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9. ABSTRACT

This study involved two distinct subject matter areas, one the study of soil aluminum and the other the Cerrado areas of central Brazil. The materials used in the study were soil samples taken from selected sites in the Cerrado in September 1973, but the actual laboratory work and growth of plants were done at Ohio State University. The Cerrado area is of interest as having great agricultural potential, though currently this area is little used for intensive agriculture. Some attempts at utilizing it have failed and after several preliminary studies of the native vegetation and field trials, the initial results lean toward native soil aluminum as the major problem. Thus, aluminum-tolerant varieties of field crops are being sought as possible solutions to the problem. Because of the problem with aluminum in these soils, the second area of study involved an attempt to characterize the phytotoxic aluminum in some representative soils of Cerrado regions. Extraction of soil samples with 1N KC1, a traditional method, and a modified F-titration procedure, a new technique, were used to estimate the level of phytotoxic aluminum in these soils. These methods then were correlated with plant growth on the soil samples.

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RELATIONSHIP OF FLUORIDE REACTIVE SOIL ALUMINUM TO PLANT GROWTH IN CERRADO SOILS OF BRAZIL

DISSERTATION

Presented in Partial Fulfillment of the Requirements

for the Degree Doctor of Philosophy

in the Graduate School of

The Ohio State University

By

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* * * * *

The Ohio State University

1975

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There is much more to a doctoral program than merely completing a research project. A multitude of factors are involved

in the education of a professional agronomist. One description of this process is that it is an integration of knowledge, skills and attitudes. Though this idea seems foreign to many, it appears very real and valid in my education at Ohio State University.

There have been many sources for each major factor, but a few stand out. For the source of my knowledge I thank all the instructors of my many classes. Some contributed more than others, but all did contribute.

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My sources for professional attitudes are many and varied. However, one particular source deserves laudable mention; the OSU Graduate Council. Through my participation I was able to observe the highest caliber of intellect apply abstract educational philosophy to concrete problems. I found participation in this process to be both enlightening and invigorating.

I am also indebted to many faculty in my own department who have revealed their personal professional attitudes and values to me. They have given me much insight into the character of the profession.

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INTRODUCTION

This study involved two distinct subject matter areas; one being the study of soil aluminum and the other the Cerrado areas of central Brazil. The materials used in the study were soil samples taken from selected sites in the Cerrado in Sept. 1973. The actual laboratory work and growth of plants was done at Ohio State University.

The Cerrado area is of interest because many persons believe it has great agricultural potential. At the present time, there is little utilization of these areas for intensive agriculture. Some of the attempts have ended in failure. After several preliminary studies of the native vegetation and field trials, the initial results tend to point towards native soil aluminum as the major problem. For this reason, aluminum tolerant varieties of field crops are being sought as possible solutions to the problem.

Because of the problem with aluminum in these soils, the second area of study involved an attempt to characterize the phytotoxic aluminum in some representative soils of Cerrado regions. Extraction of soil samples with 1N KCl, a traditional method, and a modified F^- titration procedure, a new technique, were used to estimate the level of phytotoxic aluminum in these soils. These methods were then correlated with plant growth on the soil samples.

REVIEW OF LITERATURE

The two subject matter areas of interest are the Cerrado areas and soil aluminum. Although they are related, each is a field by itself and because of this each will be reviewed separately.

THE CERRADO

The particular definition of Cerrado is that of "open pasture with patches of stunted vegetation".[58] Botanists tend to use an even more specific definition stating that Cerrado is "a regional large-scale vegetation type that forms both a vegetational and floristic province".[21]

The problem of discussion about Cerrado is further complicated by a large number of names denoting inter-grades across the range of vegetation called Cerrado. Some of these names which have been used in various publications are: Cerradão, Campo Cerrado, Campo Limpo, Campo Sujo, Caatanduva, Caapão, Caatininga, Mata Campestre, Campo Baixo and Scrub Savanna. Some of the terms are equivalent while others are misnomers or used in error. When it is necessary to delineate subtypes of Cerrado, the terms used here will be those defined by Eiten.[21] These are: Cerradão (xeromorphic low forest, low arboreal woodland, closed scrub or slightly open scrub), Campo Cerrado (xeromorphic well-open low woodland, well open scrub, arboreal

savanna, tree and scrub savanna, or scrub savanna), Campo Sujo (xeromorphic very open scrub savanna, very scattered but visible shrubs and tree-like scrub elements up to 2-3m tall), Campo Limpo (pure xeromorphic grassland, or grassland with herbs; dwarf shrubs and semi-shrubs, if present, generally hidden in the grasses). In general usage, the word Cerrado covers all of these variations and will be used as such in this writing unless otherwise noted.

Areas of Cerrado

Because of the profusion of various terms for Cerrado type vegetation it is difficult to define its actual extent. Most estimates center around an area of 1.8 million square km. which is roughly 20% of the land area of Brazil. It occurs from approximately 4° N to 24° S latitude and from 42° to 65° longitude at elevations of 100 to 1240 m. above msl.[60] The largest parts of Cerrado fall within the Central-East region of Brazil. The major continuous areas of Cerrado are within the states of Goiás, Minas Gerais, Mato Grosso and the Federal District around Brasilia. Smaller, discontinuous areas are found in many other states, a few being São Paulo, Bahia, Piauí and Maranhão.[38] The most recent estimate of the areas of occurrence of Cerrado is by Ranzani and is shown in Fig. 1.[60]

Origin of Cerrado

Since the first description of this unique vegetative association by Eugen Warming in 1881 there has been speculation as to the reasons for its existence. The first, proposed by Warming, simply asserted that Cerrado was a particular association of plant

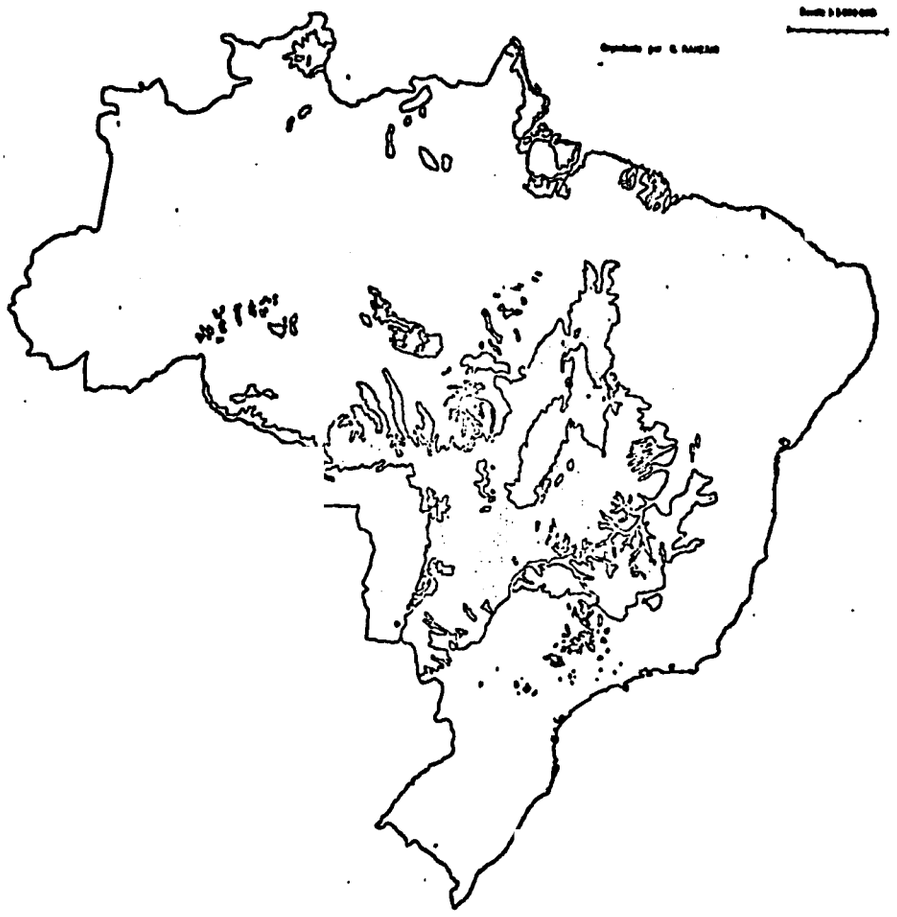


Figure 1. Approximate Geographical Distribution of Cerrado in Brazil (60)

species. This theory was accepted for several years until a better knowledge of Brazilian botany disproved it. It was easy to demonstrate that species present in the Cerrado areas are also present in non-Cerrado areas and possess normal form and appearance. So it became evident that there was something special about the geographic area of Cerrado that was responsible for its unique characteristics.

Again Eugen Warming put forth a hypothesis in 1900 stating

that the marked dry season caused the vegetation to become xeromorphic.[33] There was little argument at the time since the existence of a dry season was well acknowledged and many of the features of Cerrado such as stunted growth, contorted tree and shrub growth and predominance of grasses tended to support this hypothesis. Although it cannot be denied that these xeromorphic features do exist in Cerrado, Rawitscher and Ferri were able to disprove the xeromorphic hypothesis in the 1940's.[79] They noted that many of the large plants have large, soft leaves, not a xeromorphic feature. They also noted that the soil below 2 m depth in Cerrado areas was moist the year round. Since Cerrado plants have very deep root systems (easily extending 2-7 m below the surface) it could be argued that the plants have access to sufficient moisture during the entire year.[79] As if to show that they do not suffer from lack of water, many Cerrado plants flower profusely during the dry months of June-September. The final blow to the xeromorphic hypothesis was dealt when stomate opening studies showed that Cerrado plants transpire freely even in the midst of the dry season. Because of these findings, it became clear that the extended dry season was not an adequate explanation for Cerrado.

Another hypothesis concerning the origin of Cerrado centers around the frequent fires that occur during the dry season. Several features of the Cerrado vegetation can be explained by the effects of fire. The tortuosity of the trees and shrubs is seen as the result of fire damage to terminal buds. Later growth goes in a lateral direction until subsequent destruction of the terminal bud again alters the direction of growth. The overall result is the characteristic

twisted conformations of the trees and shrubs. A second feature mentioned in defense of the fire hypothesis is the thick cuticle possessed by most woody plants in the Cerrado regions. This is viewed as an adaptation by plants which protects against the heat of fires. Another Cerrado feature cited as being fire-caused is the presence of enlarged basal sections of woody stems (sylopodia). This is also viewed by proponents as an adaptation to the frequent fires.

Certainly there is merit to this hypothesis, especially concerning the tortuosity characteristic. But observations by Eiten argue against this view. He notes that in areas protected from fire, the vegetation only proceeds to a Cerradão and not a forest. In other parts of the world, when forests in dry climates have been burned, Cerrado-like vegetation does not develop. Adjacent regions in Brazil which have been burned as a practice of intensive agriculture have not developed Cerrado. For these reasons Eiten maintains that fires only affect Cerrado and do not act to cause or maintain Cerrado. Unfortunately there is not a wealth of empirical evidence on either side.

Another hypothesis which has greater backing in empirical evidence is that Cerrado is caused by the inherent low fertility of the soils. There is considerable evidence of low levels of extractable N, P, Zn, B, Mo, Cu, Mn, Ca, Mg and S in various Cerrado soils.[47] Although not all of these elements are limiting on all soils, it is almost always certain that additions of N and P are necessary to produce an acceptable yield of a crop.

In experiments involving fertilization of corn with large amounts of superphosphate and minimal levels of other elements, excellent growth has been obtained. These particular plots were observed in September 1973 in Brasilia. Rates of up to 1900 kg P_2O_5 were used and compared with high levels of lime. In general, the superphosphate plots had better growth than plots where lime was applied alone. In those plots that received no phosphate, the maize plants were less than 6 inches tall at the end of the growing season. Other evidence of low nutrient status is also noted in attempts to grow field crops in Cerrado areas. These trials all show similar nutrient deficiencies.[11, 29, 30, 49, 53]

Although large scale soil testing data are still not available from many parts of the Cerrado, there are some data which indicate the levels of nutrients available. A summary of 1200 analyses performed in 1962-66 in Sete Lagoas showed that those soils exhibited a uniformly high acidity, presence of extractable Al, low levels of exchangeable bases and low organic matter contents.

This rather well authenticated low fertility status has served as the starting point for the most convincing explanation of the origin of Cerrado. Work at the Univ. of São Paulo originated the concept of "oligiotrophic scleromorphy".[4] Study of plants growing on soils severely deficient in minerals has lead to the conclusion that the scleromorphic features of Cerrado vegetation are primarily due to the low nutrient status of the soils. The results of soil analyses have showed deficiencies of Ca, P, S, N, Zn, Mo and B. Since shortages of these elements limit protein synthesis, and since

both water and sunlight are not limited, there is an accumulation of carbohydrates in the plants. These surplus carbohydrates are then utilized for formation of thick cellulose cuticle or sclerenchyma. This excess carbohydrate material simulates xerophytic features (thick cuticles, thick leaves, prominent veins, etc.) but is actually induced by nutrient deficiencies. This lack of nutrients is probably caused or further aggravated by the low acidity and by phytotoxic Al.[34]

Another notable characteristic of Cerrado plants is their ability to tolerate Al. Some species may accumulate several thousand ppm (on a dry weight basis). These accumulators are a very significant part of the biomass, being dominant in over 30% of the stands studied.[35] This tolerance for Al is theorized to be a key factor in Cerrado formation. These soils are quite old and well leached with resulting high levels of extractable Al. Because forest vegetation has not been able to adapt to such high Al levels and low nutrient status, the Cerrado vegetation has a competitive advantage over forest vegetation.[21] In summary, this hypothesis states that Cerrado vegetation is a result of both the low nutrient status of the soils and the presence of high levels of phytotoxic Al.

Soils of Cerrado Areas

Given the hypothesis that Cerrado is most likely caused by soil factors, a review of the characteristics and distribution of various soil groups is in order.

The knowledge of underlying soils in Cerrado regions can at present be described as sparse. Some small areas have been mapped

and described at the reconnaissance survey level. These are usually areas of special interest such as agricultural resettlement areas or experiment stations.[23] Some surveys have also been compiled from results of experimental plots or individual sampling of profiles.[41] But overall, there is no source of detailed data for large areas under Cerrado.

