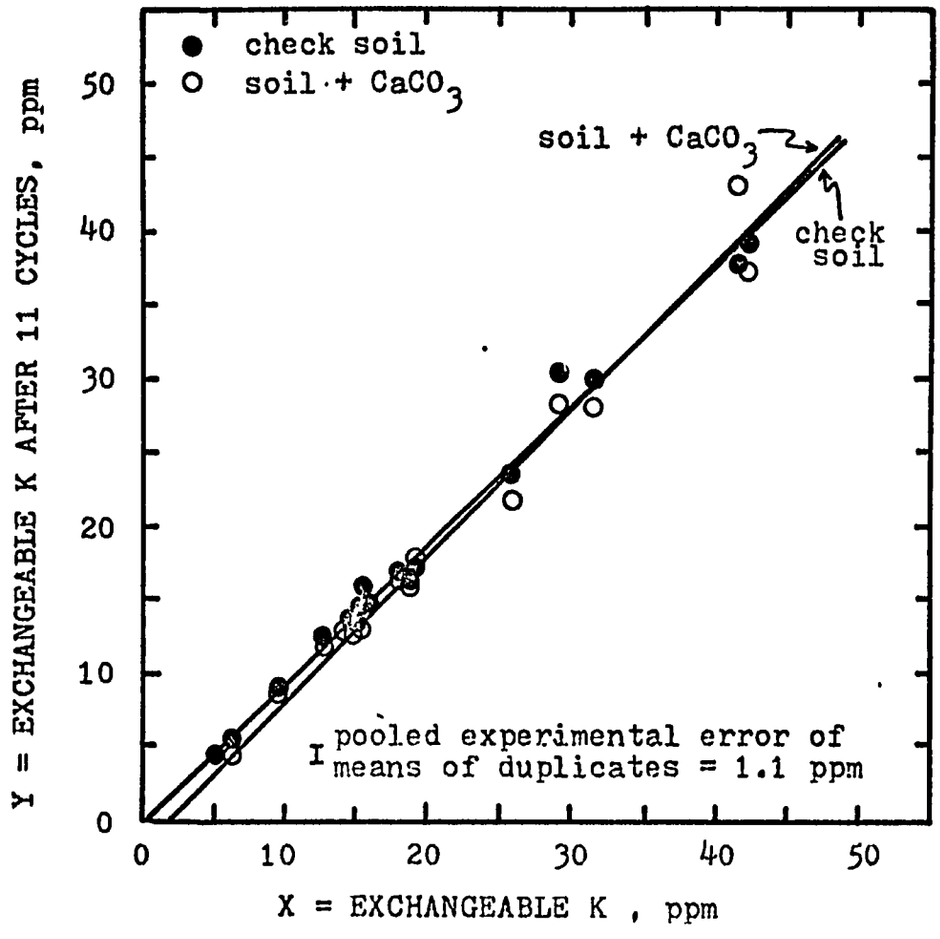

FIGURE 6. INITIAL EXCHANGEABLE K vs EXCHANGEABLE K AFTER 11 WETTING AND DRYING CYCLES (MEANS OF DUPLICATES).

Check soil: $Y = -0.369 + 0.948X$; $r = 0.994$; $S_{y \cdot x} = 1.2$

Soil + $CaCO_3$: $Y = -1.972 + 0.991X$; $r = 0.990$; $S_{y \cdot x} = 1.7$

The exchangeable K tended to remain about the same or to increase with the increase of the number of W-D cycles, specially in the $CaCO_3$ treatments. However, the only statistically significant increase occurred in the sample MR-15.

---0---

By looking at Tables 17, 18, and 19, it is observed that the soils leached with 10^{-3}M HCl showed larger levels of exchangeable Ca, Mg, and K (considering the respective amounts extracted with HCl) after 11 W-D cycles than the check soils or the soils that received $CaCO_3$. Except in a few samples, the differences were not statistically significant. To distinguish between the possible effect of the incubation itself, i.e. the wetting and drying process and the possible immediate effect of the leaching with HCl, the data corresponding to 11 W-D cycles were plotted again in Figure 7. In this Figure, the Ca, Mg, and K extracted with 10^{-3}M HCl plus the following extraction with N NH_4OAc (set 9122 + set 9124) were plotted against the Ca, Mg, and K extracted with HCl (set 9111) plus the Ca, Mg and K extracted with N NH_4OAc after 11 W-D cycles. The respective regression lines and equations are also shown. It is clear that in most of the samples there was no direct effect of the incubation, and so the slightly higher amounts of exchangeable cations found in the HCl-treated soils after incubation were due generally to the leaching with HCl and not to the incubation.

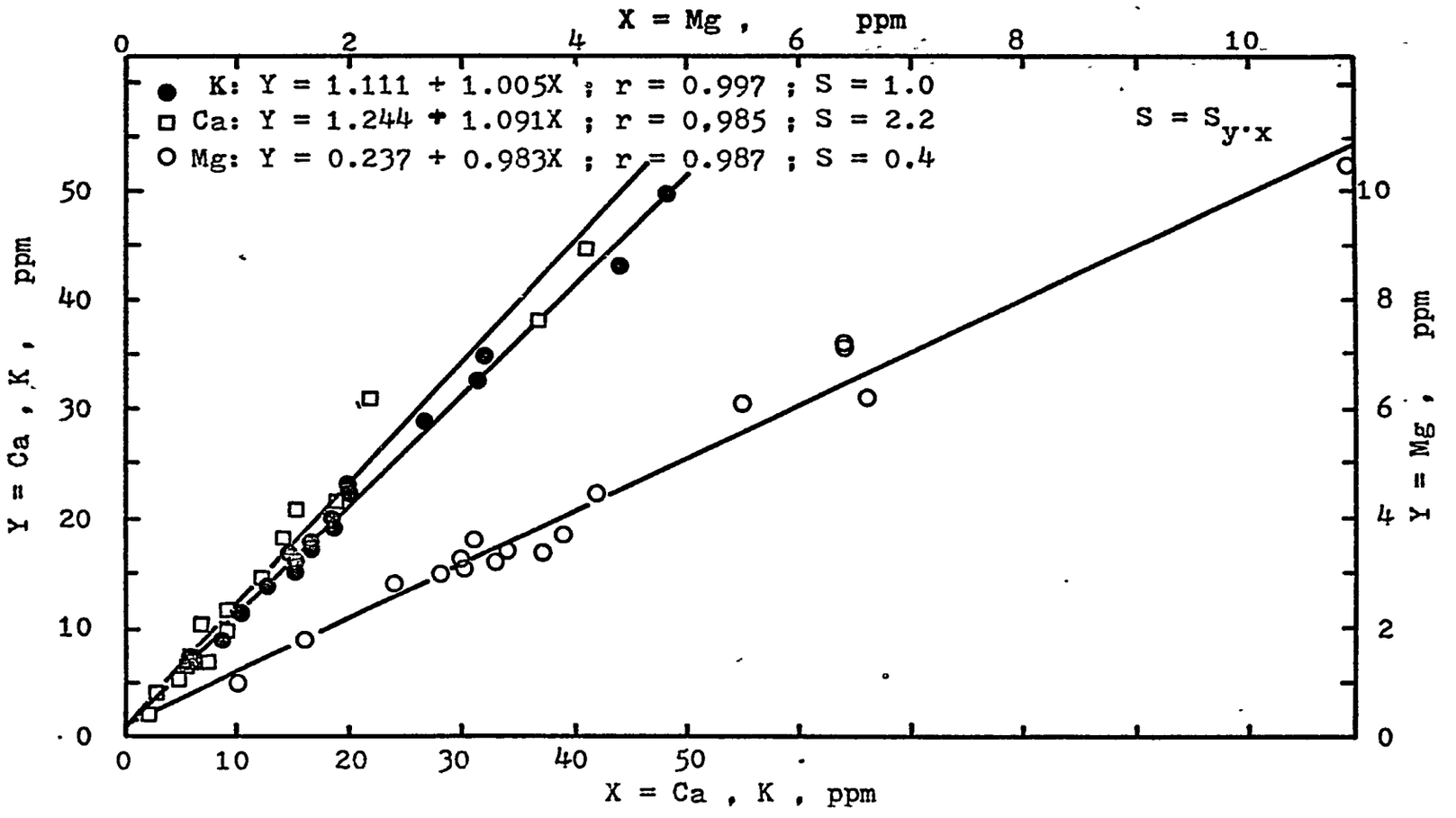

FIGURE 7.(Ca, K, AND Mg EXTRACTED WITH 10^{-3} M HCl FOLLOWED BY EXTRACTION WITH N NH_4OAc) = X vs (Ca, K, AND Mg EXTRACTED WITH 10^{-3} M HCl PLUS Ca, K, AND Mg EXTRACTED WITH N NH_4OAc AFTER 11 WETTING AND DRYING CYCLES) = Y. (MEANS OF DUPLICATES)..

4.4.2.1.2 Extra treatments

Summary: in the 3 soils to which the treatments 10 to 20 were applied, the changes in the exchangeable Ca, K, and Mg upon incubation were small in most of the cases (see Table 20) and of the same magnitude as those observed in the basic treatments. The case of Ca in the treatments that received $CaCO_3$ is discussed in the next section. A detailed analysis of the effect of the extra treatments is given next.

Addition of $CaCO_3$ (1:1). With the addition of $CaCO_3$ the exchangeable Mg was significantly lower (LSD = 1 ppm) after incubation than before and it was also significantly lower than in the incubated check soils. The exchangeable K decreased significantly (LSD = 3.9 ppm) upon incubation in the samples MR-1 and Cl-18. The sample Cl-18 had also a significant decrease in the exchangeable K in the treatments with $CaCO_3$ (2:1) and it seems safer to accept the conclusion reached earlier that although the exchangeable K decreased upon incubation in the treatments that received $CaCO_3$ (2:1), the difference was not significant in most soils. Both the exchangeable Mg and K increased with increasing the number of W-D cycles. Comparing the two levels of $CaCO_3$ added (1:1 vs 2:1), the exchangeable Mg after incubation was significantly (a = 1%) higher in the 1:1 treatments. In the case of K, there was no significant difference between the 1:1 and the 2:1 levels, although in most cases the exchangeable K was lower in the 1:1 level.

TABLE 20. Exchangeable Ca, Mg, and K after incubation (Extra treatments).

Sample	Exch. Cation	Exchang. cation after HCl extraction		Exchangeable cation after incubation										
				Treatment										
				10	11	12	13	14	15	16	17	18	19	20
				soil + $CaCO_3$ (1:1)			HCl-wet		HCl-200 ml		--HCl---		--check---	
											dry	35°C	dry	35°C
				wetting and drying cycles										
		100 ml	200 ml	2	5	11	5	11	5	11	5	5	5	5
	Ca, ppm													
MR-1	12.1	0.3	0	460	540	570	2.8	--	4.3	3.9	4.9	4.4	11.7	13.0
	11.9	0.0	0	500	460	570	2.8	3.6	4.3	4.1	4.0	6.5	13.3	15.4
	12.0	0.2	0	480	500	570	2.8	3.6	4.3	4.0	4.4	5.4	12.5	14.2
Cl-18	30.1	1.0	3.1	520	620	550	2.6	2.8	2.6	3.5	4.4	3.2	33.3	28.5
	32.0	3.0	---	520	660	600	---	3.6	2.6	4.1	3.4	3.8	33.3	28.5
	31.0	2.0	3.1	520	640	575	2.6	3.2	2.6	3.8	3.9	3.5	33.3	28.5
MR-15	15.2	3.5	3.5				3.8	4.3	5.4	6.3	5.6	6.2	16.5	---
	16.5	3.5	---				5.0	4.3	5.4	6.3	6.0	5.9	16.8	16.5
	15.8	3.5	3.5				4.4	4.3	5.4	6.3	5.8	6.0	16.6	16.5
	Mg, ppm													
MR-1	5.2	0.4	0.5	3.8		5.3	0.6	0.7	1.0	1.0	0.9	0.8	5.0	5.4
	5.2	0.1	0.5	3.8		5.3	0.6	0.6	1.0	1.0	0.7	1.2	5.2	5.8
	5.2	0.2	0.5	3.8		5.3	0.6	0.6	1.0	1.0	0.8	1.0	5.1	5.6
Cl-18	9.5	1.0	0.6	7.8		8.5	0.4	0.2	0.7	0.7	0.8	0.8	9.2	9.0
	9.9	1.3	---	7.8		8.8	0.5	0.4	0.7	0.8	0.7	0.9	9.4	9.0
	9.7	1.2	0.6	7.8		8.6	0.4	0.3	0.7	0.8	0.8	0.8	9.3	9.0
MR-15	5.2	1.2	0.8				0.5	0.5	0.5	0.6	0.6	0.7	5.0	6.5
	5.7	1.2	---				0.5	0.5	0.5	0.6	0.6	0.7	5.0	5.6
	5.4	1.2	0.8				0.5	0.5	0.5	0.6	0.6	0.7	5.0	6.0

(cont'd.)

TABLE 20. Exchangeable Ca, Mg, and K after incubation (Extra treatments).

Sample	Exch. Cation	Exchang. cation after HCl extraction		Exchangeable cation after incubation										
				Treatment										
				10	11	12	13	14	15	16	17	18	19	20
				soil + $CaCO_3$ (1:1)			HCl-wet		HCl-200 ml		--HCl---		--check--	
											dry	35°C	dry	35°C
				wetting and drying cycles										
		100 ml	200 ml	2	5	11	5	11	5	11	5	5	5	5
	K, ppm													
MR-1	31.2	8.1	7.4	24.2	25.7	29.3	8.8	9.7	9.6	10.8	10.0	10.7	29.0	29.7
	31.5	7.7	7.4	25.5	26.9	29.7	8.7	9.5	9.6	9.8	10.0	11.3	29.5	31.5
	31.4	7.9	7.4	24.8	26.3	29.5	8.8	9.6	9.6	9.9	10.0	11.0	29.2	30.6
Cl-18	42.1	11.8	7.5	33.9	34.2	36.0	9.7	10.6	9.3	10.6	11.3	11.7	36.0	33.3
	42.1	11.8	---	33.9	35.5	36.7	9.1	10.1	9.9	10.7	10.7	11.7	36.5	34.0
	42.1	11.8	7.5	33.9	34.8	36.4	9.4	10.4	9.6	10.6	11.0	11.7	36.2	33.6
MR-15	30.0	11.5	6.9				9.1	9.8	10.1	11.2	10.9	12.3	23.0	28.5
	27.9	11.7	---				8.8	9.8	9.6	10.7	11.0	12.0	23.5	26.0
	29.0	11.6	6.9				9.0	9.8	9.8	11.0	11.0	12.2	23.2	27.2

Effect of keeping the soils always wet. Assuming that the maximum release, if any, of cations would occur in the HCl-treated soils, it was decided to apply this treatment (always wet) to soils leached with 10^{-3}M HCl. The object was to partially simulate the conditions of those soils in poorly drained areas ("bajos") which remain flooded for several months during the rainy season. The LSD's (1%) are 4.7 ppm for Ca and K, and 1.3 ppm for Mg. There were no significant changes in the exchangeable Ca, K, or Mg by keeping the soils wet for either 130 or 286 days.

Effect of leaching the soils with 200 ml of 10^{-3}M HCl per 10 g of soil.

The exchangeable Ca, Mg, and K did not change significantly upon incubation (LSD's as above), although they were higher than before incubation. There were no significant differences between leaching the soils with 100 and 200 ml of 10^{-3}M HCl in relation to the exchangeable cation after incubation.