The results of most compilations seem to agree with that of Jacomine.[41] The most widespread soil groups are the Dark Red Latosols and the Red-Yellow Latosols. Both of these groups fall within the 7th Approximation Oxisol order, many types falling within the great group Acrustox. These soils have low base saturation, low CEC, low pH, are very permeable and well drained. They are usually deep and very uniform throughout the upper 2 m. Minerals of the clay fraction are quartz, kaolinite, gibbsite and goethite. In lower horizons some 2:1 clays may be present. Slopes are gentle, usually being between 1-5%. A second group of soils found in Cerrado areas is made up of Lithosols and Plinthitic soils. These are also deep, well drained soils located toward the upper regions of slopes or on plateaus. Generally the occurrence of thin, broken plinthite does not restrict water movement or root penetration. Of more limited areas of occurrence are the groups of sandy soils, podzolic soils, hydromorphic soils and brown acid soils.

Rather than go into detailed profile descriptions, it would be better to cite the statistics by J. F. Mendes.[52] A summary of 1200 soil samples is shown in Table 1.

Table 1. Chemical properties of 1200 soils samples tested in Sete Lagoas during 1962-66. (52)

Property	Value (% of samples in the range)
pH	<4.3 (33%), 4.3-5.5 (66%)
Exch. Al	<.5 me/100 g (28%), .5-1.0 me/100 g (18%), >1.0 me/100 g (54%)
Exch. Ca	<1.0 me/100 g (59%), 1.0-2.0 me/100 g (36%)
Exch. Mg	<.20 me/100 g (61%), .3-.6 me/100 g (23%), .6-1.0 me/100 g (11%)
Exch. K	<.10 me/100 g (53%), .1-.24 me/100 g (30%), .25-.60 me/100 g (16%)
Base Sat.	<25% (83%), 25-50% (16%)
Organic Matter	1.2-1.8% (18%), 1.8-2.6%, >2.6% (20%)

The most notable points from these data are the uniformly low pH, low base saturation and high extractable aluminum. Although physical properties are generally good, the chemical properties make commercial cropping of these soils difficult. Another presentation of the variation of chemical properties with depth was given by Ranzani.[61] In general, it was observed that there is a decrease of CEC and exchangeable bases with depth but that pH increases with depth. The low level of exchangeable bases was further exaggerated by the fact that the base saturation of the soils ranged from about 10-20%. Since in most cases the CEC was less than 10 me/100 gms, it

is clear that the absolute amount of exchangeable nutrients was quite low. This fact, in itself, is enough to explain much of the observed poor plant growth on these soils. When the low pH and relatively high Al levels are considered, added to the problem of low exchangeable bases, we begin to see how several soil characteristics unite to discourage normal plant growth. Findings such as this support the hypothesis of oligiotrophic scleromorphism, and further aids in understanding the reasons for the lack of success of common field crops in Cerrado areas.

Agricultural Potential of the Cerrado

Because Cerrado occupies such a large area of Brazil, the national government has been involved in research to make more intensive use of this land. The construction of the capital, Brasilia, was the first major step in the program to encourage migration and settlement of Cerrado areas. Although some areas in São Paulo state have been successfully utilized for intensive agriculture, most of the Cerrado remains untouched by agriculture.

Because of the year-round availability of water and the gently rolling topography, much of the initial research effort was directed towards intensive agricultural use of Cerrado. As recently as 1967 it was estimated that up to 80% of the Cerrado could be converted to agricultural crop production.[56] One of the earliest recorded experimental works was done at the Sete Lagoas experiment station from 1944 to 1949.[11] This work was the first to show that Cerrado could be used for crop production. The key ingredients were

lime, superphosphate and green manure. Other field plot work since then has been done using various crops, such as paddy rice, upland (dry) rice, sweet corn, soybeans, cotton, field corn, pineapple and wheat.[14, 15, 16, 20, 29, 30, 31, 47, 72] Although results are not always in perfect agreement, they all show the need for lime and heavy fertilization with macro- and micro-nutrients. Without lime and/or superphosphate, there were generally very poor yields.

Major emphasis is being placed on forage production. The largest part of the research effort in this area has been devoted to screening of varieties and development of suitable fertilization practices. Many of the species being tested are legumes adapted to tropical conditions, such as perennial soybean, siratro, Kudzu and centrosema.[28] Elephant grass has also been tested on plots at Sete Lagoas.[57] The research effort in grasses is still gaining momentum and much remains to be done, but the prospects for success are better than for intensive cropping.

THE STUDY OF SOIL ALUMINUM

One of the major problems which beset any research into reactions of soil aluminum is the problem of making a quantitative estimate of soil aluminum which is representative of that fraction being studied. In most cases, the research is related to plant growth and crop yields, and so the ultimate "judge" in these cases is the plant. But, because plant uptake and yield studies are relatively expensive and time consuming, many faster, less expensive soil extraction methods have been tested as alternates for estimating levels of phytotoxic Al.

Forms of Soil Aluminum

Unfortunately, the estimation a aluminum in a soil involves more than a simple displacement of Al^{3+} from a colloid surface and its subsequent measurement in an extracted solution. Aluminum is present in many forms in soils and, in any given natural soil, several compounds and minerals which contain aluminum will be present. In a single soil sample, aluminum will normally be present as a constituent of crystalline clay mineral structures, hydroxide forms of aluminum (such as Gibbsite and Goethite) in various stages of crystallinity, aluminum-phosphate complexes (such as $AlPO_4 \cdot 2H_2O$), various ionic species (such as Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_6(OH)_{15}^{3+}$) and many other forms of polymeric Al hydroxides.[12, 18, 77] Figure 2 shows the calculated distribution of Al hydrolysis species as a function of pH.[18] It should be remembered that this represents an idealized, equilibrium state in a solution of Al.

Because of the dynamic nature of natural soils, the proportions of total Al contained in these various forms will shift during a growing season. As the soil dries, the aluminum hydroxides act as a sink for the more soluble forms of Al.[63] Wetting reverses this reaction and results in higher levels of extractable soil Al.[80] Plant roots tend to establish zones of lower pH in the rhizosphere, dissolving weak amorphous Al complexes. Addition of chemicals, such as phosphates, may act to reduce the total Al in solution. Undoubtedly, many other factors affect the distribution of soil Al during a year. The main point here is to emphasize the complex and dynamic nature of the soil Al pool.

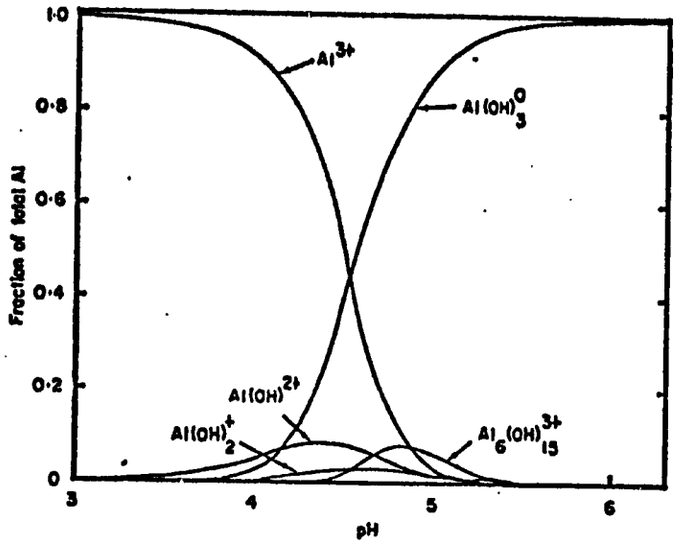


Fig. 2. The fraction of Al present in each hydrolysis species as a function of solution pH.(18)

Measuring Phytotoxic Soil Al

In spite of the difficulties caused by shifts in the various forms of soil Al during a season, a large amount of effort has been expended in attempts to find some general, quick laboratory procedure useful for estimating phytotoxic Al and determining amounts of material needed to neutralize this Al. The following is a very condensed overview of the many methods which have appeared in literature over the past few years.

Many methods involve extraction of a soil sample by a buffered salt solution with pH adjusted to between 4.5 and 5.0. One of the methods of this type uses normal NH_4OAc adjusted to pH 4.8. This pH results in extraction of more Al than at pH 7 and is often

attributed to the partial dissolution of hydrous forms of Al.[81] Other workers have postualted that the Al extracted by NH_4OAc at this pH is from pH-dependent exchange sites on organic matter complexes.[7] Although such a source of NH_4OAc-extractable Al may be possible, it does not seem likely to be a large contributor of phytotoxic Al on most soils. At this stage in our knowledge it is not clear precisely what sources of Al are measured using this method. Perhaps it was extraction of several forms of Al on some cropped Florida soils that yielded corresponding soil solution concentrations of several of hundred ppm of Al.[81]

This brings the test into question for use on these soils since only 2-3 ppm Al in a solution will severely retard plant growth. Another Canadian study using pH 4.8 and 3.0 NH_4OAc-extracted Al found that this was poorly correlated with Al uptake in barley, turnip rape and alfalfa.[37] In general, use of this method has been confined to those soils where experience has shown that the extracted Al correlates with crop responses to phytotoxic Al.

In summary, it can be said that the objectives of the many buffered extraction procedures have been two-fold. The use of the salt solution is intended as a displacing agent for Al^{n+} ions adsorbed on soil colloids. The second objectives of these salt extraction methods is to use the pH of around 4.8 to 5.0 to solubilize that Al which would presumably be soluble or active under natural acid soil conditions or in the immediate vicinity of active plant roots. Unfortunately, as stated earlier, aluminum is present in many forms in soils and all of these forms do not react similarly to high salt

concentrations or low pH. Well crystallized clay minerals are relatively unaffected by pH ranging down to pH 3. But less well crystallized clay minerals, often designated as amorphous clays, may be completely disrupted by such a low pH.

Many unbuffered salt solutions such as NH_4Cl, $BaCl_2$, $CaCl_2$, NaCl and KCl have been tried but their success has been limited.[46] The previously cited Canadian study showed a good correlation between KCl extracted Al and Al uptake by barley, turnip rape and alfalfa.[37] Although other studies have compared KCl with other extractants, such as NH_4OAc, there has been no general agreement on the suitability of KCl extractions to estimate phytotoxic Al.[2] Perhaps because of its economy and simplicity, this method is widely used as a descriptive test.[23, 59] Tamms' acid oxalate has been used by some as an extractant, but there is little agreement on the form of soil Al which this solution extracts. Some persons contend that it extracts mainly amorphous Al compounds while others claim excessive contributions from silicates.[5, 73] Solutions of $BaCl_2$ with TEA have been found adequate in some conditions but in other conditions were judged to be a poor indicator of plant uptake.[43, 69] One of the aspects of using $BaCl_2$+TEA is the complexing nature of the TEA. In one study, this resulted in a larger removal of soil Al than that by neutral salts.[81] It is beleived that this procedure results in drawing Al from both hydrous Al oxides and Al phosphates.

A major disadvantage of the unbuffered salt solutions is related to their concentrations. Precipitated Al gels tend to absorb cations which results in release of protons from the surface

HOH and OH groups of the gels.[44] If significant amounts of precipitated Al is present in a soil, with a pH near 5, addition of large amounts of an unbuffered salt solution will cause release of protons, a lowering of pH and dissolution of the less resistant gels. The overall effect is to dissolve more than the strictly exchangeable or soluble Al.[59, 62] Even field work has shown that application of chemical fertilizers alone caused increases in "exchangeable Al".[1]

Because merely lowering pH of the extracting solution or using an unbuffered salt solution has disadvantages, many researchers have turned to methods which are more selective for Al^{3+}. One of the more widely used extractants in this catagory is NH_4F. The use of NH_4F as the extracting salt is based on the formation of a stable fluoaluminate complex, $(NH_4)_3AlF_6$, in neutral to alkaline solutions.[78] Because of the pH range used this procedure has the advantage of little interference from soil Fe and organic matter and as such is sometimes also used to evaluate Al bound phosphates in soils.[24] A second advantage is that reactive Al is quickly complexed and no longer contributes to the active fraction of Al, shifting the solution equilibrium towards release of more Al^{3+}.

The major criticism is that the NH_4F procedure uses a pH which is above the range where most of the phytotoxic effects of Al are observed in soils. Because of this, it is open to criticism as a method of estimating phytotoxic Al in soils. Lowering of the pH would remove this objection and enough work has been done with NaF to make this an alternative for such a procedure.[70]

Quantitative work with the fluoride electrode has shown that under carefully controlled conditions, the total amount of solution Al present can be accurately measured using this method. The major problem lies in the precise control of pH and endpoint voltage. In any solution, the total amount of complexed F^- may be present in three forms; $Al(H_2O)_{n-1}F^{2+}$, $2Al(H_2O)_{n-2}F^{+}_2$, and $3Al(H_2O)_{n-3}F_3$. The preponderance of each form varies with pH so that the total ratio F^-/Al^{3+} varies with pH and concentration of F^- and Al^{3+}. At pH 3.80 this ratio is 2.15, pH 4.50 is 2.10, pH 5.45 is 1.72 and at pH 6.92 is 0.58.[42] Because the rate of change is least at lower pH levels, quantitative use of the F^- electrode is most effective in the range around pH 4.5. It is this method which was adapted for use in these experiments.

The testing of other Al complexing agents has also included such well known chelating agents as EDTA, DTPA, citric acid and tartaric acid.[65] Tests with these agents using Chilean soils has showed that the amount of Al extracted was primarily a function of time. These extractions were done at pH 7, but correlations were not made with plant uptake. Also, the researchers did not establish what fractions of soil Al contributed to the Al recovered. Several other Al complexing agents have been tested for Al extraction and analysis but their use is not widespread. One such method, using the fluorescence of 8-hydroxyquinoline complexed Al in chloroform, was claimed to give good estimation of active Al in North Carolina soils.[13] The accuracy was stated to be better than that of titration procedures. This procedure has not been widely used possibly because of the volatile chloroform.

Because work has indicated the presence of Al-organic matter complexes in Canadian soils, some researchers have attempted to evaluate the importance of soil organic matter in Al reactions.[66] The sites for this proposed reaction are the numerous carboxyl groups of soil organic matter, analagous to the laboratory coagulation of pectin with Al^{3+}.[3, 55] Complexes of this type have high stability constants which would tend to reduce their reaction with plant components.[67] This is a probable explanation of the observations that ligand-complexed Al^{3+} evokes little or no phytotoxic reaction in plants. In fact, some studies have shown that when Al^{3+} is ligand-complexed, the entire complex may be translocated to the leaves.[6] This could possibly be the mechanism of Al accumulation in certain Cerrado plants.

As of this date, there is no specific quantitative test for Al^{3+} held in organic matter complexes. Although use of pyrophosphate does give an indication of Al-organic matter complexes, the best method so far appears to be acid leaching with all the attendant problems of inorganic Al solubilization.[50]

Other analytical methods have also been tried, but they suffer from the requirements of expensive equipment, and/or tedious procedures which are not easily adapted to large numbers of routine determinations. However, such procedures can be useful as checks for other more simple procedures.

A procedure, which has been tested on volcanic ash soils, utilizes the formation of a Mg-Al double hydroxide at pH 8.2 to 8.5.[64] This procedure also avoids acidic dissolution of Al and gave good correlation with pH 4.8 NH_4OAc extractable Al and with phosphate

fixation. In this case, the experimental objective was to estimate the chemical activity of the soil Al, not phytotoxic Al^{3+}. The procedure consists of titration of a soil with NaOH, and after overnight incubation, measurement of pH. The activity of soil Al is estimated by pH changes during this incubation.

Another method involves the determinations of heat of neutralization of Al^{3+}-H^{+} clays.[76] Because the heats of formation of acids, the enthalpy of formation of $Al(OH)_3$, and the titratable acidity of a clay are all known factors, it becomes possible to calculate the separate contributions of Al^{3+} and H^{+} to the total heat of neutralization. On known clays, exchange resins, and natural soil clays from Argentina, satisfactory agreement was found between results by this method and the actual amounts on exchange sites.

Still another method, requiring a relatively tedious procedure, involves an isotope of Al.[54] This requires use of the $_{13}Al^{28}$ isotope of Al which has a half life of 2.3 hours. By proper corrections for interfering radiation, it was possible to achieve accurate measurements of Al in lysimeter leachates with concentrations ranging down to 50 ppb. The major problem involved in this analysis was the interference from other elements and the short half-life of the Al isotope. The major advantage of this type of analysis is the precision (a cv of approx. 2%) and the sensitivity at low concentrations.

In summary, there does not appear to be, at this time, any single, widely acceptable, simple, rapid, method available for determination of active or phytotoxic soil Al. Many methods have been tested and each has its advantages for a particular soil type and form or combination of forms of Al. Because of many forms of soil

Al which contribute to the phytotoxic pool of soil Al, it seems unlikely that a single extractant will prove useful for all soils.

The success of any single method depends on its correlation with plant growth. Therefore, to find a suitable test for phytotoxic Al on certain soils, many researchers have relied on testing as many extractants as possible, and selecting the one with the best correlation to plant growth. Hopefully, the work which follows has avoided this wide ranging approach.

MATERIALS AND METHODS

Materials - Soils

Genesis of Cerrado Soils

A major problem is encountered in attempting to describe the geology and genesis of these soils because so very little work has been done. The most information available comes from the states of São Paulo and Minas Gerais.

In the state of Minas Gerais most Cerrado soils are formed from rocks of the Bambuí series, a silurian age sedimentary formation.[8] Some areas have mesozoic sandstone covering the Bambuí rocks, while in the region of Patos in Minas Gerais, large areas are covered with volcanic ash.[9] In general, the Bambuí series is considered to be the parent rocks of most Cerrado soils. The Bambuí series has been tentatively divided into six members: Serra do Saudade (shales and slates), Três Marias (silty to sandy shales), Lagoa do Jacaré (shale plus chlorite and a calcareous base), Serro do Sta. Helena (slates), Sete Lagoas (calcareous and metamorphic calcareous rocks), and Carrancas (quartz, chlorite, slate conglomerate).[17] These rocks are generally poor in bases, and the long weathering process during soil formation has further impoverished the supply of bases.

The weathered mantle of these rocks is generally well drained. In some areas with very sandy shales there is even an absence of

streams but a good supply of underground water. Topography of Cerrado areas seems to be related to underlying geology. Slopes which are over permeable soil and sandstone tend to be relatively steep, but at the surface of shale layers the slopes become less steep.[75] In places, thin layers of nodular laterite occur in the material above the sandstone-shale boundary. These variations are attributed to ground water movements and surface creep. Over the entire area of Cerrado occurrence, the topography varies from plains to mountains.[40] The single unifying factor seems to be the low natural soil fertility.

Description of Soils Used

Five soil profiles were sampled at three locations; Brasilia, Piracicaba (in São Paulo) and Sete Lagoas (in Minas Gerais). The two profiles in Brasilia were located on the DNPEA-IPEACO (Departamento Nacional de Pisquisas e Experimentação Agropecuárias - Instituto de Pesquisas e Experimentação Agropecuárias do Centro-Oeste) Experiment Station, and were located adjacent to an area being used for field plot experiments by the University Consortium on Soils of the Tropics. The profile in Piracicaba was located on virgin soil on a private farm often used by ESALQ ("Escola Superior da Agricultura:Luiz de Queroz") soil classification classes. Samples were taken from a profile previously classified.[45] The two profiles in Sete Lagoas were located on the IPEACO Experiment Station. Both profiles had been previously described for a reconnaissance soil survey of the station. Complete profile descriptions and location sketches are given in Figures 3-7 in the Appendix.

Four of the soils fall under the Brazilian classification. of Red Latosol (three are dark-red and one is yellow-red). Profile Brasilia 2 is classed as a Humic Gley and appears to be both physically and genetically different from the others. An attempt has been made to apply classifications according to the 7th Approximation system. In some cases though, the classifications are not without question. In the case of the two soils in Sete Lagoas classified as Typic Acrohumox, the scant data available concerning soil moisture shows it to be approaching an Ustic moisture regime. In the case of Brasilia 2 classified as an Aeric Haplaquept, the Inceptisol order implies the presence of weatherable minerals such as feldspars and micas. However, this profile shows little evidence of these minerals, and has come under the Inceptisol order, more due to exclusion from the other orders than by purposeful inclusion.

Of the four latosols, only three are under Cerrado vegetation. Piracicaba profile P-2 is under broadleaf forest. Although not under Cerrado, many of its properties are similar to the Cerrado soils, and is useful for comparison and contrast. All of the latosols are deep, well drained with excellent structure. Considering physical characteristics alone, all are well suited for agricultural use.

Some physical and chemical properties are shown in Tables 2-6 in the Appendix. Particle size distribution was done by the Soil Characterization Laboratory, Department of Agronomy, Ohio State University. Dispersion was with Calgon, and silt and clay fractions were determined by the pipet method.[19] The most common characteristic of all of these profiles is the large amount of clay present. All

horizons fall within the clay textural class. In nearly every case, the largest clay fraction is that less than 0.2 micrometers. This suggests that amorphous clays may be a significant fraction of these soils. Organic carbon was determined by combustion. In all cases, it is less than 5% and usually decreased with depth. The pH values in KCl and water show a consistent pattern. In all cases ΔpH (KCl pH - water pH) is negative, indicating a net cation exchange capacity. Extractable cations were determined using pH 4.8 1N NH_4OAc. The sum of these cations predictably decreases with depth. Levels of K, Ca and Mg are highest in the upper horizons of all profiles, most likely due to retention of these bases by organic matter. The anomalous high value for K in the A1 horizon of Piracicaba profile P-2 shown in Table 3 may be attributed to base retention or to residual ash from burning. It is located in a large sugar cane farm and fires are commonly set to clear trash from surrounding fields.

Mineralogy of the upper horizon clay fractions is given in Table 7 in the Appendix. The analyses were done with a Tracor DTA using 18 mg pressed pellets in an air atmosphere.[74] The clay samples were Mg saturated.[39] The mineralogy of all samples was similar except for Brasilia profile 2. In this soil, there was no evidence of Haemitite. In Piracicaba soil P-2 the Gibbsite dehydroxylation fork showed clearly, indicating greater crystallinity and order than the other profiles.[48] All samples showed significant amounts of amorphous constituents, Gibbsite and Kaolinite.

In the case of profile samples from Brasilia 2 and Sete Lagoas 92, subsamples were treated with methyl bromide and stored in 100%

relative humidity. These were later used for comparison with the rest of the samples which were dried and crushed to pass a 2 mm seive.

Materials - Kaolin

In certain phases of the experiments, commercially purchased Spruce Pine Kaolin was used.[a] X-ray diffraction analysis showed primarily Kaolinite with small amounts of Muscovite and Gibbsite in the sample. The raw Kaolin was ground with a mortar and pestle to pass a 0.5 mm sieve. Cation exchange capacity (CEC) was 12 me/100 gms using $BaCl_2$ and the method of Frink.[32]

Materials - Monon Wheat

In the growth chamber phase of this experiment, wheat was grown in pots having various soil treatments. The cultivar used was Monon propagated at Purdue University. Monon is particularly well suited to estimate plant reactions to soil Al. Monon is relatively sensitive to Al but relatively tolerant to soil Mn, a common problem accompanying excess soil Al.[27] Monon is more sensitive than most varieties, because of its high root CEC and the root character which induces a lower pH in the rhizosphere.[26] The toxic action of Al is restricted for the most part to morphological damage to root tips shown as radically decreased root tip elongation. Lack of systemic action may have avoided possible interaction effects in other plant parts. However, the effect of radically restricted root growth was readily evident as generally reduced plant growth.

a. from Ward's Natural Science Establishment, Rochester, N.Y. 14603

Methods - Pot Study

The pot study phase of the experiment involved growth of wheat plants on samples of the surface horizons of the Brazilian soils and on treated Kaolin samples.

The purpose of growing the wheat on a Kaolin base was to estimate the effect of adsorbed Al on plant growth. In order to do this an Al saturation procedure was developed which consisted of the following steps: (1) washing of clay sample with 1N KCl four times to remove native extractable Al (2) washing with distilled water six times to remove excess KCl (3) addition of Al^{3+} as $AlCl_3$ and shaking for 30 min. (4) washing with distilled water until the supernatant was chloride free (5) washing two times with ethanol (6) overnight drying at 40°C. (7) seiving through a 0.5 mm seive.

After saturation, the clays were again KCl-extracted, and analyzed for Al as a check on the saturation procedure. During the last saturation series, it was found that the KCl-extractable Al^{3+} after saturation was essentially the same as before saturation. In effect, the Al^{3+} was not remaining on the clay surfaces. Several attempts were made to determine the cause of this problem, but no solution was found. Rechecks of several previously saturated clays showed that they had retained the added Al^{3+}. Further investigation into this problem was not undertaken.

Because a pure clay base does not permit adequate aeration for plant root growth, an aggregation procedure was developed. Polyvinal alcohol (PVA) was used as the synthetic aggregate stabilizing polymer. PVA was selected because of several advantages

over other synthetic stabilizers. Some polymers, such as Na-acrylate, have definite toxic effects on plants and are unsuitable for plant response experiments.[71] PVA has no such toxic effect on plants and does not seem to interact with normal plant metabolism.[69] The effect of small amounts of PVA (0.5% by wt.) on fine quartz sand is to produce water stable aggregates. As such, it is an acceptable polymer for stabilizing a mixture of sand and kaolin. Another advantage of PVA is associated with the fact that it is a non-ionic polymer. It is believed to bond particles by displacing adsorbed water on the particle surfaces. In the case of kaolinite, the most probable site of action is on the flat surfaces, not the edges.[22] In summary, PVA should serve the purposes of stabilizing aggregates without affecting plant growth, and without interfering with the normal exchange reactions of kaolinite. As such, it was ideally suited for use in this experiment.

Aggregation was done in a 1 gallon Nalgene container rotating at about 50 rpm. A mixture of 75% acid washed quartz sand, 25% kaolin and 0.1% PVA powder was tumbled until all aggregates were greater than 5 mm. The aggregates were then air dried. A total of 100 gms of aggregate was used for each pot.

Wax coated paper containers were used for plant growth. Because the objective was to observe effects of adsorbed Al on plant growth, an attempt was made to reduce another variable through internal pot structure. Excess soil Al is especially detrimental to seedlings, and often results in poor germination. Since excess Al prevents elongation of the radicle, plants get a very poor, uneven start. To eliminate variability due to Al effects during

germination, a type of split pot was devised. As shown in Figure 8, about 100 gms of the clay or soil sample under test was placed in the lower portion of each pot. Over this was a 5 mm layer of 3 mm PVC beads for the purpose of preventing capillary movement of water upward. A mat of open weave fiberglass cloth over the beads prevented movement of sand down into the lower portion, yet permitted easy penetration of roots. In practice, about 10 seeds were planted in the upper sand layer and watered lightly with distilled water for 5 days. At this point, the lower portion was watered from below, and watering of the upper portion slowly discontinued. The effect of this was to encourage root growth into the lower portion, and to stop root growth in the sand layer. Although somewhat complicated, this procedure had the advantage of exposing a uniform set of plants to a certain Al treatment at a fixed point in their development.

A further attempt was made to reduce variations due to nutrient differences by watering from below using 1/2 strength Hoagland's solution.[36] The solution pH was adjusted to 5.0. This pH level was chosen as one which could be expected in many field conditions, and is near the upper limit for significant Al^{3+} activity.

Plants were grown in a Sherwood growth chamber with a 12 hour day length, 18°C night temperature, 27°C day temperature, 100% R.H. at night and 80% R.H. during days. Light intensity was approximately 2000-2300 ftc.