Effect of drying the soils at 35° C. In the HCl-treated soils the only significant change upon incubation (LSD's as above) occurred in the sample MR-1, which showed a higher level of exchangeable Ca than before incubation. In the check soils (the LSD's are 3.9 ppm for Ca and K, and 1.0 ppm for Mg for comparisons between sample means) the only significant change was a decrease in the exchangeable K of sample Cl-18.

Changes in the exchangeable Ca, Mg. and K of soils kept always dry (not incubated).

In the HCl-treated soils there were no significant changes after keeping the soils for 130 days, although the exchangeable Ca showed a consistent increase in the 3 soils. In the check soils there were significant differences in the exchangeable K of samples C1-18 and MR-15 (LSD (1%) = 3.9 ppm). Except for this last two significant differences, the changes observed can be easily explained in terms of the experimental error. The two significant differences mentioned are harder to explain. It could be that they reflect real changes occurring in air-dry soils (kept tightly covered) or that the experimental error just happened to be larger in these particular cases.

4.4.2.2 Recovery of Ca in the $CaCO_3$

The recoveries of Ca in the 30-mg samples of $CaCO_3$ extracted with 100 ml of N NH_4OAc and 10^{-3}M HCl were 68.6 and 108.3%, respectively. The calculation was made assuming a 40% of Ca in the $CaCO_3$ (reagent) used. Additional comments are given in the next section. The $CaCO_3$ used in these experiments was not analyzed to check the exact carbonate content given that it was certified to meet the A.C.S. specifications (analytical reagent). An analysis of carbonate in samples of the (same brand) reagent, coming from a different bottle, showed a 92.3% of $CaCO_3$ and the equivalent of 7.7% of CaO (G. Amedee, personal communication, 1974).

4.4.2.3 Recovery of Ca in the soils treated with $CaCO_3$

The Ca added to the soils was calculated assuming 40% Ca in the $CaCO_3$ added to the soils. After incubation not all the Ca added plus initial exchangeable Ca present in the soil could be accounted for. The percentage of Ca recovered ranged from 71.4 to 86.2, from 74.4 to 99.5, and from 83.0 to 91.3 in the soil samples incubated for 2, 5, and 11 W-D cycles, respectively (see Table 21). The fact that all recoveries were below 100% indicates that it is not just a matter of normal random experimental error. The explanation lies in some systematic error in the extraction and analysis of the samples, or in the capacity of (some of) these soils to retain or "fix" calcium, or in a combination of both. A third alternative, the possibility of a Ca content well below 40% in the $CaCO_3$ was discarded because of the results obtained when 30 mg of $CaCO_3$ were extracted with 100 ml of HCl and with 100 ml of NH_4OAc (see 4.4.2.2), and because of the good recovery obtained in the blank samples after 11 W-D cycles.

In relation to the unequal recoveries obtained in the blank samples (see Table 21), the following considerations explain it satisfactorily. The blanks received 30 mg of $CaCO_3$, and after 2 and 5 W-D cycles the blanks were extracted with 100 ml of N NH_4OAc. This amount of NH_4OAc is not enough to dissolve all the $CaCO_3$ added (as evidenced by the cloudy and milky appearance of the extracts). In the blanks incubated for 11 W-D cycles a double extraction procedure

TABLE 21. Ca added and Ca recovered in the incubation experiment. (means of duplicate samples)

Sample	Depth cm	Ca added ppm	Ca added plus exch.Ca ppm	wetting and drying cycles 2 Ca recovered ppm	2 %	5 ppm	5 %	11 ppm	11 %
MR-1	0-15	1320	1332	1070	80.3	1325	99.5	1155	86.7
MR-1	0-15	660	672	480	71.4	500	74.4	570	84.8
MR-7	33-50	800	808	640	79.2	720	89.1	698	86.4
C1-18	0-20	1292	1323	1140	86.2	1305	98.6	1185	89.6
C1-18	0-20	646	677	520	76.8	640	94.5	575	84.9
C1-19	20-40	952	955	800	83.8	880	92.1	825	86.4
MR-8-9	0-20	1600	1633	1300	79.6	1420	87.0	1410	86.3
MR-10	20-38	1000	1009	810	80.3	920	91.2	885	87.7
MR-11	38-94	520	525			460	87.6	462	88.0
C2-6	0-16	1000	1007			860	85.4	885	87.9
C2-2	16-30	380	882					780	88.4
MR-15	0-15	840	856			820	95.8	795	92.9
C3-1	0-16	1360	1380					1170	84.8
C3-2	16-42	1160	1167			1110	95.1	1065	91.3
C4-1-2	0-19	1480	1493			1260	84.4	1240	83.0
C4-3	19-31	1120	1124			1025	91.2	975	86.7
Blanks	---	1200	---	940	78.3	800	66.7	1168 (960+208)	97.3 (80.0+17.3)

was used: first with NH_4OAc, as before, and then the flasks and buchner funnels were rinsed with 100 ml of diluted HCl. The NH_4OAc extracted 80.0% of the $CaCO_3$ and the HCl an additional 17.3%, for a total recovery of 97.3% of the $CaCO_3$ added to the blanks. The variation in the recoveries obtained in the blanks when using only NH_4OAc (78.3%, 66.7%, and 80.0%) can be attributed mainly to variation in the equilibrium time of the $CaCO_3$ with the NH_4OAc.

The good recoveries obtained in the blanks after 11 W-D cycles and when 100 ml of 0.1N HCl were used to extract 30 mg of $CaCO_3$ (which represent a rough average of the $CaCO_3$ added to the soils), suggest that the low recoveries obtained in the soil samples are not due only to some systematic error in the determinations but that they reflect, at least in part, a real retention of Ca by some of these soils. The possibility that the $CaCO_3$ had not reacted with the soil completely and that this unreacted $CaCO_3$ was not completely dissolved in the subsequent NH_4OAc extraction was considered. However, this seems unlikely at least after 11 W-D cycles, because: a) the $CaCO_3$ was finely divided and well mixed with the soil; b) the amount added was relatively small and would be unlikely to increase the pH much above 5.5. Even considering a "time effect" (see Discussion: Statistical considerations), the available evidence suggests that Ca "fixation" by these soils is partially responsible for the low recoveries. The large and inconsistent variations in the percentage of Ca recovered when going from 2 to 5 or to

11 W-D cycles are surprising and cannot be explained. Again, a time effect could account for some of the variation.

Table 22 shows the same results but now expressed as meq of Ca not recovered per 100 g of soil. The means for 2, 5, and 11 W-D cycles were 1.03, 0.48, and 0.68 meq of Ca not recovered/100 g of soil, respectively (notice that only 8 samples are included for the mean of 2 W-D cycles).

The percentage of recovery is defined as the ratio of exchangeable cation after the incubation to exchangeable cation before the incubation plus cation added (if any). Table 23 shows the percentages of Ca, Mg, and K recovered in the treatments that received $CaCO_3$. For comparison purposes, the cations recovered in the check soils after 11 W-D cycles are also given. It is clear that in the check soils the recoveries of Ca, Mg, and K are closer and more correlated with each other than in the treatments that received $CaCO_3$. This suggests that there is some particular effect associated with the addition of $CaCO_3$ to the soils. The correlation coefficients between the recovery of K (%) and the recovery of Ca (%), after 11 W-D cycles, were 0.10 in soils with added $CaCO_3$ (2:1) and 0.31 in the check soils. Similarly, the correlation coefficients between Mg recovered (%) and Ca recovered (%) were -0.03 and 0.47, respectively.

In order to find out if there was any relationship between the Ca not recovered and the Ca added plus the exchangeable Ca, the data were plotted again in Figure 8,

TABLE 22. Ca not recovered in the incubation experiment (treatments with $CaCO_3$) (Means of duplicate samples)

Sample	Depth cm	Ca added plus exch. Ca	Ca not recovered wetting and drying cycles 2	5	11	10% error
		meq/100 g				
MR-1	0-15	6.66	1.31	0.04	0.88	0.67
MR-1	0-15	3.36	0.96	0.86	0.51	0.34
MR-7	33-50	4.04	0.84	0.44	0.55	0.40
C1-18	0-20	6.62	0.92	0.09	0.69	0.66
C1-18	0-20	3.38	0.78	0.18	0.51	0.34
C1-19	20-40	4.78	0.78	0.38	0.65	0.48
MR-8-9	0-20	8.16	1.66	1.06	1.12	0.82
MR-10	20-38	5.04	1.00	0.44	0.62	0.50
MR-11	38-94	2.62		0.32	0.32	0.26
C2-6	0-16	5.04		0.74	0.61	0.50
C2-2	18-30	4.41			0.51	0.44
MR-15	0-15	4.28		0.18	0.30	0.43
C3-1	0-16	6.90			1.05	0.69
C3-2	16-42	5.84		0.28	0.51	0.58
C4-1-2	0-19	7.46		1.16	1.26	0.75
C4-3	19-31	5.62		0.50	0.74	0.56

TABLE 23. Percentages of Ca, Mg, and K recovered in the incubation experiment in treatments with $CaCO_3$, and in check soils (means of duplicate samples)

Sample	Cation recovered											
	soil + $CaCO_3$ (2:1)									check soil		
	wetting and drying cycles											
	2			5			11			11		
	Ca	Mg	K	Ca	Mg	K	Ca	Mg	K	Ca	Mg	K
	%											
MR-1	80.3	42.3	80.9	99.5	61.5	89.1	86.7	69.2	88.6	116.7	103.8	95.2
MR-7	79.2	37.5	71.6	89.1	37.5	82.1	86.4	43.8	90.5	137.3	100.0	93.7
C1-18	86.2	26.8	79.2	98.6	28.9	87.9	89.6	32.0	88.4	103.8	99.0	93.3
C1-19	83.8	3.2	78.2	92.1	3.2	79.2	86.4	6.5	83.0	138.2	90.3	86.7
MR-8-9	79.6	76.7	94.9	87.0	78.6	97.8	86.3	91.8	103.6	101.5	94.3	90.4
MR-10	80.3	34.3	83.3	91.2	40.0	85.6	87.7	42.8	90.6	133.3	100.0	93.3
MR-11				87.6	38.1	82.5	88.0	57.1	90.5	90.7	95.2	96.8
C2-6				85.4	9.1	72.8	87.9	12.1	79.7	102.7	72.7	90.5
C2-2							88.4	0.0	68.8	90.9	92.3	81.2
MR-15				95.8	68.5	92.1	92.9	75.9	97.2	130.4	116.7	104.8
C3-1							84.8	51.6	90.2	104.0	91.9	88.0
C3-2				95.1	21.1	80.6	91.3	26.3	87.5	97.1	97.4	90.3
C4-1-2				84.4	33.3	83.5	83.0	46.3	84.6	133.8	113.0	92.3
C4-3				91.2	23.5	80.0	86.7	32.4	82.7	126.3	100.0	92.0
	soil + $CaCO_3$ (1:1)											
MR-1	71.4	73.1	79.0	74.4	3.8	83.3	84.8	101.9	93.7			
C1-18	76.8	80.4	80.5	94.5	6.2	82.7	84.9	88.7	86.5			

and the regression equations for the sample means were calculated. From the figure, it is suggested that there seems to be some correlation between them, although it could be direct or indirect, and also that there are other variable(s) affecting the nonrecovery of Ca. The drop in the correlation coefficient for the 5 W-D cycles data is disconcerting. It is worthwhile mentioning that the level of $CaCO_3$ added was based on known or assumed values of exchangeable Al in these soils. The latter in turn is directly related to the organic matter content, CEC, and maybe clay and Al oxides present in the soil. Given that the exchangeable Ca is very low compared to the Ca added, the apparent relation between the Ca not recovered (ppm) and the Ca applied plus exchangeable Ca could be indirect through some relationship of the Ca not recovered (ppm) with anyone of the other soil variables just mentioned.

Some of the data of Table 23 were plotted in Figure 9, and it can be seen that the percentage of Ca not recovered in the treatments with $CaCO_3$ was rather uniform and independent of the Ca applied plus exchangeable Ca when all the soils were considered together.

The Ca not recovered was higher in the topsoils than in the subsoils, but the difference was not statistically significant on the average ($a = 5\%$). Plots of the total Fe content of the soils against the Ca not recovered (ppm) after 5 and after 11 W-D cycles showed no correlation between these two variables, even when the topsoils and subsoils were considered separate.

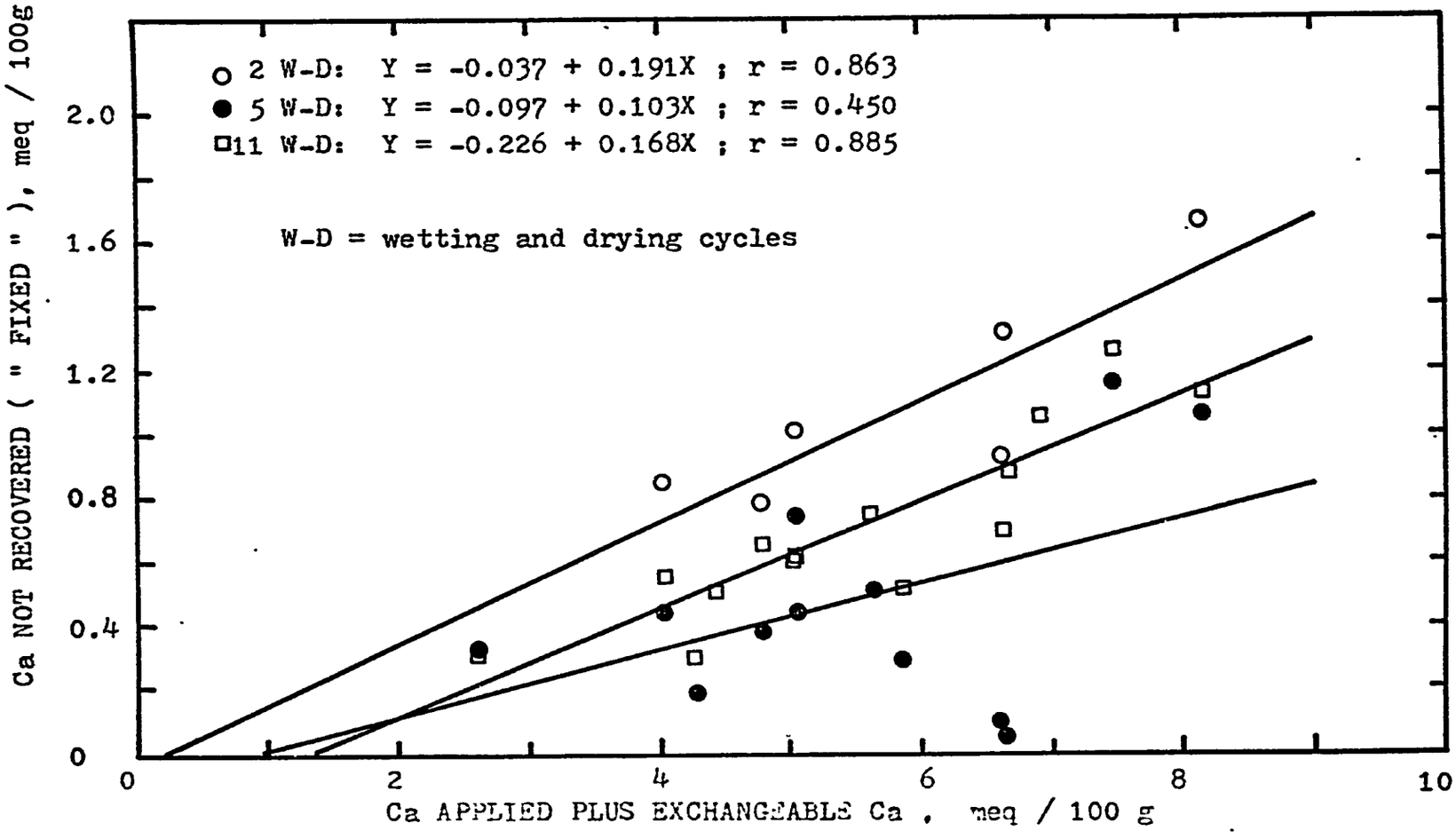

FIGURE 8. CHANGES IN THE Ca NOT RECOVERED AFTER SEVERAL WETTING AND DRYING CYCLES (MEANS OF DUPLICATES).