Harvesting was done at 2-3 weeks, and consisted of freezing the entire pot. This enabled easy separation of the dry sand layer, the tops, and two sections of roots. The roots were washed free of

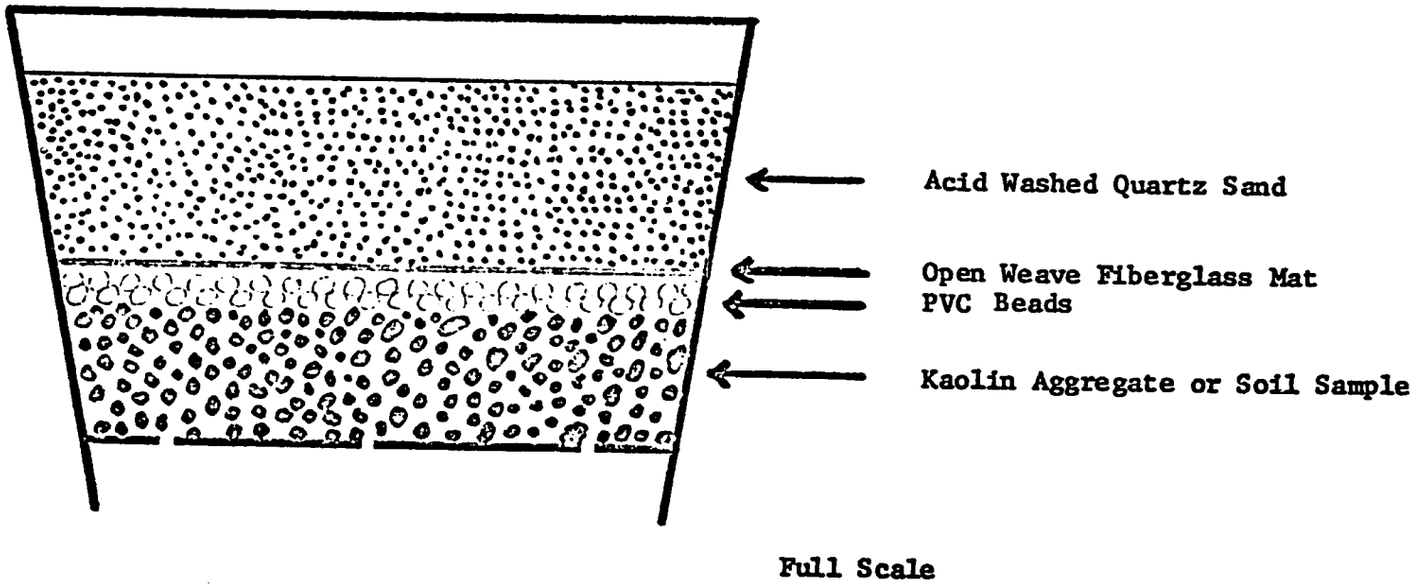


Figure 8. Arrangement of Pot Contents.

soil or clay particles. After overnight drying at 70-80° C, each plant part was weighed. In those pots where nutrient solution had seeped into the upper sand layer, the pot was discarded. All weights were adjusted to 10 plants/pot.

Methods - F^- Titration

Two methods of evaluating extractable soil Al were used. One was a relatively standard extraction with KCl. In this case, a sample was extracted five times after shaking with 1N KCl. The extract was analysed using either Eriochrome Cyanine-R or Aluminon.[51] The rationale for using KCl rather than any of the other extractants was simply that it is a common method in use in Brasilian soil laboratories to determine "exchangeable" Al^{3+}.[23]

The second method used to evaluate levels of soil Al was F^- titration. A Corning F^- electrode was used to follow levels of F^- in the sample as the titration progressed. The titration was done with 0.010M NaF, with most additions being between 0.1-3.0 ml. Two equal aliquots of F^- were added to each sample, one 60 sec. after addition of the buffer, and the second 120 sec. later.

The buffer was 0.5M NaOAc buffered at pH 4.55. Thioglycollate or thioglycollic acid was added to give a concentration of about 0.005M in the 50 ml solution being titrated for the purpose of reducing interference from Fe.[10] The final pH, after addition of the thioglycollic acid, was 4.50. During titration, a magnetic stirrer was used to ensure complete mixing.

The procedure used for titration of a sample was a follows:

(1) mix 40.0 ml of 0.5N NaOAc with 10.0 ml thioglycollic acid (dilute) (2) add this to a soil sample in a 100 ml beaker and stir for 55 sec. (3) at t = 60 sec. add an aliquot of NaF. (4) replace on stirrer and insert electrode. (5) read mv potential at 15 sec. intervals starting at t = 90 sec. (these are noted as 30, 45, 60, 75, 90, 105, and 120 sec in the data presentations). (6) at t = 180 sec. add another aliquot of NaF. (7) replace on stirrer and insert electrode (8) read mv potential at 15 sec. intervals starting at t = 210 sec. (these are noted as a subsequent series of 30, 45, 60, 75, 90, 105 and 120 sec. in the data presentations).

In fluoride titrations of Al, there are some variables which must be taken into account or controlled. The actual shape of the titration curve depends on the total soluble Al^{3+} present in a solution.[42] The reaction of F^- and Al^{3+} is not instantaneous, but progresses relatively slowly. For relatively large amounts of Al^{3+}, the time needed to complex 1/2 of the total amount present is 90 sec.[70] For smaller amounts, the times are somewhat less. Aside from Fe, both Mg and P can interfere with the titration, but in the natural soils, the low levels of nutrients made such interference unlikely.[42]

The change of free F^- over time was easily avoided by using the potential reading at 90 sec. as a reference voltage for a particular titration. The problem of varying standard curves as concentration of Al^{3+} varied was solved by plotting a 3 dimensional standard "surface". The three axes were: concentration of Al^{3+}, concentration of F^-, and mv potential observed. Given a known addition of F^- to a sample and observing the resulting mv potential,

it was possible to determine the concentration of Al^{3+} with reasonable accuracy.

RESULTS AND DISCUSSION

Results of KCl Extraction of Kaolin

As a check on the amount of Al adsorbed by the clay in the saturation procedure, each sample was extracted with 1N KCl. The samples which were used for extraction were aggregated, and as such, the total CEC for the aggregate mixture was 3 me Al^{3+}/100 gm. The total extractable Al for the three samples tested was as follows: Kaolin 1 - 0.082 me Al^{3+}/.100 gm, Kaolin 2 - 0.187 me Al^{3+}/100 gms., Kaolin 3 - 0.460 me Al^{3+}/100 gms. Kaolin 1 was KCl washed, but no Al added; in essence a blank.

Results of F^- Titration of Kaolin

For this initial treatment of titration data, the KCl extractable Al was assumed to be an accurate estimate of Al^{3+} present in a sample. With this as the basic assumption, the aliquots of NaF used in titration were based on F^-/Al^{3+} ratios varying from 0.10 up to 2.0. Previous work by Jaselskis and Bandemer has shown that at pH 4.5, the observed F^-/Al^{3+} ratio was about 2.10.[42] However, this depended on a fixed endpoint potential and in these titrations, a continuous potential was recorded. Nevertheless, for the intent of observing the pattern of reaction of adsorbed Al^{3+} with F^-, this assumed ratio is useful.

The results of the F^- titrations of the three Kaolin samples are given in Figures 9, 10 and 11. The vertical axis represents the

number of seconds after addition of an aliquot of NaF. The horizontal axis is graduated in units of R where R is the ratio (me F^- added/me Al^{3+} present in the sample). The oblique axis is plotted in units of r which is the ratio of (mv observed in the sample/mv observed in a standard). The standard in this case was a solution which contained an amount of Al^{3+} equal to the amount of KCl extractable Al present in the sample being titrated. This gave a rather fixed point of reference for each titration, and served as a point of comparison for every point observed in the sample. It should also be noted that, because of the relationship of electrode potential to F^- concentration, there is a logarithmic bias to the ratio r. The effect of this bias is to exaggerate differences between the standard and sample. The lower surface represents response to the 1st aliquot; the upper surface represents response to the 2nd aliquot.

With these points in mind, the response surfaces shown in Figures 9, 10 and 11 may be evaluated. In the case of Kaolin 1, the most marked feature is that the surfaces of both aliquots are nearly flat. Reaction time is very short, being 45-60 seconds. The second aliquot surface shows few variations which indicate very little buffering or reserve Al^{3+} entering into the reactions. The surfaces of Kaolin 2 and 3 are a bit more varied. Both show indications of greater differences between the sample and standard. But, upon addition of the second aliquot, the degree of this buffering is shown. In both cases, the ratio r indicates that the original level of Al^{3+} has been exhausted, and that the added F^- has not reacted.

By using the 3 dimensional standard surface, the titration data was converted to apparent Al^{3+} contents as shown in Figure 17. Each curve seems to peak at some maximum value of Al^{3+} and thereafter declines. Although the levels of KCl extractable Al^{3+} do not fall on these curves, they may intersect if the levels of F applied were less than 0.02 me/100 gms. These curves show relatively little in the way of unusual variations. The most useful observation of these results is that of a slow increase in apparent Al^{3+} content until a peak, after which there is a decline.

In summary, the F^- titration response surfaces of Kaolin, with primarily adsorbed Al^{3+} as the reacting cation, show a relatively featureless surface. The initial aliquot of F^- seems to react fairly uniformly and completely with the available Al^{3+}, leaving little for reaction with the 2nd aliquot.

Results of KCl Extraction of Soil Samples

The surface horizon soil samples of each soil were extracted with 1N KCl in a manner indentical to the extraction of the Kaolin samples. The levels of Al^{3+} extracted were as follows: Brasilia 1 - 0.903 me Al^{3+}/.100 gm; Brasilia 2 - 3.068 me Al^{3+}/.100 gm; Piracicaba P-2 0.040 me Al^{3+}/100 gm; Sete Lagoas 92 - 0.285 me Al^{3+}/100 gm Sete Lagoas IP-01 - 0.805 me Al^{3+}/100 gm.

Results of F^- Titrations of Soil Samples

The results of these titrations are presented as response surfaces in Figures 12 - 16. The most notable feature of all of these surfaces is the rapidly increasing differences between the