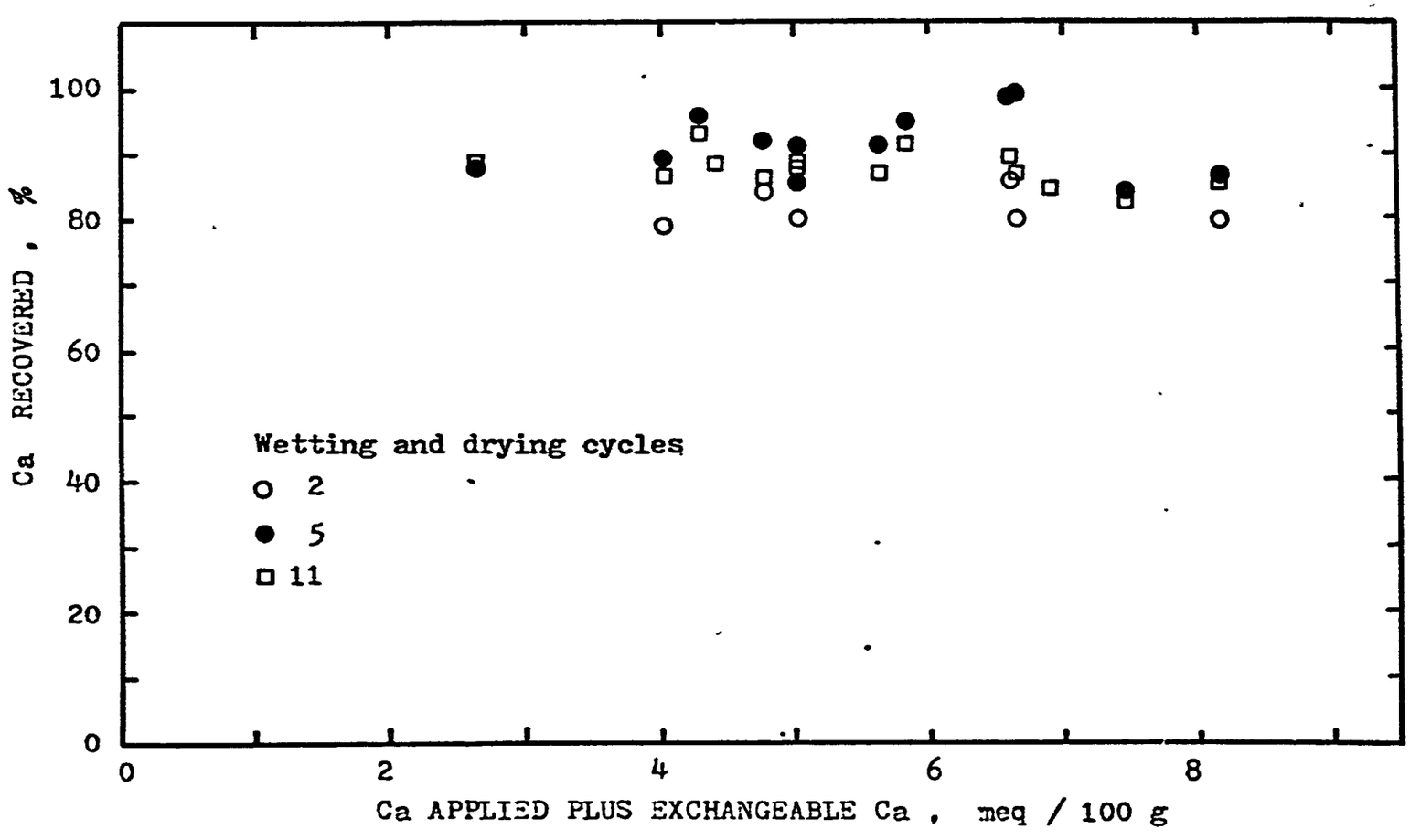

FIGURE 9. CHANGES IN THE Ca RECOVERED AFTER SEVERAL WETTING AND DRYING CYCLES (MEANS OF DUPLICATES).

In a different set of experiments, carried out at the same time by G. Amedee (personal communication, 1974), the sample MR-1 was allowed to react with an excess of $CaCO_3$ in the presence of an atmosphere enriched in CO_2. After successive extractions with water and N KCl, the Ca "fixed" was 0.96 meq/100 g (relative error: 6.2%) which is comparable to the amounts not recovered after 2 and 11 W-D cycles in the incubation experiment.

Mikami and Kimura (1964) have reported similar results of incomplete recoveries of added Ca in 3 latosols of wet regions of Hawaii. The application of lime to the subsoils significantly decreased the CEC by several meq/100 g. Under "controlled laboratory conditions" the following results were obtained:

soil	soil Ca ppm	added Ca ppm	Ca "fixed" 1 month ppm	1 month %	3 months ppm	3 months %	5 months ppm	5 months %
Akaka	28	2400	125	5.2	276	11.4	250	14.4
Manana	18	800	-4	-0.5	22	2.7	31	3.8
Lolekaa	128	800	72	7.8	114	12.3	87	9.4

Akaka is a Hydrandept and the other 2 soils are Tropohumults. However, no more details were given to critically evaluate these results. The authors suggested as possible reasons of the low recoveries the formation of insoluble organic salts (e.g. Ca oxalate), or the formation of inorganic salts ($CaSO_4 . 2H_2O$) in these relatively high sulfate containing soils. In a later paper, Uehara, et al (1972)

interpreted these results as due to Ca fixation through specific adsorption by Fe and Al oxides.

In field experiments in Hawaii, Rixon (1966) applied crushed coral stone (up to 46 ton/ha) to 3 latosols. The Ca recovered was less than that applied. However, the interpretation given later by Uehara, et al (1972) of Ca fixation is not necessarily correct. The variability in the data and other inconsistencies indicate that the low recovery of added Ca could be attributed more likely to incomplete reaction of the coral with the soil. Similarly, the variability in the CEC suggest that the reduction in CEC is more a reflection of experimental error than of Ca fixation.

Uehara, et al (1972) claim that the fraction of the applied Ca which is specifically adsorbed may be very large; however, such specifically-adsorbed Ca would be at least partially available to plants.

4.4.2.4 Exchangeable Al and pH

Both the exchangeable Al and the pH of the check soils showed only very slight changes upon incubation. Details are presented in Appendix Table 21.

4.5 Additional incubation experiment

In view of the apparent fixation of Mg and K when $CaCO_3$ was added, the additional incubation experiment described here was performed in order to study the possibility of Mg and K fixation in the absence of $CaCO_3$ addition. The results are presented in Tables 24 and 25. The percentage of recovery was defined as 100 times the ratio of cation extracted with

TABLE 24. Ca, Mg, and K extracted with NH_4OAc after two wetting and drying cycles in the additional incubation experiment.

Treatment				Cation extracted after 2 W-D cycles (ppm)								
				soil								
ppm added				MR-1			Cl-18			MR-15		
No.	Mg	K		Ca	Mg	K	Ca	Mg	K	Ca	Mg	K
1	0	0		12.6	5.6	31.6	29.6	10.3	39.6	15.5	5.6	29.7
(not incubated)				12.9	5.6	29.3	29.6	9.7	37.6	16.8	5.8	31.0
			mean	12.8	5.6	30.4	29.6	10.0	38.6	16.2	5.7	30.4
			recovery %	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2	0	0		12.0	5.6	30.6	29.6	10.3	41.0	15.7	6.1	27.5
				13.3	5.1	29.3	29.6	10.3	40.3	14.4	5.9	26.6
			mean	12.6	5.4	30.0	29.6	10.3	40.6	15.0	6.0	27.0
			recovery %	98.4	96.4	98.7	100.0	103.0	105.2	92.6	105.3	88.8
3	0	97.5		10.2	5.3	113	26.1	9.2	119	16.2	6.3	111
				10.2	5.1	113	29.6	9.9	131	14.4	6.1	111
			mean	10.2	5.2	113	27.8	9.6	125	15.3	6.2	111
			recovery %	79.7	92.9	88.4	93.9	96.0	91.8	94.4	108.8	86.8
4	0	195		10.5	5.6	202	29.6	9.9	227	15.7	6.3	204
				12.0	5.9	213	29.6	10.3	224	18.5	6.8	234
			mean	11.2	5.8	208	29.6	10.1	226	17.1	6.6	219
			recovery %	87.5	103.6	92.3	100.0	101.0	96.7	105.6	115.8	97.2
5	120	0		(26.1)	115	29.7	28.1	115	36.5	15.2	112	28.1
				10.2	115	29.7	28.1	123	40.3	15.1	115	28.4
			mean	10.2	115	29.7	28.1	119	38.4	15.2	114	28.2
			recovery %	79.7	91.6	97.7	94.9	91.5	99.5	93.8	90.7	92.8
6	240	0		11.7	244	30.6	28.1	237	37.4	14.3	224	26.1
				10.2	244	31.2	29.6	244	37.8	13.6	217	25.0
			mean	11.0	244	30.9	28.8	240	37.6	14.0	220	25.6
			recovery %	85.9	99.3	101.6	97.3	96.0	97.4	86.4	89.5	84.2

TABLE 25. Mg and K recovered in the blank samples of the additional incubation experiment.

ppm added		ppm recovered after 2 wetting and drying cycles		Recovery %	
Mg	K	Mg	K	Mg	K
0	97.5	0	97	--	99.5
		0	100	--	102.6
		0	98.5	--	101.0
0	195	0	204	--	104.6
		0	202	--	103.6
		0	203	--	104.1
120	0	118	0	98.3	--
		118	0	98.3	--
		118	0	98.3	--
240	0	251	0	104.6	--
		251	0	104.6	--
		251	0	104.6	--

NH_4OAc after the incubation to cation extracted in treatment 1 (not incubated) plus cation added before the incubation.

The analyses of the HCl extracts following the NH_4OAc extraction showed no content of Ca, Mg, and K. Before analyzing the results obtained with the soil samples it is convenient to look at the analyses of the blank samples (see Table 25). The recoveries of K and Mg in the blank samples agree very well with the expected values. The relative error was always below 5%. This indicates that the solutions used as source of K and Mg, although not true standard solutions, had a composition very close to the expected one.

All the samples of this experiment were analyzed on the same day and therefore, the "time effect" discussed before could still be present but presumably in a more restricted way. In general, it can be said that the recoveries of Ca, Mg, and K in the soil samples (see Table 24) were such that no indication exists that these soils fixed agronomically significant amounts of Ca, Mg, or K, under the conditions of the experiment. In some treatments and samples the recoveries were somewhat low (between 85 and 90%) but evey if they reflect a real process in the soils and not experimental errors, the practical importance of it is small because very small amounts are involved.

In order to analyze the data in more detail, it should be noticed that the variation between duplicates was larger, for a given element, in those treatments in which that element was applied. Therefore, the analyses of variance

will be performed in such a way as to remove the problem of non-homogeneity of variances. We know that the soils differ in the levels of exchangeable Ca, Mg, or K and so the main effect for soils is of no interest in this case. Similarly, the main effect of treatments for a given element is of no interest in those treatments that received that element. Therefore, the data will be analyzed as a factorial design, considering all the 6 treatments in the case of Ca, treatments 1, 2, 3, and 4 in case of Mg, and treatments 1, 2, 5, and 6 in the case of K.

Calcium. The experimental error (between duplicates error) was 1.0 ppm. The analysis of variance showed a statistically significant effect (at $\alpha = 5\%$) of treatments. This implies that the exchangeable Ca changed significantly with incubation in the treatments that received K or Mg, as there is no significant difference between treatments 1 and 2. The LSD (5%) for comparing means of duplicates is given by $LSD = S_D t_{0.975(18)} = 2.1$ ppm. A detailed examination of all of the sample means shows that, within soils, only 3 means differ significantly from the mean of treatment 1. Two of those means occur in soil MK-1 and at each of the low level of added K and Mg. This suggests that the differences observed are due only to experimental error (e.g. differences in the standard solutions or in the sensitivity of the spectrophotometer) and it seems reasonable to conclude that there was no real change in the exchangeable Ca either with incubation alone or with incubation following the addition

of KCl or $MgSO_4$. (Note: the value 26.1 ppm observed in soil MR-1 Treatment 5, was considered anomalous and deleted). The interaction soils x treatments was not significant (at a = 5%).

Magnesium. The analysis of variance (treatments 1 to 4) showed that the main effect of treatments was barely significant at the 5% level. The F ratio for main effect of treatments was 3.492 against a tabulated $F_{(3,12)\ 0.95} = 3.49$. The between-duplicates error was 0.27 and the LDS (5%) for comparing means of duplicates is 0.6 ppm. Comparing means within soils it can be seen that the only mean that differs significantly from the mean of treatment 1 is the mean of treatment 4 in the soil MR-15. A contrast of the mean of treatment 1 vs the average of means of treatments 2, 3, and 4 showed that in soil MR-15 inculation led to significantly higher levels of exchangeable Mg (at a = 5%). So it is possible that the soil MR-15 released a small amount of Mg from non-exchangeable into exchangeable form (0.6 ppm of Mg, on the average). This small amount could also be just a product of experimental error. The interaction soils x treatments was not significant.

In relation to the recovery of Mg in the treatments that received $MgSO_4$, the results are not fully consistent. The recovery at the low level of added Mg was about 91% for all soils, giving deficits of 10.6, 11.0, and 11.7 ppm of Mg. It is rather unlikely that all the 3 soils would "fix" almost exactly the same amounts of Mg. Besides, in the soil MR-1, the recovery at the high level of added Mg was

99.3%, i.e. 1.6 ppm of Mg were not recovered. Therefore, the experimental error for treatments 5 and 6 could be around 10 ppm. The Mg not recovered at the high levels of added Mg in soils Cl-18 and MR-15 was 10.0 and 25.7 ppm, respectively. If the experimental error is indeed around 10 ppm, the low Mg recoveries in treatments 5 and 6 would not be statistically significant. Even if they represent a real Mg "fixation" by the soils, the agronomic importance is negligible, under the conditions of the experiment.

Potassium. The analysis of variance of treatments 1, 2, 5, and 6 showed no significant main effect of treatments (at a = 5%) but the interaction soils x treatments was significant (at a = 5%). This could be attributed to the rather low recoveries of K in the soil MR-15. The experimental error (between duplicates was 1.1 ppm. The LSD (5%) for comparing means of duplicates is 2.4 ppm. The incubation led to significantly less exchangeable K (at a = 1%) only in the soil MR-15, with an average "fixation" of 3.5 ppm of K. This agrees with the results of the main incubation experiment, and so its likely that the soil MR-15 can "fix" a few ppm of K when subjected to wetting and drying, although in the long run no net fixation of K would occur in this soil.