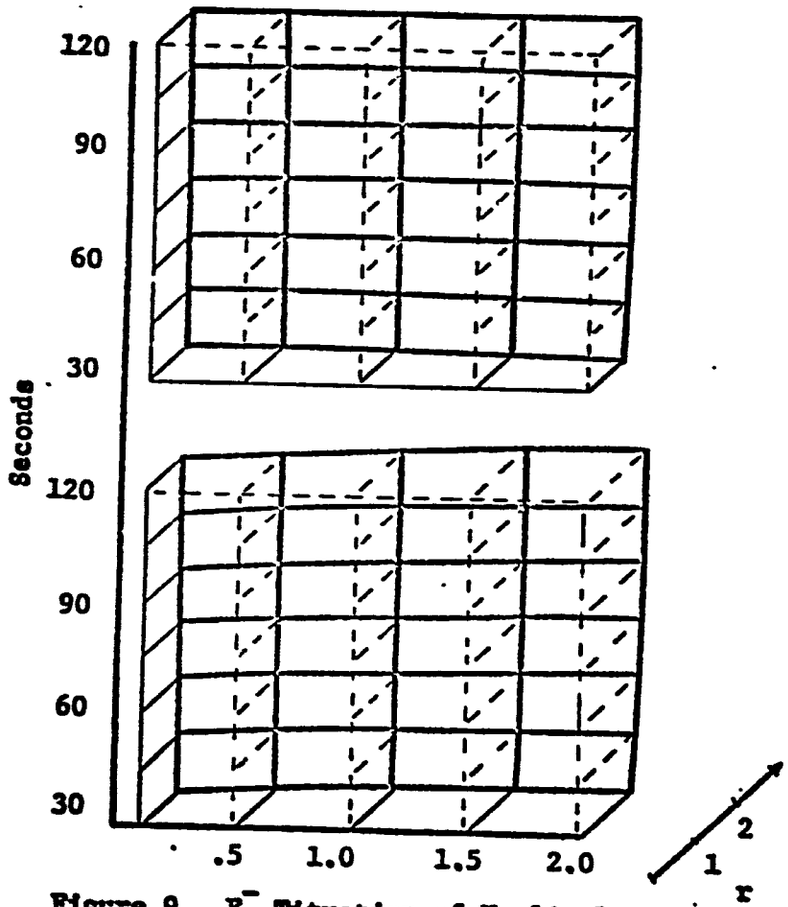


Figure 9. F^- Titration of Kaolin 1

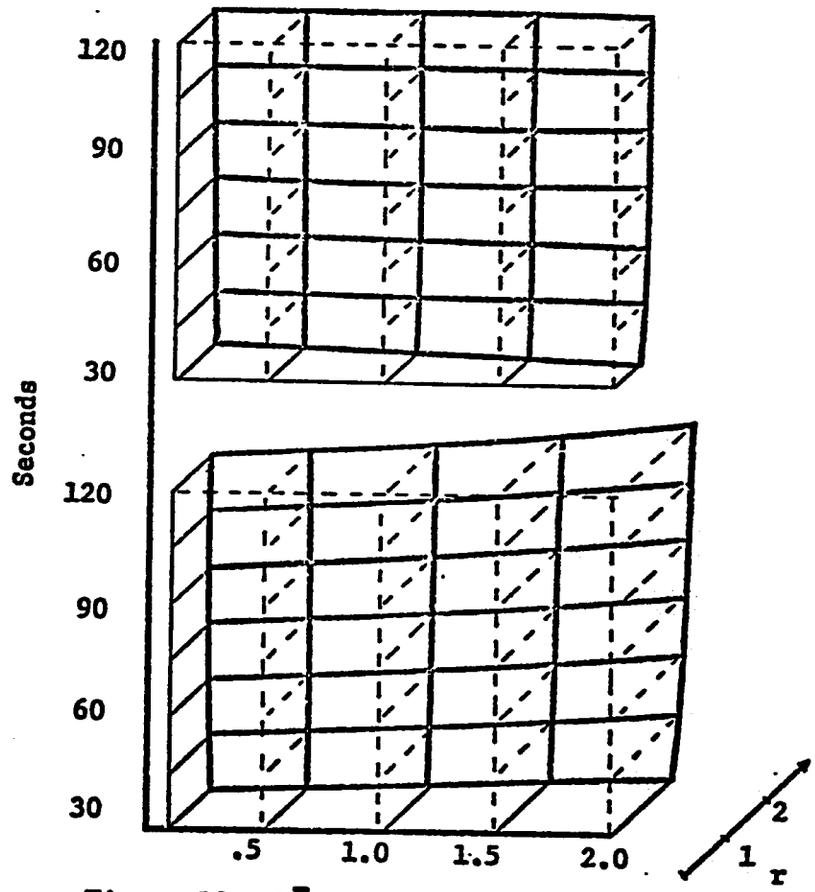


Figure 10. F^- Titration of Kaolin 2

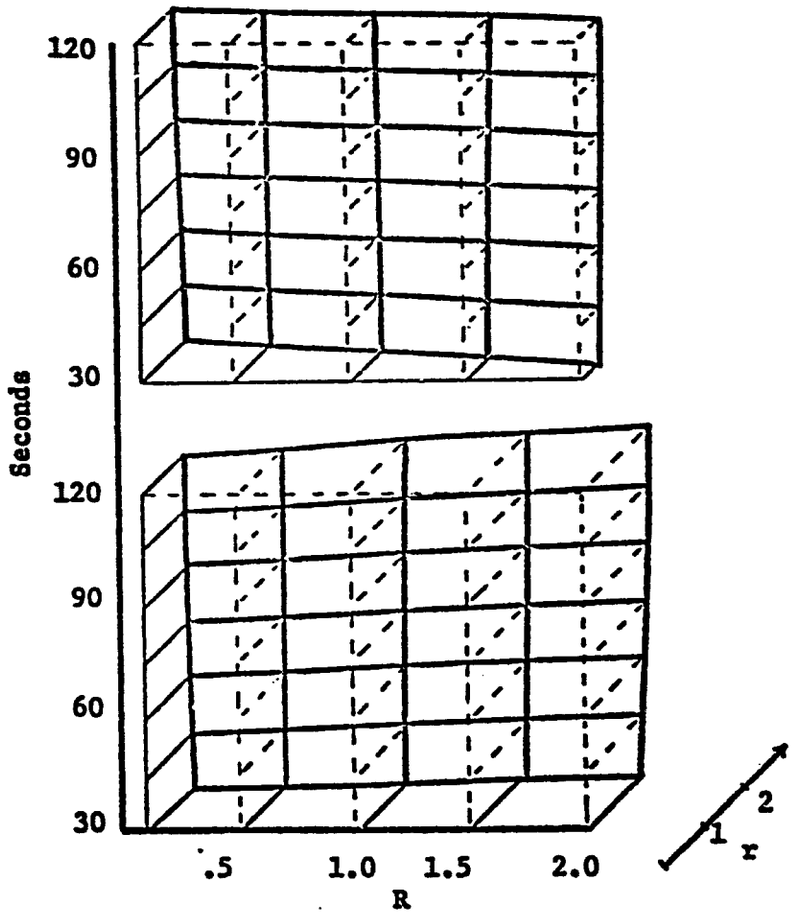


Figure 11. F^- Titration of Kaolin 3

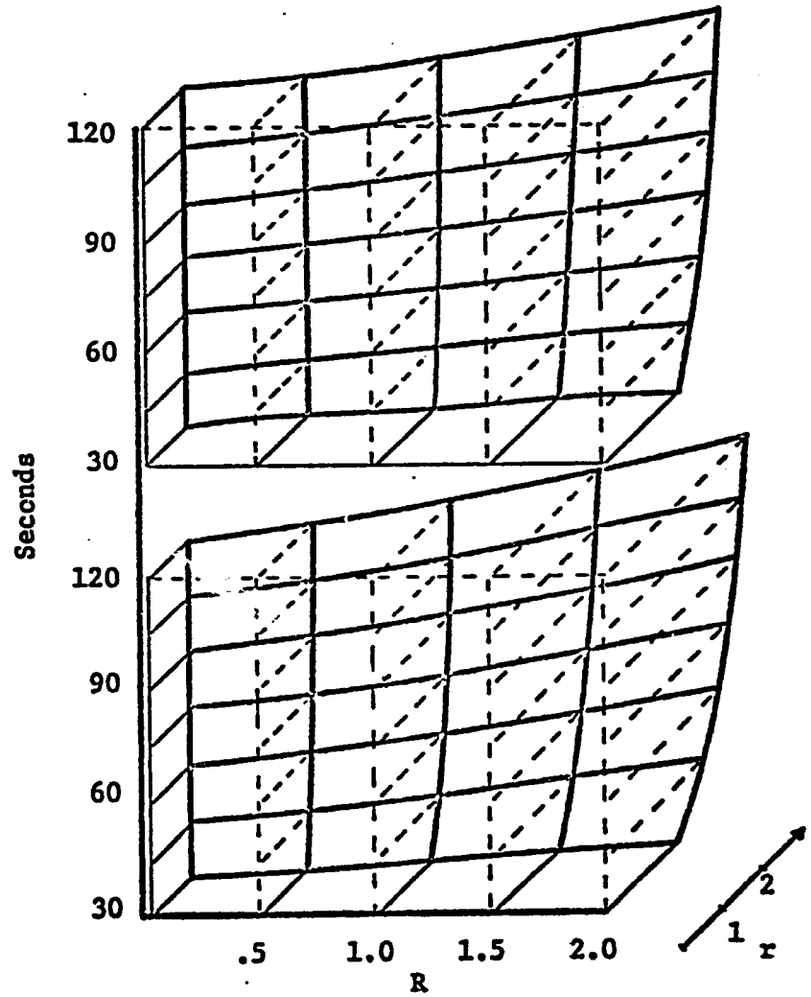


Figure 12. F^- Titration of Brasilia 1

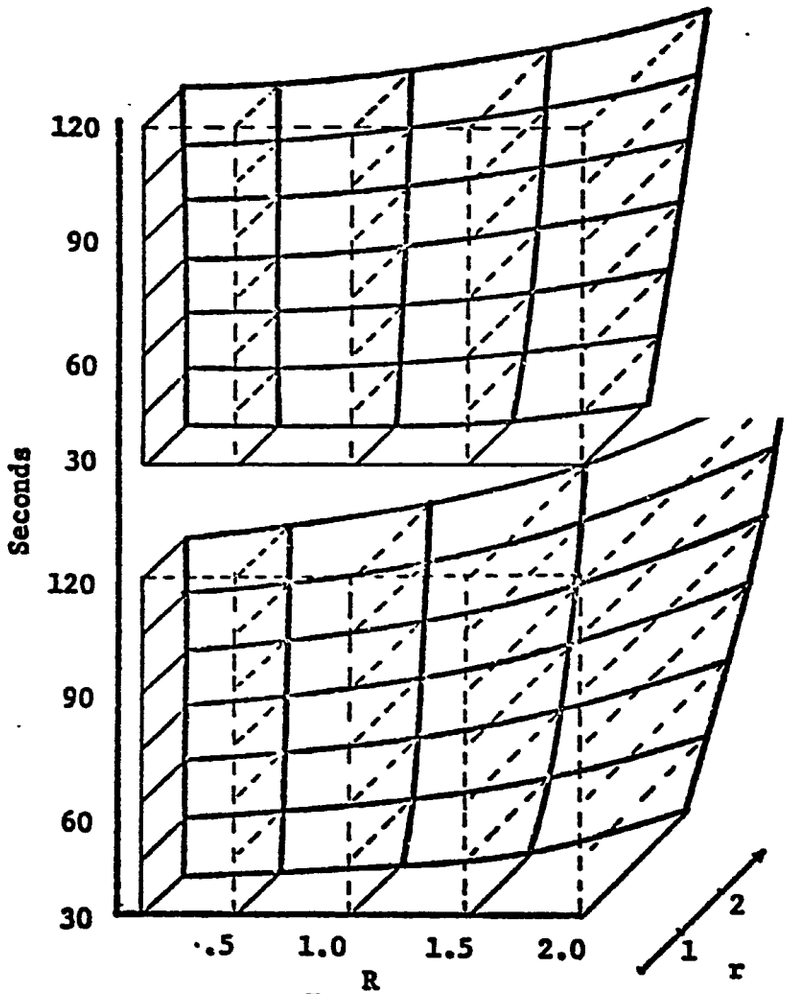


Figure 13. F^- Titration of Brasilia 2

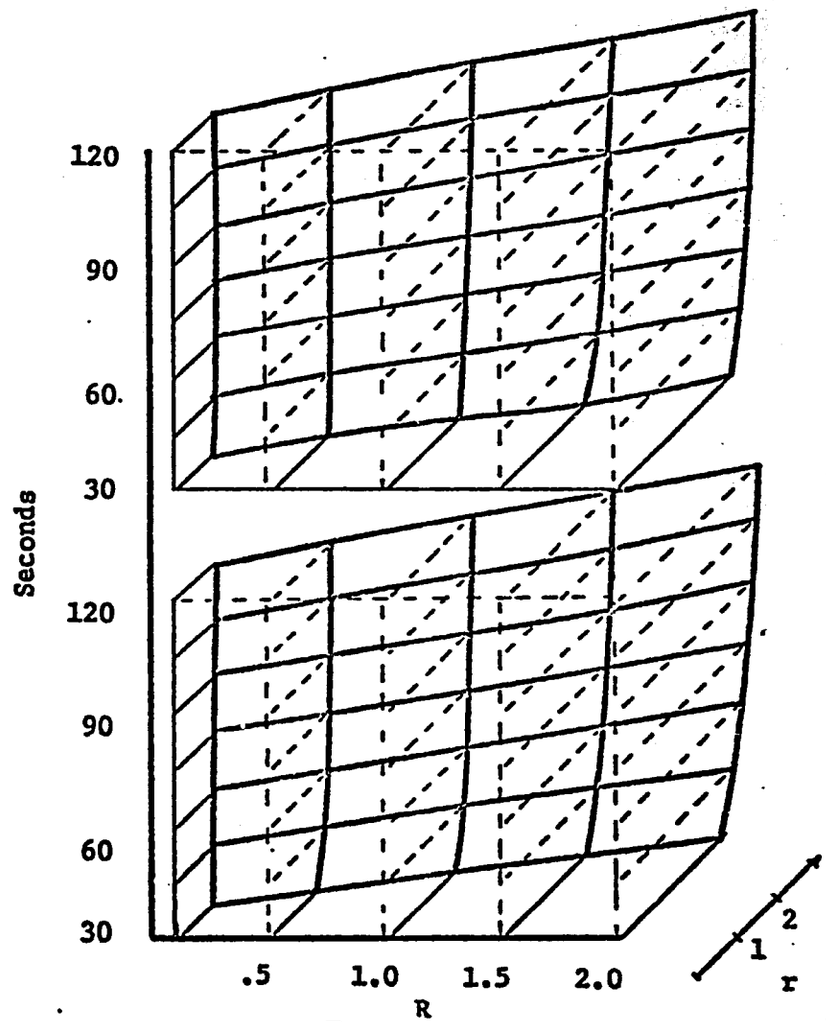


Figure 14. F^- Titration of Piracicaba P-2

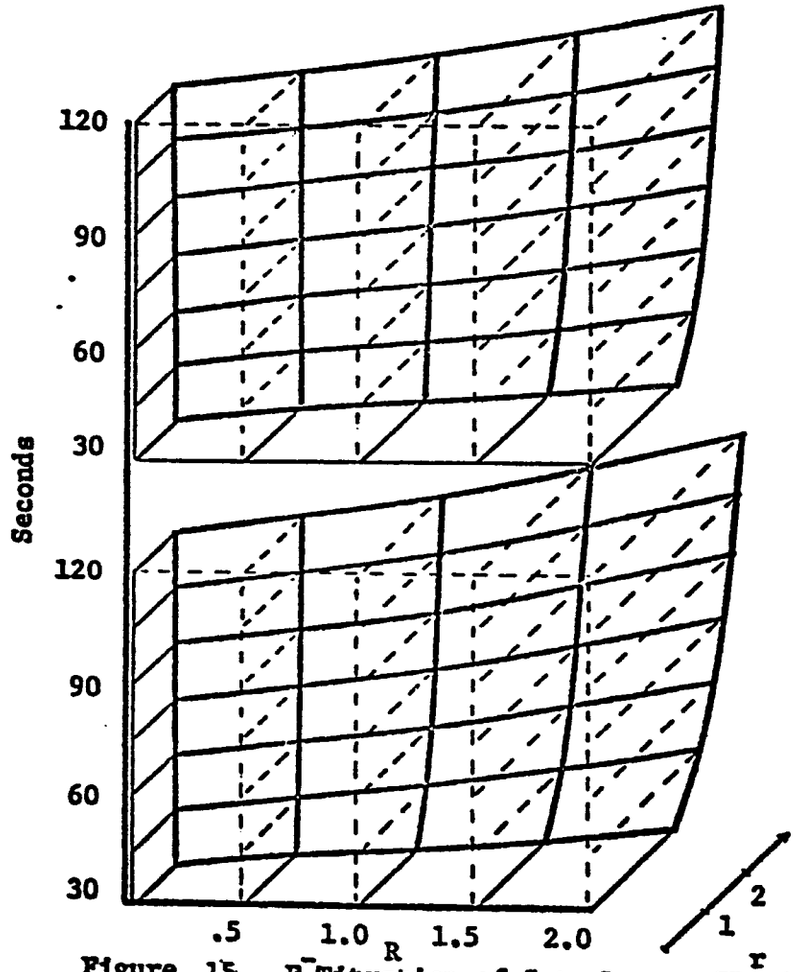


Figure 15. F^- Titration of Sete Lagoas IP-01

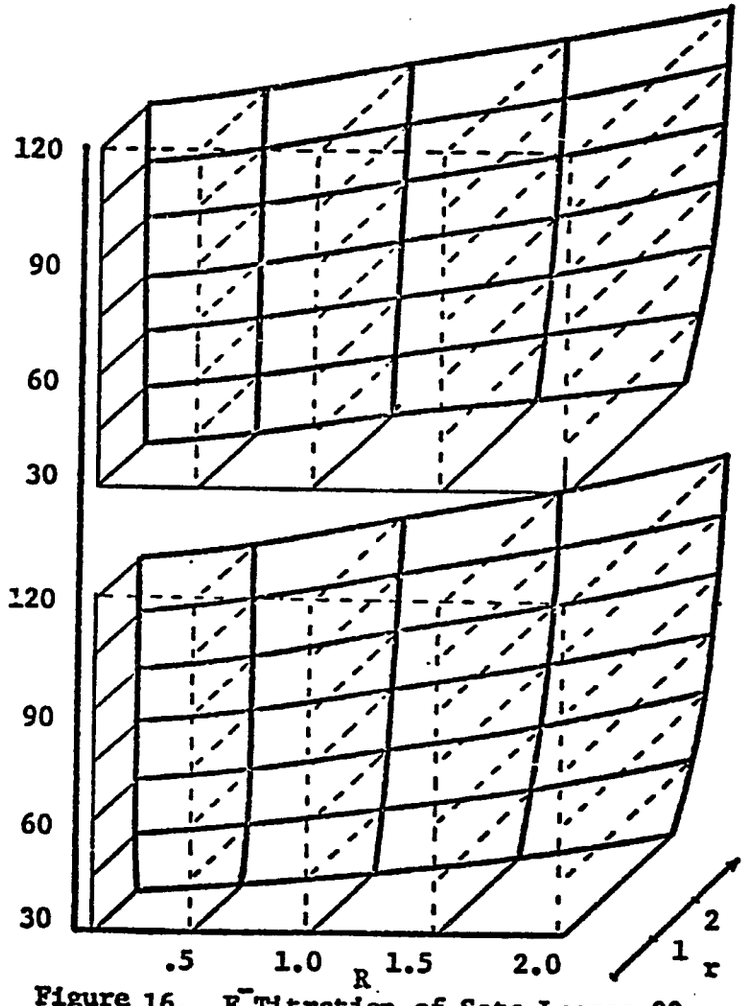


Figure 16. F^- Titration of Sete Lagoas 92

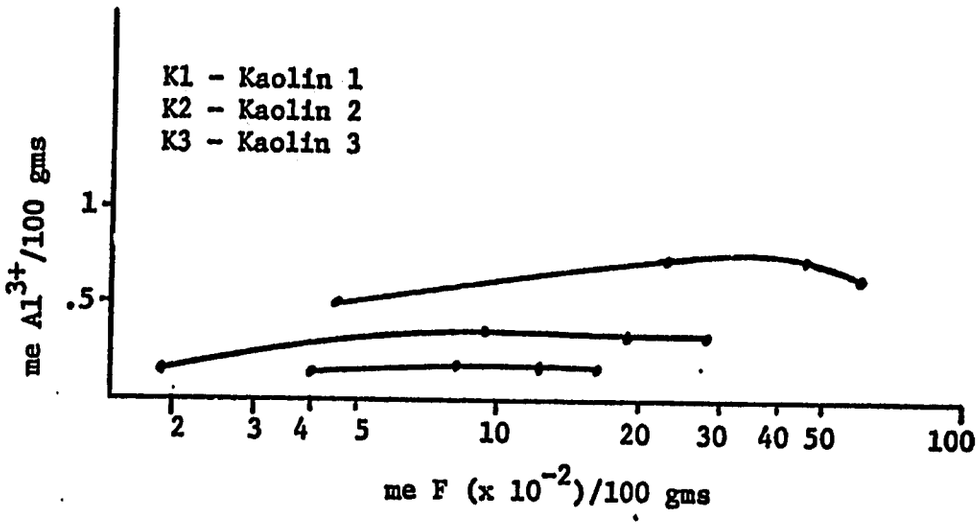


Figure 17. Apparent Al^{3+} Content of Aggregates versus F^- Applied

samples and standards as F^- additions increased. This serves as indication that larger proportions of F^- were being complexed in the samples than in the standards. The second notable feature is the great similarity between the 1st aliquot response surface and the 2nd aliquot response surface. This degree of similarity vividly demonstrates the degree to which the soil Al^{3+} is buffered in these soils. In the case of Brasilia 2, it appears to have much of its Al in a more reactive form since the 2nd aliquot response surface is noticeably lower than the 1st. However, in this soil the total amount of Al present is relatively high. This may also be a slightly different mineral form of Al, since profile classification indicates a different genesis. Although the other samples have

lower amounts of KCl-Al^{3+}, their buffer reserve is apparently adequate to instantly replenish the losses due to F^- additions.

Another noteworthy feature is the curvature of the surface along the time axis at higher F^- levels. In all cases, the surface has some curvature at the end of 120 sec., indicating that the F-complexing reactions are still in progress. With relatively small additions of F^- to the samples, as along the lines R = 0.10 and 0.50, the reactions seem to be approaching equilibrium, as shown by the nearly flat curves along the time axis. All sample surfaces show increasing r along the R axis, indicating that as larger aliquots of F^- are added, larger amounts of Al are complexed than in the standard.

Again, using the 3 dimensional standard surface apparent Al^{3+} levels were estimated. The titration curves for each sample are shown in Figure 18. The X on the lower ends of each curve represent the levels of KCl-extractable Al^{3+}. In the case of Brasilia 2, most of the points exceeded the limits of the standard surface. It is apparent that the amount of KCl-Al^{3+} is a relatively small fraction of the reactive soil Al reserve. The curves of 4 samples follow patterns similar to the Kaolin samples, showing a gradual increase up to a maximum. There are no abrupt breaks in the lower parts to indicate shifts from one form of Al to another.

Results of Wheat Growth on Kaolin

During the growth of wheat on the Kaolin aggregates, several problems became apparent. Although decreased plant weights were noted with increasing levels of adsorbed Al^{3+}, chlorosis of the leaf tips

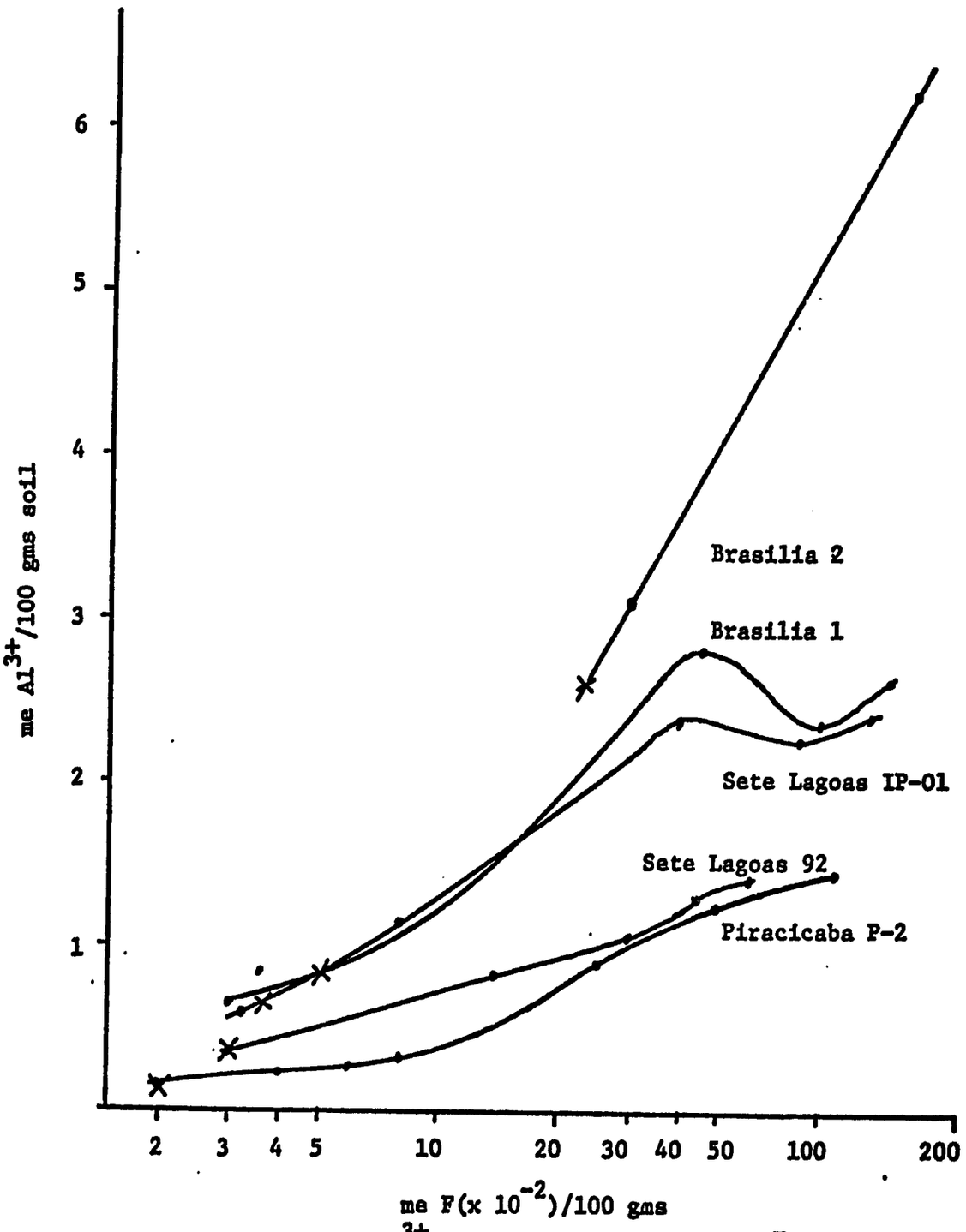


Figure 18. Apparent Al^{3+} Content of Soils Versus F^- Applied

was also evident. This appeared to be due primarily to poor aeration in the Kaolin-sand aggregate layer. In addition, analysis of the aggregates after plants were harvested showed a variation in pH similar to the changes in adsorbed Al^{3+}. Figure 19 shows this relationship graphically. As a result, the effects of the varying levels of adsorbed Al^{3+} were completely confounded with both pH and probably aeration, making statistical analysis impossible.