The recovery of K in the treatments that received KCl was between 86.8 and 97.2%. The results are consistent in the sense that they suggest some "fixation" of K at both the low and high levels of added K. The K not recovered at the low and high levels of added K was,

respectively, 14.9 and 17.4 ppm in the soil MR-1, 11.1 and 7.6 ppm in the soil C1018, and 16.9 and 6.4 ppm in the soil MR-15 (note the large variation between duplicates in the last case). In relation to the possible agronomic importance of such fixation, firstly, even if it is real, the amounts involved are rather small. In the second place, it is not known what would happen under more wetting and drying cycles, or under field conditions with leaching and removal by plants going on. It is even unknown whether or not N NH_4OAc at pH 7 extracts only K available to plants in these type of soils.

In a similar experiment, Tincknell and López (1962) found that 2 poor red latosols of Venezuela, with 44 and 36 ppm of exchangeable K, fixed only an average of 9 and 8 ppm of K upon wetting and drying after the addition of 100 ppm of K (as KCl).

It is necessary to evaluate the ability of several extractants to estimate the plant available K as well as Ca and Mg, in the soils of the Eastern Plains of Colombia. It is likely that the bases exchangeable with NH_4OAc are not equivalent to the bases available to plants. Oliveira, et al (1971) affirm that in the highly weathered soils of Rio Grande do Sul, Brazil (mostly Ultisols and Oxisols) the responses to K application were not as clear as with other micronutrients and lime, even in some soils with as little as 20 ppm of exchangeable K. They compared several extractants and found that although no one of them was better than the others, all of them extracted only a small fraction

of the K taken up by several cuttings of ryegrass in 5 months. It was speculated that the presence of interlayer Al and Fe oxides in such soils could be responsible for this behavior. Ekpete (1972,b) compared 13 laboratory methods for extracting K from 20 soils of Eastern Nigeria, some of them red soils; except for water extractions all other methods gave high correlation with the available K, as measured by uptake of millet and sorghum in pots. On the other hand plants differ in their ability to extract K from different sources in the soil. According to Tincknell and López (1962), tobacco shows deficiency symptoms when NH_4OAc exchangeable K is low even though K extracted with HNO_3 may be high, but cotton and maize do not show them unless both are low.

Another factor to take into account in relation to this experiment is the fact that only KCl and $MgSO_4$ were added to the soils. However, given the very low levels of exchangeable Ca and the very low reserves of total Ca in these soils, as well as the high acidity, application of $CaCO_3$ seems essential for crop productiot and, eventually, even for the management of improved pastures. From the results obtained in both incubation experiments, it can be said that more research is needed to study what changes occur in the exchangeable basic cations when $CaCO_3$ and K or Mg are added to these soils. It seems that the soils of the Llanos of Colombia could "fix" some Ca and Mg when $CaCO_3$ or other liming material is applied to them. The work done on oxide systems (see Literature review) and a few data reported about soil

systems as well as the experiments described here support this hypothesis. Such fixation would vary with the kinds of amendments and fertilizers added, because the specific adsorption of cations on oxides is strongly dependent on pH (Stumm and Morgan, 1970; Huang and Stumm, 1973; Breenwsma, 1973).

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No data is available to make a balance of additions and removals of bases from soils of the Llanos orientales. The magnitude of additions in the rain and potential aeolian additions have not been estimated. Not considering leaching losses, the removal of bases under the extensive livestock exploitations practiced today would be very small.

Assuming that the mineral matter content of cattle in the Llanos is Ca: 1.2%, Mg: 0.04, and K: 0.20% (see Morrison, 1961, p. 640), the removal of Ca in the cattle would be only 0.12 kg/ha/year under a system in which the load is 1 head/10 ha and the young bulls are moved to another area when they weigh 300 kg, after 3 years. The removal of Mg and K would be correspondingly smaller. Under an improved system, having 1 head/ha and removing bulls with a weight of 400 kg after 3 years, the removal of Ca would be 1.6 kg/ha/year. Losses of this magnitude can be compensated by cations apported in the rain. Recently Kozák and Mészaros (1971) reviewed the literature on addition of cations in the rain. The ranges reported were Ca, 1.0 - 83.0; Mg, 0.2 - 17.3; and K, 0.3- 39.8 kg/ha/year.

5 SUMMARY AND CONCLUSIONS

The contents of total Ca, Mg, K, and Fe, and the Ca, Mg, and K exchangeable with N NH_4OAc were determined in 19 soil samples of the Eastern Plains of Colombia, 7 of them representing surface soils. Analyses of total elemental content of the clay and silt fractions of some samples were also performed.

The exchangeable bases are extremely low and decrease sharply from the surface soil to the subsoil. The mean contents of Ca, Mg, and K were 0.083, 0.048, and 0.070 meq/100 g, respectively, in the surface soils, and 0.028, 0.025, and 0.035 meq/100 g, in the same order, in the subsoils. The highest correlation found was between the exchangeable Ca and Mg.

For the analyses of total elements two digestion procedures, HF-H_2SO_4 and HF-HCl, were compared. Both methods gave comparable results and, especially, it was found that in these soils the Ca content is not underestimated by the HF-H_2SO_4 method.

The total Ca content in these soils is extremely low (<100 ppm) and up to 50% of it or more is in exchangeable form. It seems that these low Ca reserves are associated mainly with the organic fraction. The total Mg was between 400 and 1000 ppm. The total K was between 700 and 5000 ppm, although most of the samples had around 1500-2000 ppm of K. The total Fe content was between 1.5 and 3.5%. No substantial differences were found between surface soils and

subsoils in relation to the total contents of Mg, K, and Fe, although all of them tended to be higher in the latter. The proportion of total Mg exchangeable with NH_4OAc was below 1% in all but 2 of the samples. Less than 2% of the total K was exchangeable with NH_4OAc in most of the samples. A high correlation existed in general between the total K and Mg.

Comparing the analyses of total elements in these soils with some of the data reported in the literature for highly weathered soils of the tropics, it can be said that the soils of the altillanura plana of the Eastern Plains of Colombia have generally lower contents of total K, Mg, and specially Fe and Ca. The data indicate that these soils were derived from parent materials low in mafic minerals.

In the soil samples from the Carimagua pit most of the total K, Mg, and Fe were found in the clay fraction. Almost all of the Fe was present as free iron oxides extractable with CBD.

To study the possible release of Ca, Mg, and K from non-exchangeable forms, the soils were incubated for 52, 130, and 286 days, subjected to 2, 5, and 11 wetting and drying (W-D) cycles, respectively. The incubation included check soils, soils leached with 10^{-3}M HCl, and soils that received $CaCO_3$.

The exchangeable Ca, Mg, and K showed small fluctuations, in general, upon incubation. The fluctuations were considered normal and/or related to the experimental error in most of the cases. An exception, however, was the

consistent and significant decrease in the exchangeable Mg in the soils that received $CaCO_3$, as well as the low recoveri of added Ca (as $CaCO_3$).

Considering the cations extracted with HCl before the incubation, the soils leached with HCl showed slightly higher exchangeable Ca, Mg, and K after 11 W-D cycles than the check soils or the soils that received $CaCO_3$. This was shown to be an effect of the HCl extraction and not of the incubatio itself, i.e., the HCl extraction solubilized some Ca, Mg, and K but in very small, almost negligible amounts.

There was no significant and consistent effect of increasing the number of W-D cycles on the exchangeable bases.

The effect of several additional factors during the incubation experiment was also tested in 3 soils. No difference was found between the effect on the exchangeable K of $CaCO_3$ applied at the rates of one or twice the equivalent of exchangeable Al, but the exchangeable Mg decreased significantly upon incubation at both rates of $CaCO_3$, the decrease being significantly larger at the highest rate of added $CaCO_3$. Keeping the soils wet for 130 or 286 days (after leaching with HCl) had no effect on the exchangeable bases. There were no significant differences in the exchangeable bases after incubation between the leaching of the soils with 100 and 200 ml of 10^{-3}M HCl. Drying the soils at 35°C at the end of each W-D cycle had no effect, in general, on the exchangeable bases.

Not considering the treatments in which $CaCO_3$ was added, and excepting a few cases, the soils incubated did not show

any significant "fixation" or release of Ca, Mg, or K, upon incubation. Significant in this context means greater than 4 ppm for Ca or K, and 1 ppm for Mg, roughly. The largest changes, significant or not, generally occurred in the surface soils. This could be related to the higher organix matter content in them, or also the higher content of intergradient 2:1-2:2 minerals in the surface soils. The inability of these soils to release bases, specially in the soils leached with HCl, is somewhat surprising given the presence of traces or small amounts of mica-vermiculite and intergradient type minerals or even feldspars. The possibility exists of low solubility of such minerals due to coatings by iron oxides as well as by blocking effects of hydroxy-Al and -Fe interlayers. This does not mean necessarily that this is what happens in the field. The fact that native grasses and trees and other introduced species do better than would be expected in these circumstances indicates that plants may have some mechanisms for getting more Ca, Mg, or K than the quantities indicated as exchangeable by NH_4OAc. Root exhudates could play an important role in this respect.

The Ca recovered after incubation in the treatments that received $CaCO_3$ was consistently below 100%. This could be attributed to experimental error but only in part. There are indications to suggest that these soils may specifically adsorb Ca and Mg, when $CaCO_3$ or other liming material is applied to them. Such specific adsorption would occur on Fe and Al oxide surfaces.

In an additional incubation experiment, $MgSO_4$ or KCl were added to 3 of the soils, in the absence of added $CaCO_3$. After 2 W-D cycles (52 days) it was found that the application of neither one had an effect on the exchangeable Ca. The results indicate that some of the soils could "fix" very small amounts of Mg (25 ppm or less) when up to 240 ppm of Mg were added, or very small amounts of K (20 ppm or less) when up to 195 ppm of K were added. It was considered that such "fixation", if real, does not have agronomic importance at the rates at which Mg or K were applied to the soils. However, it is necessary to study the combined effects of liming and fertilizing on the fate of the initially exchangeable and added bases.

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7 APPENDIX

Appendix Table 1. Description of the soil profile corresponding to samples MR-8-9 to MR-14 (Carimagua). Data of Guerrero, which were reported as "soil profile No. 4 - Carimagua."

Description: Pit by R. Guerrero and S. W. Buol.

Date: August 4, 1969.

Location: Approximately 300-500 meters west of the Carimagua ranch house, near and along the fence of the experimental field.

Vegetation: Treeless savanna; herding area.

Physiography. Apparently intermediate position.

Parent Material: Mixed acid alluvial sediments.

Slope: 0-1%.

Drainage: Well drained (to somewhat poorly drained?).

Erosion: None.

Depth to Water Table: Deep.

Remarks: Possibly water table at this place is influenced by the short distance to the Carimagua lake (400 meters). An apparent catena was observed along the ditch to the lake.

0 - 8 cm Very dusky red (2.5YR 2/2); silty clay loam; weak, coarse, massive that breaks into moderate, fine, subangular blocky structure, hard when dry, slightly sticky when wet; many medium and fine roots; clear, smooth boundary.

8 - 22 cm Dark reddish brown (5YR 3/4); clay loam; weak, medium subangular blocky structure; friable when moist, many, fine roots, pockets and tongues of organic material transported from first horizon; gradual, smooth boundary.

22-46 cm Yellowish red (5YR 4/8); clay loam; moderate fine subangular blocky structure, slightly sticky when wet, many roots but less than above, channels and tongues of organic materials from first horizons, gradual, wavy boundary.

46-132 cm Yellowish red (5YR 5/8)with few, faint, fine (10YR 6/6) brownish yellow mottlings; light silty clay loam; weak, fine, subangular blocky structure;friable when moist; common, fine roots; diffuse, wavy boundary.

132-140 cm Yellowish red (5YR 5/8) with common strong brown (7.5YR 5/8) and red (20 R 5/8) medium, faint mottlings; silty clay; slightly sticky; few fine roots.

Appendix Table 2. Description of the soil profile corresponding to samples C2-6, C2-2 and C2-3 (El Piñal). Data of Guerrero, which were reported as "soil profile No. 1 - El Piñal."

Description: Pit by R. Guerrero and S. W. Buol.

Date: August 2, 1969.

Locations: Approximately 1-1.5 km east of the El Piñal ranch house and about 200 meters south of the Meta cliff; southwest corner of I.C.A. 1969 experiments, between fence and air strip.

Vegetation: Treeless savanna.

Physiography: Typical river bank plain draining toward the Meta River.

Parent Material: Mixed acid alluvial sediments.

Slope: At the place, 0-1%.

Drainage: Somewhat excessively drained.

Erosion: By wind?

Depth to Water Table: Deep.

Remarks: Supposedly a site influenced by wind-blow materials, but rather local and non-representative of the whole area.

0 - 18 cm Dark reddish brown (5YR 3/3); loam; weak, medium subangular blocky structure; firm when moist, non-sticky when wet; many medium and fine roots and earthworm activity as tonguing and channels; gradual, wavy boundary.

18-30 cm Dark reddish brown (5YR 3/4); loam; weak, coarse, subangular blocky structure, at places massive; friable (brittle) when moist; less roots and worm activity than above; gradual, wavy boundary.

30-80 cm Red (2.5YR 4/6); sandy clay loam; moderate, medium subangular blocky structure; friable when moist, slightly sticky when wet; common, medium roots; gradual, wavy boundary.

80-160 cm Red (2.5YR 4/6); sandy clay; moderate, medium to coarse subangular blocky structure; sticky when wet; common medium roots; common, medium, soft plinthite nodules at 150 - 160 cm depth, clear, wavy boundary.

160-205 cm (By auger below 185 cm). Red (10 R 4/8); clay; moderate, medium, subangular blocky structure; sticky and slightly plastic when wet; less than 5% of hard but not very hard dark red (10 R 3/6) plinthite nodules about 1 cm of diameter or less; less than 5% of dark reddish brown (5YR 3/3) of organic material as vertical and/or irregular pockets which might be root fillings or animal furrows. No reaction to H_2O_2.

205-210 cm Red but lighter color than above; clay; sticky and plastic; with grayish, few, fine and distinct fibrous mottles along root channels.

Appendix Table 3. Description of the soil profile corresponding to samples C3-1 and C3-2 (Matapalito). Data of Guerrero, which were reported as "soil profile No. 3 Matapalito."

Description: Pit by R. Guerrero and S. W. Buol

Date: August 3, 1969.

Location: Approximately 1.5-2.0 km North-northwest of the Matapalito ranch house and about 2.5 km south of profile 2. Approximately at the boundary of the As-Aa F.A.O. areas (F.A.O., 1965).

Vegetation: Wet-treeless savanna, about 300 meters north of the "estero" (low lands with moriche palms); termite area.

Physiography: Low plain but not the lowest member of the catana; slightly concave position.

Parent Material: Mixed acid alluvial sediments.

Slope: 0-1%.

Drainage: Somewhat poorly drained to moderately well drained.

Erosion: None.

Depth to Water Table: 92 cm (3 ft. 1 in.).

Remarks: Soft plinthite nodules at intermediate horizons.

0 - 16 cm	Very dark gray brown (10 YR 3/2); clay loam; moderate, fine, subangular blocky structure; friable when moist; slightly sticky and plastic when wet; many, small, medium roots; clear, wavy boundary.
16 - 42 cm	Dark gray brown (10YR 3/3); clay loam; weak, fine and medium subangular blocky structure; firm when moist, slightly sticky and plastic when wet; common, fine roots; gradual, smooth boundary.
42 - 70 cm	Gray brown (10YR 5/2) with common, medium, distinct, reddish brown (5YR 4/5) and yellowish red (5YR 4/6) mottlings; clay; moderate, medium; subangular blocky structure; sticky and slightly plastic when wet; common, medium roots; gradual, smooth boundary.

70 - 145 cm	(Below 92 cm by auger). Strong brown (7.5YR 5/6) with common, fine, faint, strong brown (5YR 5/8) mottles; clay; weak, medium, subangular blocky structure; few, medium, soft plinthite nodules; sticky and plastic when wet.
145 -170 cm	Color becomes redder; clay; plastic and sticky when wet; soft plinthite about 20% of the soil.

Appendix Table 4. Description of the soil profile corresponding to samples C4-1-2 and C4-3 (El Viento). Data of Guerrero, which were reported as "soil profile No. 7 - El Viento."

Description: Pit by R. Guerrero and S. W. Buol.

Date: August 5, 1969

Location: Along fence of I.C.A. 1969A field experiments; approximately 200 meters south of the experiments and about 200 meters north of "estero" (swampy palms).

Vegetation: Treeless savanna with common hydrophytic species.

Physiography: Low member of the catena and wet savanna, but not the lowest. Termites are common.

Parent Material: Mixed acid alluvial sediments.

Slope: 0-1%.

Drainage: Somewhat poorly to moderately-well drained.

Erosion: None.

Depth to Water T.ble: 77 cm.

Remarks: Apparently worse drainage than site No. 3.

0 - 10 cm	Very dark gray brown (10YR 3/2); silt loam; weak, fine, subangular blocky structure breaking to weak, fine granular; friable when moist, slightly sticky and plastic when wet; many, fine and medium roots; clear, smooth boundary.
10 - 25 cm	Dark brown (10YR 4/3); silty clay loam; moderate medium to fine subangular blocky structure; friable when moist, slightly sticky when wet; common, fine and medium roots and pockets of organic material; gradual, smooth boundary.
25 - 44 cm	Dark yellowish brown (10YR 4/4) with brown 7.5YR 4/4) and pale brown (10YR 6/3) few, fine, distinct mottles; silty clay; weak, fine subangular blocky structure; stickier and more plastic than above when wet; common, small roots; gradual, wavy boundary.

44 - 77 cm	Strong brown matrix (7.5YR 5/6) with brown (7.5YR 5/4) common, medium, faint mottles; red plinthite nodules (10 R 3/6); silty clay; weak, fine angular and subangular blocky structure; stickier and more plastic than above in wet; few small roots; diffuse boundary.
77 - 188 cm	(By auger). Roughly the same color; clay; no plinthite nodules.

Appendix Table 5. Chemical characteristics. Data of Guerrero, which were reported as soil profiles No. 1, 3, 4, and 7 respectively.

Locality (pit)	Depth	pH H_2O 1:1	pH KCl 1:1	Organic carbon	CEC	Ca	Mg	K	Na	Exch. Al	Exch. H	Sum of cations	Base saturation by sum of cations
	cm			%	meq/100 g soil								%
	0-18	4.6	3.6	1.5	6.1	.2	.2	.1	.2	1.7	.8	3.2	22
	18-30	4.6	3.7	0.9	4.7	.1	.1	.1	<.1	1.7	.5	2.5	14
El Piñal	30-80	4.6	3.8	0.5	4.4	.1	.1	<.1	.1	1.4	.4	2.1	16
	80-160	4.8	3.9	0.2	5.4	.1	<.1	<.1	.1	0.9	.5	1.7	18
	160-185	4.9	3.7	--	5.8	.1	.1	<.1	.1	1.2	.7	2.2	16
	185-205	5.0	3.5	--	5.9	.1	.1	<.1	.2	1.8	.7	2.9	15
	205-210	5.0	--	--	--	.1	.2	<.1	.2	--	--	--	--
	0-16	4.4		1.9	13.2	.2	.2	<.1	.2	2.8	.6	4.1	16
	16-42	4.4		1.2	11.6	.2	.2	<.1	.2	2.3	.6	3.6	18
Matapalito	42-70	4.6		0.9	8.4	.2	.2	<.1	.2	1.5	.9	3.2	20
	70-92	4.8		0.6	8.0	.2	.1	<.1	.1	0.8	.7	2.0	23
	92-112	4.9		--	4.8	.2	.2	<.1	.3	0.8	.8	2.4	31
	145-170	5.1		--	6.0	.2	.2	<.1	.3	0.9	.8	2.5	30
	0-8	4.8	3.6	3.1	13.0	.6	.8	.5	.5	3.1	1.0	6.5	37
	8-22	4.7	3.6	1.7	10.1	.2	.2	.2	.2	3.2	.6	4.6	17
Carimagua	22-46	4.4	3.8	1.1	8.8	.2	.1	.1	.1	1.9	.5	2.9	17
	46-132	4.9	4.1	0.6	6.0	.1	.1	.1	.1	0.6	.4	1.4	29
	132-140	5.4	4.3	--	7.0	.2	.4	.1	.2	0.3	.4	1.6	56
	0-10	4.7	--	2.8	12.0	.4	.4	.1	.1	2.4	1.7	5.1	20
	10-25	4.5	--	1.9	10.6	.3	.4	.1	.1	2.5	.8	4.2	21
El Viento	25-44	4.6	--	1.1	6.4	.2	.3	<.1	.1	1.7	.6	3.0	22
	44-77	4.8	--	0.7	7.4	.2	.2	<.1	<.1	0.8	.5	1.8	28
	77-137	5.4	--	0.5	7.4	.2	.1	<.1	<.1	0.1	.5	1.0	40

Appendix Table 5. (continuation)

pH determined potentiometrically, after 30 min. of equilibrium. Organic carbon determined by the methods described by Peech and Walkley (Soil Conservation Service, 1967. Soil survey laboratory methods and procedures for collecting soil samples).

CEC with NH_4OAc at pH7.

Ca, Mg, Na, and K extracted with NH_4OAc; Ca and Mg determined by atomic absorption; K and Na by flame photometry.

Exchangeable Al and H extracted with N KCl and determined by titration with NaOH and HCl.

Appendix Table 6. Some chemical and physical characteristics. Data of Guerrero, which were reported as soil profiles No. 1, 3, 4, and 7, respectively.

Locality (pit)	Depth	Calgon-pipette with O. M. removed: Sand 2mm -50u	Silt 50u -2u	Clay < 2u	H_2O dispersible: Clay	Sand	H_2O at 15-bars	Clay by 15-bars	Fe_2O_3
	cm	%	%	%	%	%	%	%	%
	0-18	32	49	19	15	40	8.6	22	--
	18-30	32	48	20	19	34	8.1	20	--
El Piñal	30-80	31	46	23	21	30	9.1	23	--
	80-160	28	46	26	3	29	12.2	31	--
	160-185	28	45	27	3	28	12.4	31	--
	185-205	28	38	34	3	27	12.6	32	--
	205-210	21	40	39	3	21	--	--	--
	0-16	39	30	31	--	--	12.0	30	--
	16-42	35	31	34	--	--	12.5	31	--
Matapalito	42-70	33	32	35	--	--	12.8	32	--
	70-92	32	30	38	--	--	14.3	36	--
	92-112	32	31	37	--	--	14.0	35	--
	145-170	35	30	35	--	--	13.9	35	--
	0-8	7	58	35	27	12	14.6	37	6.0
	8-22	11	51	38	32	11	13.8	35	7.1
Carimagua	22-46	19	41	40	38	10	14.7	37	7.4
	46-132	10	47	43	3	13	14.8	37	7.4
	132-140	8	43	49	3	14	19.0	48	7.4
	0-10	15	50	35	--	--	14.3	36	--
	10-25	13	48	39	--	--	14.3	36	--
El Viento	25-44	12	45	43	--	--	15.6	39	--
	44-77	11	45	44	--	--	16.1	40	--
	77-137	11	46	43	--	--	17.1	43	--

H_2O at 15-bars pressure was determined by pressure membrane equipment. The clay percentage was calculated by multiplying the weight percentage of water retained by the factor 2.5.

Fe_2O_3 extracted with citrate-dithionite.

Appendix Table 7. Selected chemical characteristics of some samples

Locality	Sample	Depth cm	pH		Exch. Al		Exch. bases c			organic matter %	P ppm
			H_2O 1:1	N-KCl 1:1	a	b	Ca	Mg	K		
			------ meq/100 g ---------								
Carimagua	MR-1	0-15	3.95	3.72	3.98	2.63	0.125	0.062	0.064	3.6	0.5
	MR-7	33-50	3.90	---	---	2.50	0.125	0.042	0.019	1.6	0.5
La Libertad	Cl-18	0-20	3.79	3.77	3.58	2.78	0.125	0.104	0.096	4.0	0.5
	Cl-19	20-40	4.08	---	----	3.19	0.125	0.042	0.042	2.6	0.5
El Piñal	MR-15	0-15	4.00	3.87	2.47	1.88	0.125	0.062	0.058	1.6	0.5

pH determined after 1 hour of equilibrium, with calomel electrode in the supernatant liquid.

a) Exchangeable Al with N KCl

b) Exchangeable Al with Morgan solution (Sodium acetate - acecit acid, pH 4.8)

c) Extraction with Morgan solution

Appendix Table 8. Mineralogical analyses of selected horizons. Data of Guerrero.

Locality	Depth cm	Particle size, microns			
		<.2	.2-2	2-5	5-20
North Beach (Meta River)[a]	0-10	$K^3M^2 2:1^1$	$K^3I^TM^2 2:1^1$	$K^1I^2M^2Q^2F^T$	$K^2M^2Q^3F^1$
Tabarís [b]	20-34	$K^3I^2P^1$	$K^2I^2P^1$	$K^1I^1P^1Q^3$	$K^TI^1P^TQ^3$
	178-208	$K^3I^1P^T$	$K^3I^1P^2M^1V^2$	$K^1I^TP^1M^1Q^3F^1$	$K^1I^TP^1M^1P^1Q^3$
Carimagua[c]	8-22	$K^3I^3P^T$	$K^2I^3P^1$	$K^1I^1P^TM^TQ^3S^T$	$K^TQ^3V^T$
	132-140	$K^3I^2P^T$	$K^2I^2P^1$	$K^1I^1P^TM^TQ^2F^T$	$K^1I^TP^1 M^TQ^3F^1$
Carimagua[d]	12-32	$K^3I^2P^T$	$K^3I^3P^1S^T$	$K^2I^1P^1M^1Q^3V^T$	$K^1I^TP^1M^1Q^3F^1S^1$
	88-148	K^3I^2	$K^2I^2P^1M^1F^1S^1$	$K^1I^1P^1M^1Q^3F^2S^1$	$K^1P^1M^1Q^3F^1S^1V^T$
El Viento[e]	10-19	$K^3I^2P^T$	$K^2I^2P^1$	$K^1I^1P^1Q^3S^1$	$K^1I^1P^TM^TQ^3F^1$
	105-140	K^3I^1	$K^3I^2P^1$	$K^1I^TP^1M^1Q^2S^1$	$K^1I^TP^1M^1Q^3F^TS^1$

KEY: K - Kaolinite
I - Intergradient 2:1 - 2:2
P - Pyrophyllite
M - Mica
Q - Quartz
F - Feldspars
V - Vermiculite
S - Vermiculite-Mica Stratification
2:1 - Smectite

Semi-Quantitative Estimation: (by visual comparison of the height and width of the X-ray diffractogram peaks)
3 - Abundant (>50%)
2 - Medium (25-50%)
1 - Small (10-25%)
T - Trace (<10%)

a. sample taken 7 km NE of El Piñal
b. Tabarís is a farm midway between El Piñal and Matapalito (10 km apart approximately).
c. Same pit as samples MR-8-9 to MR-14
d. pit at 5 km NE of pit c.
e. pit at 2 km N of samples C4-1-2, C4-3.

Appendix Table 9. Mineralogical composition of the clay size fraction of the Carimagua pit. Data of Weaver.

sample	depth cm	Mica	Vermic	Al-chlor	Kaol	Gibb	Amorp	Total
MR-9	8-20	8	4	27	31	1	20	91
MR-11	38-94	8	3	23	31	1	21	87
MR-14	94-114	10	3	23	31	1	21	89
MR-13	114-137	11	4	14	40	1	21	91

Based on X-ray diffraction and differential thermal analysis. The quantitative estimates are based on chemical techniques and thermal gravimetric analysis.

Appendix Table 10. **Mineralogical analyses of samples from La Libertad and El Piñal.** Data of León (X-ray diffraction). **Relative amounts** are indicated by the number of + 's

Soil	depth (cm)	mineral contents												
		< 2 μ clay								silt 2-50 μ				
		Mt	Mi	Vr-C	K	G	H	Q	A	F	Q	Cr	Cm	FeOX
La Libertad	0-14	0	+	+++	++	+	0	+	+	0	+++++	0	0	0
	14-39	0	+	+++	++	+	0	+	+	0	+++++	0	0	0
El Piñal	0-21	0	0	++	+++	tr	0	tr	+	0	+++++	0	tr	tr
	21-60	0	0	++	+++	tr	0	tr	+	0	+++++	0	tr	tr

Mt montmorillonite
Mi mica
Vr-C vermiculite-chlorite
K kaolinite
G goethite
H hematite
Q quartz
A amorphous

F feldspars
Cr K-cristobalite
CM clay minerals
FeOX iron oxides
tr traces

Samples from El Piñal appear to contain ilmenite and talc.

Appendix Table 11. Water retention at several tensions.

Locality	Sample	Depth cm	Water hold (percent by weight) tension (bars)				
			1/3	2/3	1	5	15
El Viento	C4-1	0-10	34.2	29.5+	27.2	21.1	17.7
	C4-2	10-19	32.8	27.0+	25.8	20.4	17.3
	C4-3	19-31	32.4	27.1	25.2	20.0	17.4
	C4-5	31-105	33.0	27.4	25.6	20.5	18.2
Matapalito	C3-1	0-16	23.5	20.8	18.6	13.7	11.6
	C3-2	16-42	22.4	19.7	17.8	13.5	11.8
	C3-3	42-72	19.8	17.2	16.0	13.2	12.0
	C3-4	72-92	20.0	18.0	16.6	14.2	12.7
	C3-5	145-175	23.2	---	18.2	---	13.2
El Piñal	C2-6	0-16	21.0	---	13.3+	---	---
	C2-2	18-30	19.4	16.6	13.0	9.8	8.3
	C2-3	30-80	16.6	14.6+	12.2	10.2	9.0
	C2-4	80-160	17.4	15.2	13.4	11.6	10.2
	C2-5	160	19.5	19.0+	15.2	13.6	12.0
La Libertad	C1-18	0-20	23.5	20.8	18.2	17.3	12.6
	C1-19	20-40	22.8	19.9	19.5	17.0	15.1
Carimagua	(a)	0-20	31.0	27.2	24.0	20.9	17.2
Carimagua	(b)	0-20	37.1	29.8	24.4	17.4	13.6

(a) sample taken in the agronomy field, close to the Carimagua pit.

(b) sample taken a few meters apart from sample MR-1

Determinations done with the pressure membrane equipment.

Figures are averages of two determinations, except those marked with (+)

Appendix Table 12. Determination of exchangeable Ca, Mg, and K. Comparison of several methods in the handling of the NH_4OAc extracts.

The NH_4OAc extracts were obtained as described under Materials and Methods. The experiment was conducted as a CRD, with 2 replications, and using the soils MR-1 and MR-15.

A. - Treatments

1) Handling of the NH_4OAc extracts as described in Materials and Methods under Exchangeable Ca, Mg, and K. Parafilm plastic was used when it was necessary to cover the erlenmeyer flasks.