However, one observation is possible. By examination of the more flat portion of the curve for plant weights, it does seem that above a certain level of adsorbed Al^{3+}, plant response shows little variation. This may be due to a "saturation" of the sites of root damage.

Results of Wheat Growth on Soil Samples

In all presentations of plant growth data, only whole plant weights have been used. Initial analysis of the variability within each component measured (tops, upper roots and lower roots) showed that use of the total 10 plant weights gave the best estimate of overall plant response.

Wheat growth on the soil samples did not have the problems of the wheat grown on Kaolin. The total plant weights did vary with soil Al contents. Figure 20 shows the relationship between plant weights and apparent soil Al^{3+} levels. The apparent Al^{3+} levels were estimated by taking the point at which the curves shown in Figure 18 reached a maximum level. This level was then assumed to be the maximum level of Al^{3+} which could readily enter into complexing

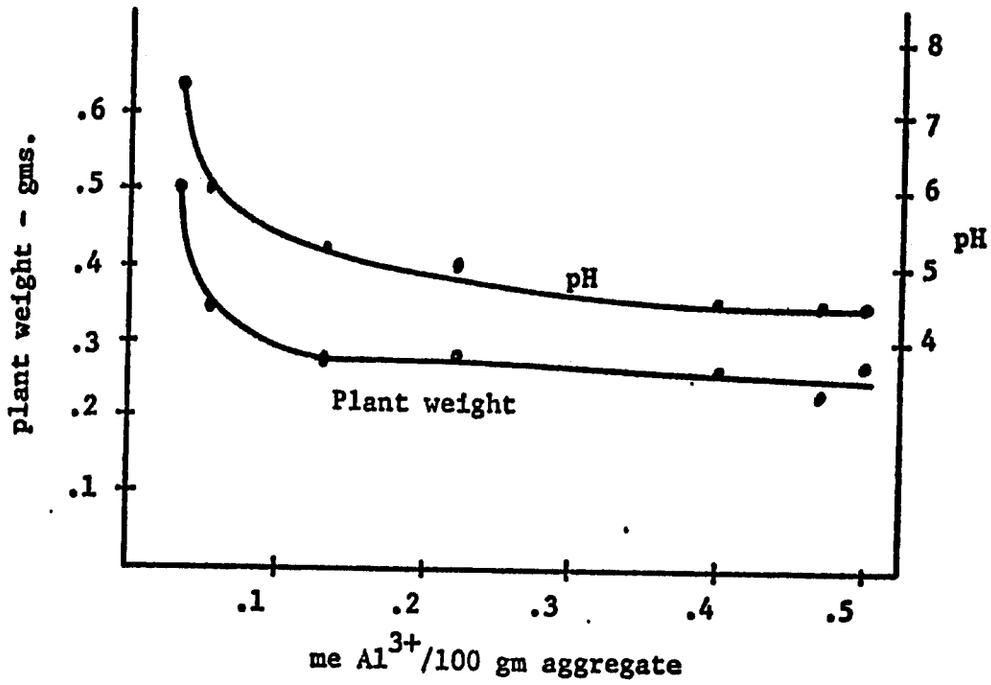


Figure 17. Variation of Plant Weights and pH versus Adsorbed Al^{3+}

reactions under natural conditions. The Brasilia 2 sample was not included since it was not possible to plot a peak for this sample. The data are shown in Table 8. The figures shown for Plant Weights are the mean weights of three pots having ten plants per pot. Regression of the log of plant weight on these apparent Al^{3+} levels gave a formula of $\hat{Y} = 0.3203 - 0.17647 (\log x)$ where $\hat{Y}$ is the resulting plant weight and x is the apparent level of soil Al^{3+}. The correlation coefficient, r was .9851 and was significant at the 5% level. The level of r^2 was .970. According to these figures then, the variation in apparent soil Al^{3+} was associated with 97% of the variation in plant weights.

Table 8. Plant weights versus Al^{3+} content of samples

Soil	me Al^{3+}/100 gms		10 plant weights - gms			
	KCl-Al	F-Al	lower roots	upper roots	tops	total
Brasilia 1	0.903	2.8	0.19	0.11	0.35	0.64
Brasilia 2	3.068	>10	0.13	0.14	0.33	0.60
Piracicaba P-2	0.040	1.5	0.41	0.15	0.59	1.15
Sete Lagoas 92	0.285	1.4	0.38	0.15	0.62	0.83
Sete Lagoas IP-01	0.805	2.4	0.22	0.14	0.48	0.83

Discussion of Results - Kaolin Titrations

While the results of the Kaolin titrations were not marked by definite differences, much can be learned by noting what did not occur. One concern with F^- was that it might attack the crystalline clay Al. From the results of the titration on the blank, Kaolin 1, it appears that within the range of F^- used, there was no observable increase in the apparent Al^{3+} content of the samples. If the clay structure were being attacked, certainly much larger variations would have been noted.

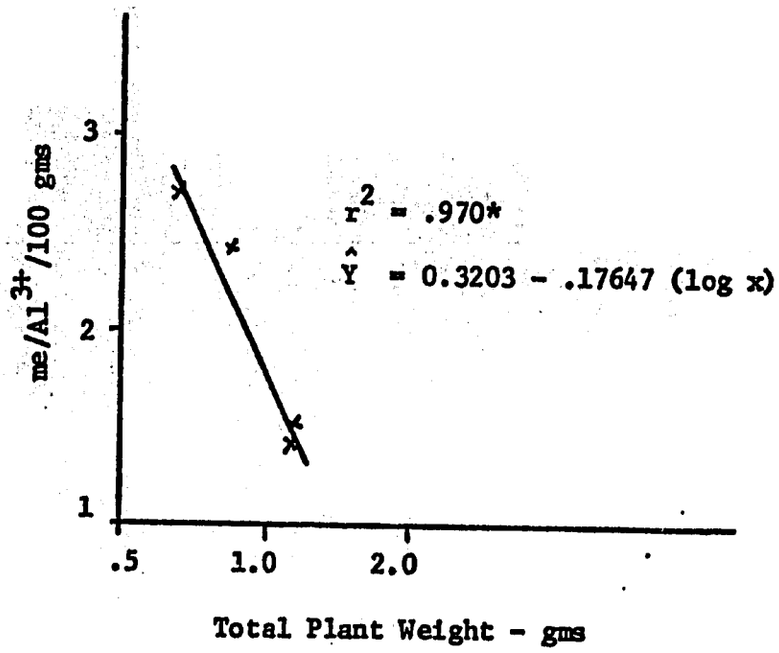


Figure 20. Plant Weights versus apparent Al^{3+} content of Soils

Adsorption of F^- on clay surfaces was also not a significant problem. During titration of the clays, differing weights of sample were sometimes used to yield certain low values of R. The lower portions of most of the curves were achieved by increasing amounts of sample in the titration procedure. If adsorption of F^- had been a significant part of the reaction, the apparent Al^{3+} would have shown an increase in this area. Instead, the uniformly decreasing values demonstrate the independence of apparent Al^{3+} values from total clay content and surface area.