2) The same as treatment 1 (T-1), but, instead of Parafilm plastic, rubber stoppers were used when the soil suspensions were shaken during the equilibration of the samples with 20 ml of NH_4OAc, and whenever it was necessary to cover the containers.

3) The same as T-1, but watch glasses were used during the several evaporations to dryness. The watch glass was rinsed with distilled water (into the container).

4) The same as T-3, but watch glasses were used only during the evaporation to dryness of the 10 ml of H_2O_2:H_2O (1:1).

5) The same as T-1, but only 4 ml of HCl:H_2O (1:1) were added (trying to rinse the container walls) before the final evaporation to dryness.

6) The same as T-1, but, instead of destroying the organic matter with H_2O_2, the samples were put in the muffle furnace

at 480°C, for 9 hours, covered with watch glasses. Then, 20 ml of HCl: H_2O (2:8) were added and evaporated to dryness in the hot plate (as in T-1).

7) The same as T-1, but, when the 10 ml of H_2O_2: H_2O were added, the samples received 10 ml of HCl: H_2O (1:4), to get an acid solution and were covered with watch glasses during this evaporation to dryness.

Two blank samples were also ran for each one of the 7 treatments. The samples were sent to the Analytical Service Laboratory for analysis of Ca, Mg, and K by atomic absorption.

B. - Results

The analyses are presented in Appendix Table 12.1.

C. - Comments

The very high Ca values obtained in treatments (T) 4 and 7 in the soil MR-15 seemed quite abnormal and were checked several times immediately after the first analysis. The same solutions were analyzed again 13 days later and the values obtained were the following:

T-4: 28.0 and 26.0 (original values : 92.0 and 92.0)

T-7: 32.0 and 26.0 (original values : 94.0 and 94.0)

No explanation was found for either the high values or the sharp differences between the 2 dates of analysis.

Appendix Table 12.1

Comparison of several methods in the handling of NH_4OAc extracts for the determination of exchangeable Ca, Mg, and K.

Method \ Soil	Ca, ppm		Mg, ppm		K, ppm	
	MR-1	MR-15	MR-1	MR-15	MR-1	MR-15
1	13.0	19.0	4.9	5.9	29.5	28.9
	14.2	19.0	7.9	6.1	32.5	29.2
	13.6	19.0	6.4	6.0	31.0	29.0
2	13.4	25.4	5.5	6.4	30.8	29.5
	13.4	17.4	5.5	6.0	30.8	29.2
	13.4	21.4	5.5	6.2	30.8	29.4
3	15.0	20.2	5.7	6.6	32.5	31.2
	15.0	22.8	5.7	6.8	29.2	32.5
	15.0	21.5	5.7	6.7	30.8	31.8
4	14.0	92.0	5.2	6.1	30.8	30.8
	15.5	92.0	5.6	6.1	30.8	30.4
	14.8	92.0	5.4	6.1	30.8	30.6
5	14.0	18.6	5.3	6.1	28.7	26.7
	14.0	18.6	5.3	6.0	29.2	26.7
	14.0	18.6	5.3	6.0	29.0	26.7
6	12.7	15.1	6.1	6.7	0	0
	12.7	16.6	5.9	6.9	0	0
	12.7	15.8	6.0	6.8	0	0
7	15.2	94.0	5.6	6.9	30.2	31.2
	15.0	94.0	6.0	7.1	31.6	30.6
	15.1	94.0	5.8	7.0	30.9	30.9

Appendix Table 12. (continued)

In relation to the low K values found in T-6, it is explained by complete volatilization of K at the high temperature used in the muffle furnace (480°C).

D. Statistical Analysis

The data were analyzed with the fixed effects model (7 x 2 factorial).

ANOVA Table

Source	d.f.	Mg F	K F	Ca F	$F_{.95}$
methods	6	1.08	599.65**	859.5**	2.85
soils	1	9.31**	3.84	3089.5**	4.60
inter-action	6	0.75	1.65	805.5**	2.85
error M.S.	14	0.3461	0.8746	1.5621	

The above F tests are not of much interest, with the exception of the interaction methods x soils. The highly significant methods effect (at a = 1%) in the case of K can be attributed mainly to the low K levels found in T-6. The high significance obtained for methods and the interaction, in the case of Ca, is due mainly to the very high Ca values found with T-4 and T-7 in the soil MR-15 (but not in the soil MR-1). Of more practical interest are comparisons of the different Treatments, specially in relation to T-1 (considered as a control). Contrasts of the type $C = \bar{X}_1 - \bar{X}_i$, for i = 2,3,...,6, were

Appendix Table 12. (continued)

used to compare the different treatments against the control (T-1), where $\bar{X}i$ is the mean of the i th treatment. Although the 6 contrasts obtained for each element (Ca, Mg, and K) are not orthogonal, they are valid because they were planned before doing the experiment. These contrasts, tested using student-t tests, showed that:

a) For Mg: none of contrasts were significant at a = 5% and even at a = 10%. It should be noted that the high variation between duplicates in T-1, soil MR-1, is giving a high standard error both in the ANOVA and the t-tests. Considering, however, the overall results of the experiment for Ca, Mg, and K, no further attention was given to this fact.

b) For K: The only treatments significantly different (at a = 1%) from T-1 were T-5 and T-6.

c) For Ca: There were not significant differences between each one of treatments 2 to 6 and the control (T-1) in the case of soil MR-1 (even at a = 10%). In the case of soil MR-15, the treatments 4, 6, and 7 were significantly different from T-1 (at a = 5%). Here, again, the high variation between duplicates in T-2 (soil MR-15) is giving a high error.

E. - Conclusions

The most pertinent conclusions drawn from this experiment are:

1) The use of rubber stoppers seems to be a potential cause of contamination, but such contamination is not always present, or if present, does not necessarily affect all the values obtained for Ca, Mg, and K in the same sample.

Appendix Table 12. (continued)

2) The use of only 4 ml of HCl: H_2O (1:1) sometimes gave smaller values than the use of 20 ml of HCl: H_2O (2:8), before the final evaporation to dryness (T-5 vs T-1). The difference was significant only in the case of K (at a = 5%).

3) The use of watch glasses during the evaporations to dryness did not lead to higher values of Ca, Mg, and K than when they were not used.

4) High variation between duplicates may be exceptionally found in some values of a set of analyses. Curiously, this occurs in only one of the elements analyzed but not in the other two (in the same samples).

5) Exceptionally high values were found for Ca in 2 of the treatments and in only one soil. It seems to the author that errors of this magnitude are not present in the other data reported in this study. No explanation was found for this nor for the changes that were found when the analysis was repeated (see comments).

Appendix Table 13. Particle size distribution, Tamm extractable, and CBD extractable Fe_2O_3 and Al_2O_3 in soil samples of the Carimagua pit (Data adapted from Weaver. Organic matter content adapted from Guerrero).

Sample	Depth	Organic Matter	Sand	Silt	Clay	Tamm		CBD		Total
						Fe_2O_3	Al_2O_3	Fe_2O_3	Al_2O_3	
	cm	%								
MR-8	0-8	6.2	9.5	51.1	27.8	0.29	0.36	3.6	1.3	100.15
MR-9	8-20	3.6	9.7	52.5	28.5	0.30	0.37	3.7	1.3	99.97
MR-8-9	0-20	4.2	9.6	51.9	28.2	0.30	0.37	3.7	1.3	99.27
MR-10	20-38	2.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
MR-11	38-94	1.4	9.6	50.9	31.6	n.d.	n.d.	4.6	2.1	100.20
MR-12	94-114	1.1	8.1	50.6	33.4	n.d.	n.d.	4.8	1.9	99.90
MR-13	114-137	1.0	8.1	44.2	39.7	0.17	0.21	5.1	1.5	99.98

Appendix Table 14. Exchangeable Ca, Ca extracted with 100 ml of 10^{-3}M HCl, and Ca extracted with NH_4OAc after the HCl extraction.

Locality	Sample	Depth cm	Exchang. Ca	Ca extracted with 10^{-3}M HCl		Ca extract. with NH_4OAc after HCl	set 9122 plus set 9124	Exch. Ca after HCl extraction. Aver. of set 1 minus set 9111
			set 9112	set 9111	set 9122	set 9124	set 1	
			ppm					
Carimagua	MR-1	0-15	12.1	13.6	12.5	1.5	14.0	0.3
			11.9	13.9	12.2	1.5	13.7	0.0
			12.0	13.8	12.4	1.5	13.9	0.2
	MR-7	33-50	8.0	9.3	8.1	0.9	9.0	0
			8.6	---	---	---	---	---
			8.3	9.3	8.1	0.9	9.0	0
La Libertad	C1-18	0-20	30.1	35.6	34.7	1.8	36.5	1.0
			32.0	33.6	34.7	2.0	36.7	3.0
			31.0	34.6	34.7	1.9	36.6	2.0
	C1-19	20-40	3.2	5.4	5.5	0.0	5.5	0.1
			3.5	---	5.5	0.0	5.5	---
			3.4	5.4	5.5	0.0	5.5	0.1
El Viento (pit)	C4-1-2	0-19	12.1	12.0	10.6	4.3	14.9	3.0
			14.5	---	11.7	3.5	15.2	---
			13.3	12.0	11.2	3.9	15.0	3.0
	C4-3	19-31	3.4	3.9	4.5	0.8	5.3	1.4
			4.2	---	---	---	---	---
			3.8	3.9	4.5	0.8	5.3	1.4

Appendix Table 14. Exchangeable Ca, Ca extracted with 100 ml of 10^{-3}M HCl, and Ca extracted with NH_4OAc after the HCl extraction. (cont'd.)

Locality	Sample	Depth cm	Exchang. Ca	Ca extracted with 10^{-3}M HCl		Ca extract. with NH_4OAc after HCl	set 9122 plus set 9124	Exch. Ca after HCl extraction. Aver. of set 1 minus set 9111
			set 9112	set 9111	set 9122	set 9124	set 1	
			ppm					
El Piñal	MR-15	0-15	15.2	15.7	16.6	2.6	19.2	3.5
			16.5	15.7	16.6	2.6	19.2	3.5
			15.8	15.7	16.6	2.6	19.2	3.5
El Piñal (pit)	C2-6	0-16	7.4	6.7	6.4	0.1	6.5	0.7
			---	---	---	---	---	---
			7.4	6.7	6.4	0.1	6.5	0.7
	C2-2	18-30	2.2	2.5	2.5	0.3	2.8	0.3
			---	---	---	---	---	---
			2.2	2.5	2.5	0.3	2.8	0.3
	C2-3	30-80	1.5	1.3	2.0	0.0	2.0	0.7
			0.8	---	2.0	0.0	2.0	---
			1.2	1.3	2.0	0.0	2.0	0.7
Matapalito (pit)	C3-1	0-16	19.6	22.1	15.9	6.0	21.9	0
			20.0	---	---	---	---	---
			19.8	22.1	15.9	6.0	21.9	0
	C3-2	16-42	7.0	7.6	7.6	1.3	8.9	1.3
			---	---	---	---	---	---
			7.0	7.6	7.6	1.3	8.9	1.3

Appendix Table 14. Exchangeable Ca, Ca extracted with 100 ml of 10^{-3}M HCl, and Ca extracted with NH_4OAc after the HCl extraction.

(cont'd.)

Locality	Sample	Depth cm	Exchang. Ca	Ca extracted with 10^{-3}M HCL		Ca extract. with NH_4OAc after HCl	set 9122 plus set 9124	Exch. Ca after HCl extraction. Aver. of set 1 minus set 9111
			set 9112	set 9111	set 9122	set 9124	set 1	
			ppm					
Carimagua (pit)	MR-8-9	0-20	32.0	33.6	31.3	11.1	42.4	7.4
			33.8	---	27.7	11.9	39.6	---
			32.9	33.6	29.5	11.5	41.0	7.4
	MR-10	20-38	9.0	11.2	10.8	0.9	11.7	0.9
			9.0	---	11.7	0.8	12.5	---
			9.0	11.2	11.2	0.8	12.1	0.9
	MR-11	38-94	5.4	5.5	4.8	1.0	5.8	0.3
			---	---	---	---	---	---
			5.4	5.5	4.8	1.0	5.8	0.3
	MR-12	94-114	6.4	3.8	4.3	1.5	5.8	2.2
			5.5	---	3.8	2.0	5.8	---
			6.0	3.8	4.0	1.8	5.8	2.2
	MR-13	114-137	3.9	2.2	2.6	1.8	4.4	2.3
			3.7	---	2.3	2.3	4.6	---
			3.8	2.2	2.4	2.0	4.5	2.3
	MR-14	150	6.4	4.7	5.7	1.7	7.4	2.7
			---	---	---	---	---	---
			6.4	4.7	5.7	1.7	7.4	2.7

Appendix Table 15. Exchangeable Mg, Mg extracted with 100 ml of 10^{-3} M HCl, and Mg extracted with NH_4OAc after the HCl extraction.

Locality	Sample	Depth cm	Exchang. Mg. set 9112	Mg extracted with 10^{-3}M HCl set 9111	Mg extracted with 10^{-3}M HCl set 9122	Mg extract. with NH_4OAc after HCl set 9124	set 9122 plus set 9124 set 1	Exch. Mg after HCl extraction. Aver. of set 1 minus set 9111
			ppm					
Carimagua	MR-1	0-15	5.2	5.1	5.2	0.4	5.6	0.4
			5.2	5.4	5.0	0.4	5.4	0.1
			5.2	5.2	5.1	0.4	5.5	0.2
	MR-7	33-50	3.3	3.0	3.2	0.2	3.4	0.4
			3.2	---	---	---	---	---
			3.2	3.0	3.2	0.2	3.4	0.4
La Libertad	C1-18	0-20	9.5	9.9	10.6	0.3	10.9	1.0
			9.9	9.6	10.6	0.3	10.9	1.3
			9.7	9.8	10.6	0.3	10.9	1.2
	C1-19	20-40	3.0	2.8	3.2	0.1	3.3	0.5
			3.2	---	3.2	0.1	3.3	---
			3.1	2.8	3.2	0.1	3.3	0.5
El Viento (pit)	C4-1-2	0-19	5.2	5.4	5.0	1.5	6.5	1.0
			5.7	---	5.2	1.1	6.3	---
			5.4	5.4	5.1	1.3	6.4	1.0
	C4-3	19-31	3.3	2.8	2.9	0.8	3.7	0.9
			3.5	---	---	---	---	---
			3.4	2.8	2.9	0.8	3.7	0.9

(cont'd.)

Appendix Table 15. Exchangeable Mg, Mg extracted with 100 ml of 10^{-3}M HCl, and Mg extracted with NH_4OAc after the HCl extraction.

Locality	Sample	Depth cm	Exchang. Mg.	Mg extracted with 10^{-3}M HCl		Mg extract. with NH_4OAc after HCl	set 9122 plus set 9124	Exch. Mg after HCl extraction.
			set 9112	set 9111	set 9122	set 9124	set 1	Aver. of set 1 minus set 9111
			ppm					
El Piñal	MR-15	0-15	5.2	5.4	6.3	0.3	6.6	1.2
			5.7	5.4	6.1	0.4	6.5	1.2
			5.4	5.4	6.2	0.4	6.6	1.2
El Piñal (pit)	C2-6	0-16	3.3	3.0	2.9	0.2	3.1	0.3
			---	---	---	---	---	---
			3.3	3.0	2.9	0.2	3.1	0.3
	C2-2	18-30	1.3	1.4	1.4	0.2	1.6	0.2
			---	---	---	---	---	---
			1.3	1.4	1.4	0.2	1.6	0.2
	C2-3	30-80	1.0	0.8	0.9	0.0	0.9	0.2
			0.8	---	1.0	0.0	1.0	---
			0.9	0.8	1.0	0.0	1.0	0.2
Matapalito (pit)	C3-1	0-16	6.1	5.9	5.2	1.2	6.4	0.5
			6.4	---	---	---	---	---
			6.2	5.9	5.2	1.2	6.4	0.5
	C3-2	16-42	3.8	4.2	3.8	0.4	4.2	0.0
			---	---	---	---	---	---
			3.8	4.2	3.8	0.4	4.2	0.0

Appendix Table 15. Exchangeable Mg, Mg extracted with 100 ml of 10^{-3}M HCl, and Mg extracted with NH_4OAc after the HCl extraction.
(cont'd.)

Locality	Sample	Depth cm	Exchang. Mg. set 9112	Mg extracted with 10^{-3}M HCl set 9111	Mg extracted with 10^{-3}M HCl set 9122	Mg extract. with NH_4OAc after HCl set 9124	set 9122 plus set 9124 set 1	Exch. Mg after HCl extraction. Aver. of set 1 minus set 9111
			ppm					
Carimagua (pit)	MR-8-9	0-20	16.1	17.2	14.6	3.1	17.7	0.8
			15.7	---	15.0	3.3	18.3	---
			15.9	17.2	14.8	3.2	18.0	0.8
	MR-10	20-38	3.5	3.2	3.6	0.3	3.9	0.7
			3.5	---	3.6	0.3	3.9	---
			3.5	3.2	3.6	0.3	3.9	0.7
	MR-11	38-94	2.1	2.4	2.0	0.4	2.4	0.0
			---	---	---	---	---	---
			2.1	2.4	2.0	0.4	2.4	0.0
	MR-12	94-114	2.6	2.1	2.2	0.9	3.1	0.9
			2.9	---	1.9	1.1	3.0	---
			2.8	2.1	2.0	1.0	3.0	0.9
	MR-13	114-137	2.3	1.4	1.5	1.3	2.8	1.4
			2.2	---	1.3	1.4	2.7	---
			2.2	1.4	1.4	1.4	2.8	1.4
	MR-14	150	2.7	2.3	2.0	1.0	3.0	0.7
			---	---	---	---	---	---
			2.7	2.3	2.0	1.0	3.0	0.7

Appendix Table 16. Exchangeable K, K extracted with 100 ml of 10^{-3}M HCl, and K extracted with NH_4OAc after the HCl extraction.

Locality	Sample	Depth cm	Exchang. K	K extracted with 10^{-3}M HCl		K extracted with NH_4OAc after HCl	set 9122 plus set 9124	Exchang. K after HCl extraction. Aver. of set 1 minus set 9111
			set 9112	set 9111	set 9122	set 9124	set 1	
			ppm					
Carimagua	MR-1	0-15	31.2	23.7	22.8	9.4	32.2	8.1
			31.5	24.1	22.4	9.1	31.5	7.7
			31.4	23.9	22.6	9.2	31.8	7.9
	MR-7	33-50	9.5	5.5	5.1	5.0	10.1	4.6
			9.5	---	---	---	----	---
			9.5	5.5	5.1	5.0	10.1	4.6
La Libertad	Cl-18	0-20	42.1	32.0	34.3	9.4	43.7	11.8
			42.1	32.0	34.3	9.6	43.9	11.8
			42.1	32.0	34.3	9.5	43.8	11.8
	Cl-19	20-40	18.3	13.5	13.2	5.0	18.2	5.3
			19.3	---	13.2	5.2	18.4	---
			18.8	13.5	13.2	5.1	18.3	5.3
El Viento (pit)	C4-1-2	0-19	25.7	17.3	16.3	10.8	27.1	9.4
			26.4	---	16.9	9.4	26.3	---
			26.0	17.3	16.6	10.1	26.7	9.4
	C4-3	19-31	14.6	8.6	10.3	4.7	15.0	6.4
			15.4	---	---	---	---	---
			15.0	8.6	10.3	4.7	15.0	6.4

Appendix Table 16. Exchangeable K, K extracted with 100 ml of 10^{-3}M HCl, and K extracted with NH_4OAc after the HCl extraction.
(cont'd.)

Locality	Sample	Depth cm	Exchang. K	K extracted with 10^{-3} M HCl		K extracted with NH_4OAc after HCl	set 9122 plus set 9124	Exchang. K after HCl extraction. Aver. of set 1 minus set 9111
			set 9112	set 9111	set 9122	set 9124	set 1	
			ppm					
El Piñal	MR-15	0-15	30.0	19.9	21.4	9.7	31.1	11.5
			27.9	19.7	21.4	10.4	31.8	11.7
			29.0	19.8	21.4	10.0	31.4	11.6
El Piñal (pit)	C2-6	0-16	15.8	12.4	12.4	4.1	16.5	4.1
			---	---	---	---	---	---
			15.8	12.4	12.4	4.1	16.5	4.1
	C2-2	18-30	6.4	5.8	5.8	2.6	8.4	2.6
			---	---	---	---	---	---
			6.4	5.8	5.8	2.6	8.4	2.6
	C2-3	30-80	5.7	4.1	4.1	2.0	6.1	1.9
			4.8	---	3.9	1.9	5.8	---
			5.2	4.1	4.0	2.0	6.0	1.9
Matapalito (pit)	C3-1	0-16	19.0	14.2	12.6	7.6	20.2	6.0
			19.6	---	---	---	---	---
			19.3	14.2	12.6	7.6	20.2	6.0
	C3-2	16-42	14.4	10.9	9.9	5.1	15.0	4.1
			---	---	---	---	---	---
			14.4	10.9	9.9	5.1	15.0	4.1

Appendix Table 16. Exchangeable K, K extracted with 100 ml of 10^{-3}M HCl, and K extracted with NH_4OAc after the HCl extraction. (cont'd.)

Locality	Sample	Depth cm	Exchang. K	K extracted with 10^{-3}M HCl		K extracted with NH_4OAc after HCl	set 9122 plus set 9124	Exchang. K after HCl extraction. Aver. of set 1 minus set 9111
			set 9112	set 9111	set 9122	set 9124	set 1	
			ppm					
Carimagua (pit)	MR-8-9	0-20	41.5	33.5	34.8	13.1	47.9	14.5
			41.5	---	33.6	14.5	48.1	---
			41.5	33.5	34.2	13.8	48.0	14.5
	MR-10	20-38	18.0	12.1	12.6	5.4	18.0	6.7
			18.0	---	13.5	6.0	19.5	---
			18.0	12.1	13.0	5.7	18.8	6.7
	MR-11	38-94	12.6	7.8	6.4	6.5	12.9	5.1
			---	---	---	---	---	---
			12.6	7.8	6.4	6.5	12.9	5.1
	MR-12	94-114	14.6	6.1	7.5	7.4	14.9	8.7
			15.1	---	6.9	7.2	14.1	---
			14.8	6.1	7.2	7.3	14.5	8.7
	MR-13	114-137	14.8	5.7	6.1	10.0	16.1	10.9
			16.0	---	6.0	11.0	17.0	---
			15.4	5.7	6.0	10.5	16.6	10.9
	MR-14	150	20.0	11.7	10.0	10.1	20.1	8.4
			---	---	---	---	---	---
			20.0	11.7	10.0	10.1	20.1	8.4

Appendix Table 17

Estimation of the time effect in the analysis of total K, Mg, and Fe

Procedure

Duplicate samples (and blanks) of several soils were digested for analysis of total Fe, Mg, and K.

Samples 9 and 10 were digested on 2/22/73 and analyzed on 3/11/73 (F.N. 8951). The respective blanks showed no content of Ca, Fe, Mg, and K. The rest of the samples were digested on 5/26/73 and analyzed on 5/30/73 (F.N. 9027). Hereafter all these analyses are designated as "9027".

After the analysis, the samples (solutions) were kept in the original containers with the caps or lids tight to avoid loss of liquid by evaporation. Samples 1 to 8 were in polypropylene containers (with polypropylene caps) and samples 9 to 12 were in volumetric flasks.

On 8/21/73 the solutions in volumetric flasks were transferred to polypropylene containers and all the samples (1 to 12) were sent to the Analytical Service Laboratory (Agronomy Department), as before, for analysis of K, Mg, and Fe. The new analysis was done on 8/24/73 (F.N. 9114) and is designated hereafter as "9114". All the analyses were done using atomic absorption techniques.

The results are reported in Appendix Table 17.1 and the ratio of the results on both dates is also given.

Notes: a) The values reported in the samples 1 and 2 in the set 9114, were 528 and 388 ppm of Mg, respectively, and no error in calculations was

Appendix Table 17.1 Total Fe, K, and Mg in some soils of Colombia. The same solutions were analyzed on two different dates several months apart.

Sample no	Fe (%)			K (ppm)				Mg (ppm)			
	9027 x	9114 y	$(\frac{x}{y})100$	9027 x	9114 y	$(\frac{x}{y})100$	$(\frac{x}{y-\overline{BI}})100$	9027 x	9114 y	$(\frac{x}{y})100$	$(\frac{x}{y-\overline{BI}})100$
1	1.96	2.10	93.3	600	724	82.9	89.3	340	392*	86.7	90.2
2	1.96	1.90	103.2	600	736	81.5	87.7	340	380*	89.5	93.2
mean	1.96	2.00	98.0	600	730	82.2	88.5	340	386	88.1	91.6
3	2.40	2.10	114.3	2000	2120	94.3	96.7	770	744*	103.5	105.6
4	2.40	2.40	100.0	2000	2052	97.5	100.0	770	780	98.7	100.6
mean	2.40	2.25	106.7	2000	2086	95.9	98.3	770	762	101.0	103.1
5	1.50	1.40	107.1	4500	4560	98.7	99.8	850	820	103.7	105.6
6	1.54	1.40	110.0	4500	4740	94.9	96.0	870	848	102.6	104.4
mean	1.52	1.40	108.6	4500	4650	96.8	97.9	860	834	103.1	105.0
9	2.34	2.00	117.0	2200	2180	100.9	103.4	750	732	102.5	104.6
10	2.34	2.20	106.4	2200	2180	100.9	103.4	750	744	100.1	102.9
mean	2.34	2.10	111.4	2200	2180	100.9	103.4	750	738	101.6	103.7
11	2.46	2.30	107.0	1900	2052	92.6	95.0	810	760	106.6	108.7
12	2.52	2.30	109.6	1800	1940	92.8	95.3	780	760	102.6	104.7
mean	2.49	2.30	108.3	1850	1996	92.7	95.2	795	760	104.6	106.7
7	0.03	0		0	76			0	18		
8	0	0		0	28			0	12		
mean (Blanks)	0	0		0	52			0	15		

*See notes on text

$\overline{BI}$ = mean of blanks

found. The solutions were analyzed ten days later with the following results

sample no	Mg (ppm)	K (ppm)	Fe(%)
1	392	716	2.10
2	380	724	2.04

b) In view of the rather high values found for the blanks (samples 7 and 8) in the set 9114, the analysis was repeated and the new values were as follows

sample no	Mg (ppm)	K (ppm)
7	18	72
8	12	32

Statistical Analysis

The data were analyzed using paired t-tests for both the individual samples and the means of duplicates. In the first case the statistical singificance of the difference between the sets of analysis 9027(x) and 9114(y) is evaluated for individual samples, whereas in the latter case it is evaluated for the means of duplicates, i.e. for soils.

In the case of Fe the average of the blanks was taken to be zero. In the case of K and Mg the t-tests were done both by substracting and by not substracting the means of the blanks.

The assumption is made that the differences between values of x and y (or their means for a given soil) come from a normal population. The hypothesis tested are

H_o : $W_D = 0$, or $W_d = 0$

H_1 : $W_D \neq 0$, or $W_d \neq 0$

W_D is the expected value of $\bar{D}$, where $D = x - y$

W_d is the expected value of $\bar{d}$, where $d = x - (y - \overline{BI})$

x = set 9027

y = set 9114

$\overline{BI}$ = average of blanks for either K or Mg.

The t-tests gave the following results

a) means of duplicates

The critical t-value was $\pm t_{(4)0.975} = \pm 2.776$, at a level of significance of 5%.

The t-values for $\bar{D}$ were 2.78*, =3.10*, and 0.50 for Fe, K, and Mg, respectively.

The t-values for $\bar{d}$ were -1.46 and 1.56 for K and Mg, respectively.

b) individual samples

The critical t-value was $\pm t_{(9)\ 0.975} = \pm 2.262$, at a level of significance of 5%.

The t-values for $\bar{D}$ were 2.97*, -3.85*, and 0.69 for Fe, K, and Mg, respectively.

The t-values for $\bar{d}$ were -1.81 and 2.17 for K and Mg, respectively.

Comments

Although the hypothesis $W_D = o$ (or $W_d = o$) was accepted or rejected in the same cases when using the means of duplicates than when using individual samples, the level of significance was not the same. In the latter case we

have more degrees of freedom and the critical absolute value of t for rejection of the null hypothesis decreases ($\pm$ 2.776 vs $\pm$ 2.262), whereas the calculated t-statistic increased in absolute value.

In the case of Fe, the difference between both sets of analyses is significant (at a = 5%). As the mean of the blanks was zero, it was not necessary to perform t-tests for both D and d. In the case of K and Mg the t-tests were performed for both D and d because it is not easy to explain the differences found in the analyses of the blanks on both dates. For K, $D = x - y$ was significant (at a = 5%) but $d = x - (y - \overline{BI})$ was not significant. In the case of Mg the differences D and d were not significant (at a = 5%).

However, even in the case that we had not found any significant difference for Fe, K, and Mg, the variation between both sets of analyses is disturbing enough. This can be appreciated better by looking at the ratios $(x/y)100$ or $(x/(y-\overline{BI}))100$:

For Fe, the range of the ratio $(x/y)100$ goes from 93.3% to 117% and the mean is 106.8%.

For K, the range of the ratio $(x/(y-\overline{BI}))100$ is 87.7 - 103.4% and the mean is 96.7%.

For Mg, the range of the ratio $(x/(y-\overline{BI}))\ 100$ is 90.2 to 108.8% and the mean is 102.0%.

In the cases in which the difference (D or d) was significant, the conclusion to be drawn is that there is one (or more) systematic error or bias in one set of analyses in relation to the other, besides the natural or common random

errors found or present in any set of measurements.

In those cases in which the difference was not significant, the evidence is not statistically enough to conclude the presence of a systematic error or bias between the two analyses. However, the fact that most of the differences for a given element are either positive or negative suggests the presence of a systematic error, whereas the range in ratios or differences indicates either large random errors or the presence of more than one systematic error acting in different directions in some samples.

Among the possibilities to be considered to explain the differences found, we may include:

a) changes of the stored solutions (samples) with time.

b) reactions of the solutions with the containers.

c) variation in the dilution of solutions (samples) when preparing them for analysis in the spectrophotometer.

d) changes in the standard curves.

e) changes or contamination in the atomic absorption spectrophotometer.

f) errors in reporting (or calculating) the results.

The fact that $\bar{D}$ (or $\bar{d}$) is not consistently positive or negative for the 3 elements analyzed indicates that a systematic error due to evaporation of solutions (samples) and/or to a constant change in the aliquots taken for analysis was not present or, if present, it was not the major

contributor to the differences found. This can be appreciated too by looking at the means of the ratios $(x/(y - \overline{BI}))100$: 106.8% for Fe, 96.7% for K and 102.0% for Mg. The means of the ratios $(x/y)100$ were: 106.8% for Fe, 93.7% for K and 99.7% for Mg.