It was noted that the F^- titration yielded more apparent Al^{3+} than was KCl-extractable. If it is assumed that KCl wholly replaced the adsorbed Al^{3+}, then this extra Al must have come from a source other than the added Al^{3+} or the clay crystal. Amorphous Al solids in various stages of crystallinity are a most likely source.

It is also possible that the KCl did not displace all of the Al^{3+} adsorbed on the Kaolin surfaces. Various surface charge densities would act to hold the Al^{3+} ions with varying degrees of force. It is easy to imagine stearic configurations of this electrical field which would make it extremely difficult for K^+ ions to displace Al^{3+} ions. Such a mechanism could account for a part of the discrepencies noted. Most likely, a combination of this stearic selectivity and contributions from solid Al forms are the sources of the additional Al^{3+} available for reaction with F^-.

Discussion of Results - Soil Titrations

One significant observation of the titration curves in Figure 18 is that there is a smooth increase in the F^- complexed Al^{3+} up to a maximum. If several distinct and separate forms of Al were contributing to the reactive pool of Al^{3+}, some breaks in these curves would be expected. However, the curves actually show a continuum of Al^{3+} complexing. The placement of KCl-Al^{3+} on these curves indicates that KCl-extractable Al is a relatively minor fraction of the total soil Al^{3+} pool. Although it is reasonable to assume that KCl extracts much of the adsorbed Al^{3+}, it is also highly probable that it removes a significant amount of Al^{3+} from part of the amorphous clay fraction

by proton release.[44, 62]

It is most likely that this amorphous clay fraction is the major contributor to the pool of Al^{3+} complexed by F^-. There is certainly a nearly infinite number of possible hydroxy-aluminum combinations that can be postulated as occurring in a soil. These various combinations could also be arranged in an order in which the bonding energies of Al^{3+} within the structure becomes greater and greater. This would then give a continuum of amorphous forms of Al having the Al^{3+} held in progressively stronger bonds. If progressively stronger disturbing forces (i.e. F^-) were introduced into this system at equilibrium, the effect would be for the force to interact with progressively stronger bonded Al. At a point where the force of bonding of Al is equal to the strength of the disturbing force, a new equilibrium is reached. It is possible that the upper limits of the curves in Figure 18 represent such an equilibrium. This then may be thought of as a measure of the amount of Al^{3+} in a soil which is held in various bonding patterns with less than a certain energy.

The next pertinent question, then, becomes one of whether this level of bonding energy is at all similar to that of the Al^{3+} - cell protein bond, where much of the phytotoxic Al^{3+} reactions are still open to debate, the answer is uncertain. In this case, the correlation between apparent Al^{3+} measured by F^- and plant growth seems to suggest that the energy of bonding by F^- may approximate that of the wheat in this experiment.

It is certainly apparent that the shifts in equilibrium to restore a balance towards Al^{3+} is quite rapid in these soils. The

titration pH of 4.5 was chosen to show precisely this shift. According to the work of Dalal, the neutral forms of soil Al would be the greatest contributors.[18] This also points to the amorphous clay fraction components. The speed of this shift is easily seen on the surfaces shown in Figures 12 - 16. In many cases where very small shifts in the equilibrium are made, the time required is only 30 - 45 seconds. When the disturbance is greater, it appears that 120 seconds is not enough. Certainly, under conditions of plant growth, there is enough time for such a shift to occur to near completion. Therefore, with the plant root acting as a sink for Al^{3+}, the buffering reserve of Al becomes more significant than soluble or adsorbed Al^{3+}. The amount and form of this reserve appears to determine the actual level of phytotoxic Al^{3+} in these Cerrado soils.

There are, of course, a large number of possible tests and alternate experiments that could be undertaken with such F^- titrations. Further refinement of the technique may enable resolution of certain inflections in the titration curves. These could, in turn, be related to curves of known Al complexes to define the contributing sources of Al^{3+} in natural soils. Study of the complexing reaction over longer time periods is certainly needed. Higher levels of F^- may also reveal more about the buffering reserve of these soils. It would also be useful to know the relative bonding energies of organically-held Al^{3+} and F^--complexed Al^{3+}. If they are indeed quantitatively similar, as implied in this study, the validity of F^- as an indicator of phytotoxic Al would be enhanced. At this point these questions must await more long-term reserach.

Conclusions

In this study, soil samples from the Brazilian Cerrado were used to determine a correlation between wheat growth and native soil Al^{3+}. The levels of soil Al^{3+} indicated by F^- titrations were greater than those of soil Al^{3+} extracted by 1N KCl. The most likely sources of Al which reacted with F^- were adsorbed Al^{3+} and weakly amorphous Al. The use of F^- titration enabled an estimate of the buffering reserve of phytotoxic Al over time. The estimate of soil Al^{3+} obtained by use of the F^- titration data was significantly correlated with total plant growth on the soils. This procedure of F^- titration has potential for defining the nature and type of phytotoxic Al in a soil sample.

A P P E N D I X

Profile Brasilia 1

Soil Type: Dark Red Latosol (Latosolos vermelho escuro Distrofico, textura argilosa) Acrorthox, clayey, kaolinitic, thermic.

Location: DNPEA-IPEACO Experiment Station, D.F., Brasil. about 2.5 km from BR41 along station entrance road, and about 100 m NE of road in virgin cerrado. Pit located 71 m NE of the corner marker of the Cornell lime plot on a line 82 m SE from the E corner of the Cornell P plot.

Physiography: Dissected peneplain

Parent Material: Silurian clayey schists and shales (Bambuí series)

Elevation: 985 meters

Topography and slope: gently rolling, 5% slope

Drainage: Well Drained

Permeability: Rapid

Vegetation: Cerrado with extensive ground cover by molassas grass (barba de bode)

Remarks: Slope facing N-NE; slight to no erosion; roots present at 160 cm depth; soil profile was dry at surface becoming slightly moist at 160 cm; Of the color chips available, 10 R 3/6 was the best choice; 7.5 R may have been better but was not available; very little diffentiation between horizons; pit was about 2 m E from a hive of wild bees.

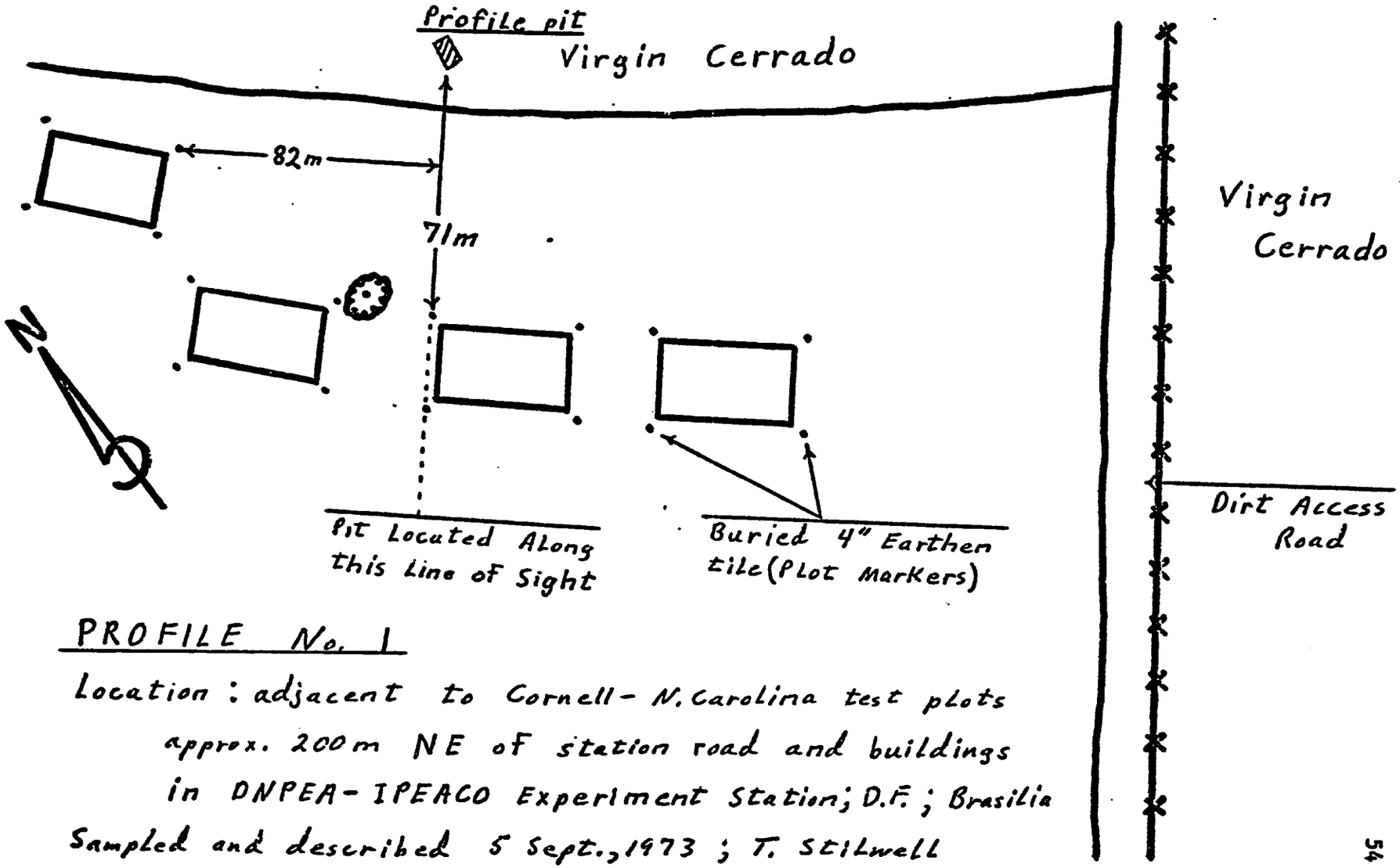
Depth & Horizon	PROFILE DESCRIPTION
0-22 cm A1	Dark red (10 R 3/6) moist and dark red (2.5 YR 3/6) dry sandy loam; weak, medium, granular structure; friable moist, firm dry; abundant roots; no stones; diffuse, smooth boundary.
22-53 A3	Dark red (10 R 3/6) moist, dark red (2.5 YR 3/6) dry, sandy loam; weak, very fine subangular blocky structure; friable moist and firm dry; many roots; no stones; diffuse, smooth boundary.
53-160 B1	Dark red (10 R 3/6) moist, dark red (2.5 YR 3/6) dry, sandy clay; weak very fine subangular blocky structure; friable moist and firm dry; many roots; no stones.

Collector: T. Stilwell

Date: 4 Sept., 1973

Weather: clear, warm with occasional bees

Figure 3a: Soil Profile Description - Brasilia 1



PROFILE No. 1

Location: adjacent to Cornell-N. Carolina test plots approx. 200m NE of station road and buildings in DNPEA-IPEACO Experiment Station; D.F.; Brasilia

Sampled and described 5 Sept., 1973; T. Stilwell

Figure 3b: Profile Location - Brasilia 1

Table 2a. Particle size distribution of Brasilia soil 1

Horizon	%Sand very coarse	coarse	medium	fine	very fine	total	%Silt fine	coarse	total	%Clay fine	coarse	total	texture
mm	1-2	.5-1	.25-.5	.1-.25	.05-.1	.02-2	2-20	20-50	2-50μ	<2	.2-2	< 2μ	
A1	.3	3.1	7.5	18.8	4.3	34.0	7.5	14.0	21.5	23.3	21.2	44.5	clay
A2	.2	2.0	7.1	16.6	9.6	30.5	7.4	3.2	10.6	53.8	5.1	58.9	clay
B1	.2	1.7	7.5	18.0	5.1	32.5	6.4	2.3	8.7	36.5	22.3	58.8	clay

Table 2b. Chemical properties of Brasilia soil 1

Horizon	organic C %	1:2 pH KCl	1:2 pH water	ΔpH	Exch. cations as me/100 gm soil Al^{3+}	Ca^{2+}	Fe^{3+}	K^{1+}	Mg^{2+}	Σ
A1	2.40	4.0	4.7	-0.7	.81	.16	1.45	.08	.09	2.59
A2	1.65	4.1	4.8	-0.7	.58	.04	.81	.03	.04	1.50
B1	.93	4.7	4.7	0	.56	.05	.16	.01	.02	.80

Profile Brasilia 2

Soil Type: Humic Gley (Gley Pouco Húmico Distrófico de várzea) Aeric Haplaquept, clayey, kaolinitic, thermic

Location: DNPEA-IPEACO Experiment Station, D.F., Brasil about 1.25 km from BR 41 along córrego Serandi and 200 m SW of cofrego Serandi. Pit was located 50 m E-SE of fence line on a line perpendicular to the fence line starting from a post marked X which in turn is 53 m N=NE from a tree on the fence line and E of a pond.

Physiography: dissected peneplain

Parent Material: Alluvial clay sediment

Elevation: 965 meters

Topography and slope: Gently rolling to flat, 0.5% slope

Drainage: fair drainage

Permeability: moderate

Vegetaion: Primarily virgin grasses with few, small woody plants (campo limpo or campo de varzea)

Remarks: Slope facing E, no erosion, free water at 175 cm depth, upper horizon was slightly moist becoming wet at 175 cm depth, mottles noted in C1 horizon had a value higher than those present on the 10R color chart (could possibly have been 10 R 7/6), pit was located on a sloping terrace above 2 m above floodplain where vegetation became strictly grass (campo de várzea) and no woody shrubs were present, all colors are for moist soil, the B1 horizon has some inclusions of material from the A horizon due to animal activity or movement through root channels.