The variation "within times" (between duplicates) was smaller than the variation "among times" (between dates of analysis) for all three elements. The pooled within times and among times errors were: 0.09 vs 0.12%, 55 vs 83 ppm, and 14 vs 21 ppm for Fe, K, and Mg, respectively. (The among times error was calculated using the means). No statistical F test of the respective variances was performed due to the lack of independence of all of the observations.

Appendix Table 18

Estimation of the time effect in the extraction and analysis of the exchangeable Ca, Mg, and K.

Duplicate 10-g samples of 3 soils were taken from the same jars and analyzed for exchangeable Ca, Mg, and K, using the same procedure, on three occasions, as follows: set 9069 on 7/12/73, set 9112 on 8/27/73, and set 9126 on 9/18/73 (in the last set one of the soils was not included).

The results are shown in Appendix Table 18.1. It should be noted that the soil samples in the jars had been ground, passed through a 2.38-mm sieve, and well mixed.

The analysis of variance is shown in Table 6-11 together with other estimates of the variation "among times" and "within times." The variation "within times" refers to the pooled variance between duplicates (i.e. it is the usual estimate of the experimental error mean square). The variation "among times" is the among treatments mean square, where the treatments are the different sets of analyses (i.e. the different times in which the analyses were done.)

Appendix Table 18.1 Exchangeable Ca, Mg, and K determined on three different dates using the same method and soil samples from the same jars.

Soil	Ca (ppm)			Mg (ppm)			K (ppm)			Range (means)		
	9112	9126	9069	9112	9126	9069	9112	9126	9069	Ca	Mg	K
MR-1	12.1	12.6	13.0	5.2	5.6	4.9	31.2	31.6	29.5			
	11.9	12.9	14.2	5.2	5.6	7.9	31.5	29.3	32.5			
	12.0	12.8	13.6	5.2	5.6	6.4	31.4	30.4	31.0	1.6	1.2	1.0
Cl-18	30.1	29.6	n.d.	9.5	10.3	n.d	42.1	39.6	n.d.			
	32.0	29.6		9.9	9.7		42.1	37.6				
	31.0	29.6		9.7	10.0		42.1	38.6		1.4	0.3	3.5
MR-15	15.2	15.5	19.0	5.2	5.6	5.9	30.0	29.7	28.9			
	16.5	16.8	19.0	5.7	5.8	6.1	27.9	31.0	29.2			
	15.8	16.2	19.0	5.4	5.7	6.0	29.0	30.4	29.0	3.2	0.6	1.4
									$\bar{x}$ =	2.1	0.7	2.0

n.d.: not determined

Appendix Table 19

Estimation of the time effect in the analysis of Ca, Mg, and K in 10^{-3}M HCl soil extracts

Soil extractions with 10^{-3}M HCl were obtained as described before. The same solutions were evaporated to dryness and analyzed on two different dates: set 9035 on 6/11/73 and set 9111 on 8/23/73. The results appear in Appendix Table 19.1.

The statistical analysis using paired t-tests and considering all the observations showed : the critical t-value was $\pm$ t (8) 0.975 = $\pm$ 2.306 (5% level of significance).

Defining D = (set 9035) - (set 9111), the t-values for $\bar{D}$ were 2.62*, 0.85, and -1.58 for Ca, Mg, and K, respectively.

Comments

A significant t-value indicates a systematic difference or bias in one set in relation to the other, i.e. a systematic time effect. Only Ca showed this systematic bias. However, the fact remains that even when the differences between sets of analyses are not systematic, there is a variation among times that is larger than the variation within times (i.e. between duplicates). The variation among and within times is shown in Table 6-11. It should be noted that because of nonindependence (the samples came from the same solutions) a formal test of mean squares cannot be performed). Besides, the variation within times was calculated using the samples of which duplicates were available, but these samples happened to have the largest values of Ca, Mg, and K and this may be related to the sensitivity and error in the analysis

Appendix
Table 19.1 Comparison of analyses of 10^{-3}M HCl soil extracts. The same solutions were evaporated to dryness and analyzed on two different days

ppm

Soil	Ca		Mg		K	
	9035	9111	9035	9111	9035	9111
MR-1	13.8 13.8 13.8	13.6 13.9 13.8	4.5 4.3 4.4	5.1 5.4 5.2	23.8 23.8 23.8	23.7 24.1 23.9
C1-18	38.1 38.1 38.1	35.6 33.6 34.6	11.0 11.0 11.0	9.9 9.6 9.8	31.4 31.8 31.6	32.0 32.0 32.0
MR-15	17.1 17.1 17.1	15.7 15.7 15.7	6.0 5.8 5.9	5.4 5.4 5.4	20.0 20.4 20.2	19.9 19.7 19.8
MR-7	9.8	9.3	3.2	3.0	5.1	5.5
MR-11	6.2	5.5	2.5	2.4	4.4	7.8
C2-3	1.6	1.3	0.7	0.8	2.2	4.1

Appendix Table 20

Recovery of Ca, Mg, and K from the standard solutions.

The recoveries of Ca, Mg, and K when the standard solution A-4 was used were very good in the case of Ca but consistently low for Mg and K (see Appendix Table 20.1). The way the percentage of recovery varied for the 3 elements suggests that a physical loss of sample was not the cause of it. The concentration of the standard solution A-4 had been checked by the same laboratory a few days earlier. This indicates that the reason for the low recoveries of Mg and K may be attributable to some differential loss or to some changes or variation in the equipment or solutions involved in the determination. It is interesting to note the closeness of the duplicates. The difference between the observed and the expected values can be considered another proof of the "time effect" discussed earlier.

Appendix Table 20.2 shows the recoveries of Ca, Mg, and K when the standard solution S-9 was used. In this occasion, the recovery of K was good but not the recoveries of Ca and Mg, which were generally low specially in the more concentrated samples. As above, physical loss of sample alone could not account for the variation observed. The differences between sets A and B are very definite and they suggest either a significant change in the way the author handled the samples or a real difference between the composition of the standard solutions from which sets A and B came (it was the same solution, labeled S-9, but coming from different bottles). Note again the

Appendix Table 20.1 Recovery of Ca, Mg, and K from the standard solution A-4.

Added			Recovered			Recovery		
Ca	Mg	K	Ca	Mg	K	Ca	Mg	K
γ/ml						%		
12.0	5.3	15.7	12.0	5.0	13.8			
			12.0	5.0	13.6			
			12.0	5.0	13.7	100.0	94.3	87.3
36.0	16.0	47.2	36.6 (a)	14.6	41.2	101.7	71.2	87.3

(a) duplicate sample was lost.

Appendix Table 20.2 Recovery of Ca, Mg, and K from the standard solution S-9. Final residue dissolved in a HCl-La solution.

	added			recovered			recovery		
set	Ca	Mg	K	Ca	Mg	K	Ca	Mg	K
	γ/ml						%		
A	12	4	16	12.5	4.1	15.7			
				12.5	3.9	15.7			
				12.5	4.0	15.7	104.2	100.0	98.1
	36	12	48	32.0	11.2	47.9			
				32.0	11.2	47.9			
				32.0	11.2	47.9	88.9	93.3	99.8
B	12	4	16	11.1	3.7	15.9			
				11.1	3.7	15.1			
				11.1	3.7	15.5	92.5	92.5	96.9
	36	12	48	30.6	10.9	46.8			
				30.6	10.6	46.1			
				30.6	10.8	46.4	85.0	90.0	96.7

Both sets, A and B, were analyzed on the same date, but they came from different stock standard solutions.

closeness of the duplicates. The "time effect" is also evident here. The standard solution S-9 already had La and more La was added when the residue was dissolved for analysis. Thus, a possible interference due to a high La concentration was suggested, as the cause of the low recoveries in sets A and B.

To test the above hypothesis, new samples were prepared with the standard solution S-9, but making the final dilution in a HCl solution without La. The results are shown in Appendix Table 20.3. The recovery of Mg can be considered acceptable but not so the recoveries of Ca in one pair of duplicates and of K. The duplicates were very close except for the low value obtained for Ca in one sample. Both sets, A and B, were practically equal. No reason was found for the impossibility of making a reading for the more concentrated samples. According to the Laboratory, it was the first time that something like this ever happened. One thing clear in this set of analyses is the "time effect". Although many things remain unclear, no further analyses of standard solutions were performed.

Appendix Table 20.3 Recovery of Ca, Mg, and K from the standard solution S-9. Final residue dissolved in a HCl solution.

set	added			recovered			recovery		
	Ca	Mg	K	Ca	Mg	K	Ca	Mg	K
	γ/ml						%		
A	12	4	16	11.7	3.8	14.6			
				13.2	3.8	14.4			
				12.4	3.8	14.5	103.3	95.0	90.6
	36	12	48	---- see note ----					
B	12	4	16	13.2	3.8	14.2			
				13.2	3.8	14.4			
				13.2	3.8	14.3	110.0	95.0	89.4
	36	12	48	---- see note ----					

set A: container walls rinsed with HCl: H_2O and 10 ml of H_2O

set B: container walls rinsed with HCl: H_2O.

Sets A and B analyzed on the same date.

Note: For unexplained reasons, it was impossible to get a reading in the spectrophotometer. Apparently something clogged the burner each time that a lecture was attempted.

Appendix Table 21. Effect of the incubation on the exchangeable Al and pH

The pH of the 3 check soils incubated changed only slightly after the several W-D cycles (see Appendix Table 21.1). The change in pH occurred mainly in the first 2 W-D cycles when it increased by 0.2 units or less. This implies that the H^+ concentration in solution decreased by less than 1/3 of the initial level. The analysis of variance showed that the main effects of soils and of W-D cycles, as well as the interaction were statistically significant (at a = 0.1%). However, even though the changes in pH were statistically significant, the practical significance, i.e. importance, of the changes in pH is negligible.

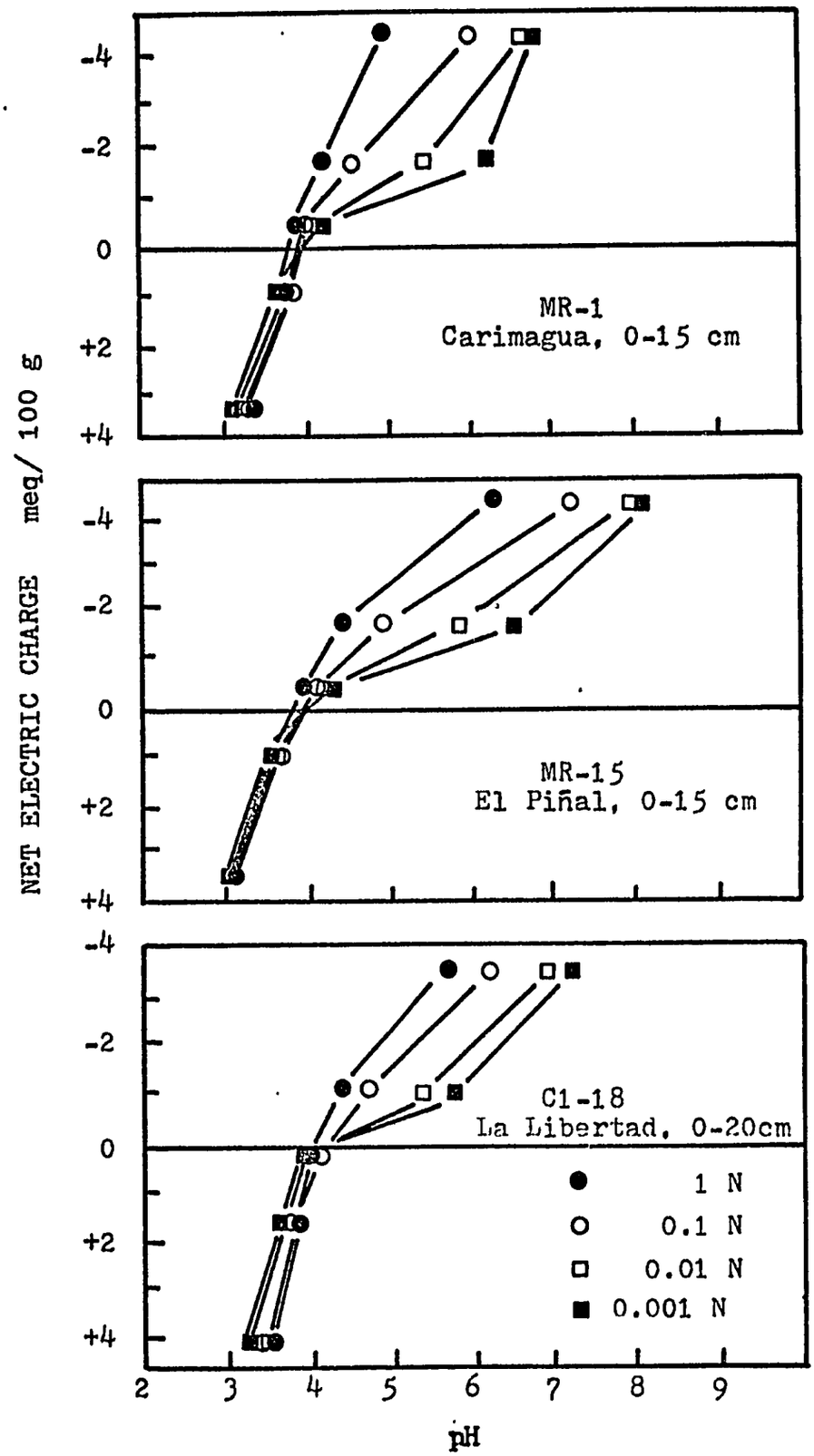
The changes in the exchangeable Al (see Appendix Table 21.2) were also small although more pronounced than the changes in pH. The changes in both variables in each soil tended to be negatively correlated, and although a better degree of correlation could be expected, notice that both variables were measured in different soil samples. As in the case of pH, the analysis of variance showed a significant main effect of soils, of W-D cycles, and a significant interaction (at a = 0.1%). Again, the changes in the exchangeable Al do not seem to have practical importance, although the reason for the changes in the exchangeable Al upon wetting and drying is unclear.

Appendix Table 21.1 Effect of wetting and drying on the pH of some soil samples.

Sample	wetting and drying cycles			
	0	2	5	11
MR-1	3.95	4.15	4.17	4.09
	3.95	4.17	4.13	4.08
	3.95	4.16	4.15	4.08
C1-18	3.79	3.84	3.85	3.87
	3.79	3.85	3.85	3.87
	3.79	3.84	3.85	3.87
MR-15	4.00	4.14	4.14	4.12
	4.00	4.14	4.14	4.13
	4.00	4.14	4.14	4.12

APPENDIX TABLE 21.2 Effect of wetting and drying on the exchangeable Al of some soil samples

Sample	wetting and drying cycles			
	0	2	5	11
	meq/100 g			
MR-1	3.99	3.49	3.68	3.72
	3.97	3.49	3.75	3.67
	3.98	3.49	3.72	3.70
C1-18	3.57	3.39	3.66	3.32
	3.59	3.37	3.75	3.34
	3.58	3.38	3.70	3.33
MR-15	2.40	2.35	2.23	2.37
	2.54	2.40	2.28	2.35
	2.47	2.38	2.26	2.36



APPENDIX FIGURE 1. pH - SURFACE CHARGE RELATIONSHIPS IN 3 SOILS. (Data of Uehara and Keng, unpubl.)