Depth & Horizon	PROFILE DESCRIPTION
0-14 cm A1	Gray brown (10 YR 5/2) sandy loam; moderate, medium crumb structure; friable moist, stickey wet; abundant roots; no stones; clear smooth boundary.
14-58 B1	Very pale brown (10 YR 7/3) silt; very weak small subangular blocky structure; friable moist and sticky wet; many roots; no stones; diffuse smooth boundary.
58-84 B2	Very pale brown (10 YR 7/3) silt; very weak medium subangular blocky structure; friable moist and sticky wet; many roots; no stones; clear smooth boundary.

Figure 4a. Soil Profile Description - Brasilia 2

84-120 C1	Light gray (10 YR 7/2) silty clay with few, fine distinct light red (10 R 6/6) mottles; moderate, medium subangular blocky structure; firm moist and very sticky wet; few roots, no stones; smooth, diffuse boundary.
120-170 C2	Light gray (10 YR 7/1) silty clay; weak, medium subangular blocky structure; firm moist and very sticky wet; few roots; no stones.

Collector: T. Stillwell
Date: 4 Sept., 1973 Weather: clear, warm

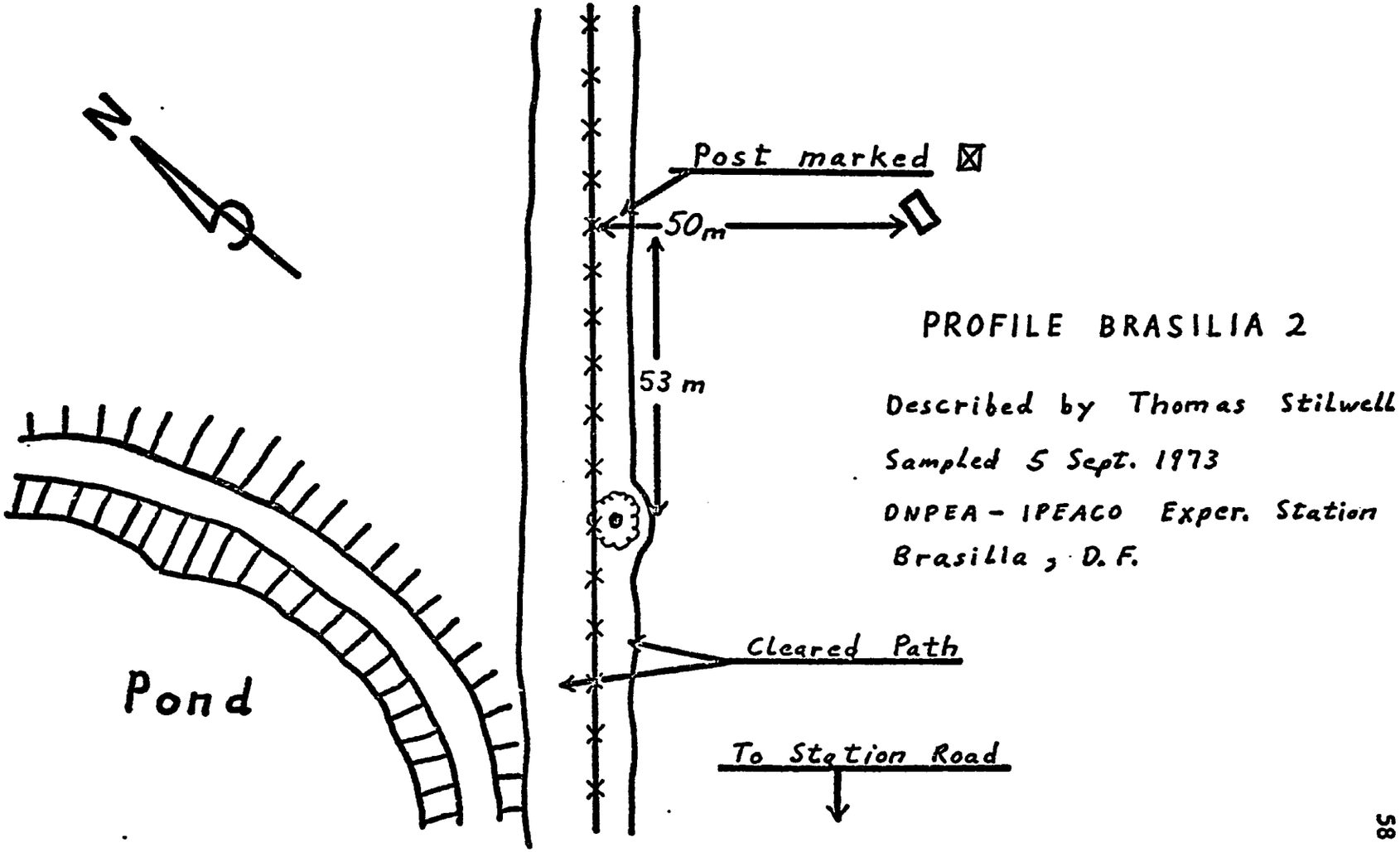


Figure 4b. Profile Location - Brasilia 2

Table 3a. Particle size distribution of Brasilia soil 2

Horizon	%SAND very coarse	coarse	medium	fine	very fine	total	%SILT fine	coarse	total	%CLAY fine	coarse	total	texture
mm	1-2	.5-1	.25-.5	.1-.25	.05-.1	.05-2	2-20	20-50	2-50μ	<2	.2-2	<2μ	
A1	.4	1.3	4.6	13.5	4.9	24.7	8.8	11.4	20.2	37.3	17.8	55.1	clay
B1	.1	.8	4.0	12.3	5.5	22.7	11.3	3.2	14.5	46.3	16.5	62.8	clay
B2	0	.7	3.7	11.3	5.5	21.2	9.2	4.4	13.6	48.6	16.6	65.2	clay
C1	.2	.7	3.6	11.0	5.5	21.0	8.5	3.4	11.9	52.7	14.4	67.1	clay
C2	.2	.9	3.2	10.4	5.4	20.1	9.5	3.6	13.1	48.0	18.8	66.8	clay

Table 3b. Chemical properties of Brasilia soil 2

Horizon	Organic C %	1:2 pH KCl	1:2 pH water	ΔpH	Exch. cations as me/100 gm Al^{3+}	Ca^{2+}	Fe^{3+}	K^{1+}	Mg^{2+}	Σ
A1	2.24	3.8	4.6	-0.8	1.04	.08	1.02	.11	.09	2.34
B1	1.14	3.8	4.7	-0.9	.76	.04	.54	.03	.05	1.42
B2	.62	3.8	4.9	-1.1	.70	.06	.16	.02	.03	.97
C1	.62	3.9	5.3	-1.4	.70	.02	.11	.01	.02	.86
C2	.56	3.8	5.1	-1.3	.65	0	0	.02	.03	.70

Profile IP-01

Soil Type: Red yellow latosol (Latossolo vermelho amarelado) Typic Acrohumox, clayey, kaolinitic, thermic
Location: IPEACO Experiment Station, Sete Lagoas, Minas Gerais. Pit located on hill about 80 m above entrance road and about 100 m N of entrance road and about 200 m E of BR-040, in pasture.
Physiography: dissected peneplain
Parent Material: Silurian schists and shales (Bambuí series)
Elevation: Approx. 750 meters
Topography and slope: undulating, 5-10% slope
Drainage: Well drained
Permeability: rapid
Vegetation: Presently used as pasture (capim gordura) previously was cerrado
Remarks: This description was made by Bernardo C. de Avelar for the reconnaissance (group level) soil survey of the experiment station. This description is a translation of his description plus added items from other sources (such as location, elevation, parent material, etc). Erosion is moderate. Some stones present in the profile.

Depth & Horizon	PROFILE DESCRIPTION
0-14 cm A1P	Yellowish red (5 YR 5/6) clay; weak, medium granular structure; plastic and very sticky wet; abundant fine to medium roots; few, moderate clay skins; diffuse, smooth boundary.
14-30 A3P	Yellowish red (5 YR 5/7) clay; weak medium subangular blocky structure; plastic and sticky wet; common fine and medium roots; few moderate clay skins; gradual boundary.
30-48 B1	Yellowish red (5 YR 5/8) clay; massive to weak, medium to large subangular blocky structure; very few, moderate clay skins; plastic and sticky wet; common, fine and medium roots; diffuse boundary.
48-83 B21	Yellowish red (5 YR 5/8) clay; massive to weak, large subangular blocky structure; very porous; plastic and sticky wet; few, fine and medium roots; diffuse boundary.

Figure 5a. Soil Profile Description - Sete Lagoas IP-01

83-130 B22	Yellowish red (5 YR 5/8) clay; massive to very weak, large subangular blocky structure; very porous; plastic and sticky wet; few fine roots; diffuse boundary.
130-176 B3	Yellowish red (5 YR 5/8) clay; massive to very weak, large subangular blocky structure; very porous; plastic and sticky wet; few, fine roots.

Translated by T. Stilwell

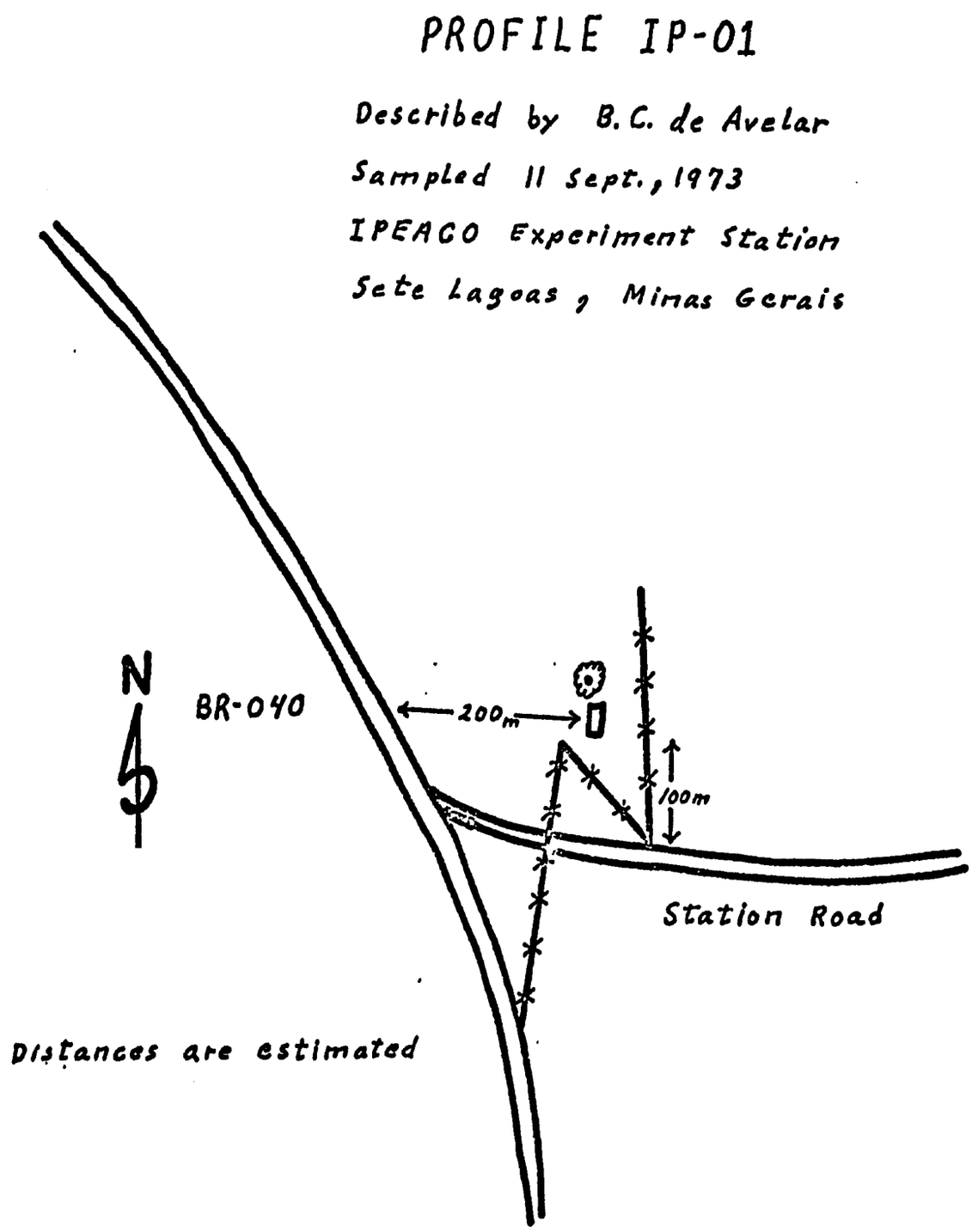


Figure 5h. Profile Location - Sete Lagoas IP-01

Table 4a. Particle size distribution of Sete Lagoas soil IP-01

Horizon	%SAND very coarse	coarse	medium	fine	very fine	total	%SILT fine	coarse	total	%CLAY fine	coarse	total	texture
mm	1-2	.5-1	.25-.5	.1-.25	.05-.1	.05-2	2-20	20-50	2-50μ	<2	.2-2	<2μ	
A1P	3.3	3.4	2.1	3.8	1.3	13.9	11.5	5.7	17.2	28.8	40.1	68.9	clay
A3P	2.9	3.6	1.9	3.4	1.5	13.3	9.3	0.5	9.8	72.4	4.5	76.9	clay
B1	2.6	2.9	1.7	3.4	1.5	12.1	7.2	0.7	7.9	39.8	40.2	80.0	clay
B21	3.2	3.4	1.4	3.3	1.7	13.0	8.3	0.4	8.7	41.7	36.6	78.3	clay
B22	2.6	3.0	1.8	3.2	1.3	11.9	4.6	5.6	10.2	42.3	35.6	77.9	clay
B3	3.3	3.2	1.6	3.5	1.7	13.3	9.0	0.8	9.8	41.7	35.2	76.9	clay

Table 4b. Chemical properties of Sete Lagoas soil IP-01

Horizon	Organic C %	1:2 pH KCl	1:2 pH water	ΔpH	Exch. cations as me/100 gm soil Al^{3+}	Ca^{2+}	Fe^{3+}	K^{+}	Mg^{2+}	Σ
A1P	1.99	4.0	4.7	-0.7	.72	.97	1.61	2.20	.25	5.75
A3P	2.32	3.9	4.7	-0.8	.76	.15	1.40	.11	.07	2.49
B1	1.75	4.0	4.5	-0.5	.53	.09	.43	.04	.05	1.14
B21	1.16	4.0	4.8	-0.8	.49	.07	.32	.06	.03	.97
B22	.82	4.2	5.0	-0.8	.56	.02	.21	.04	.04	.87
B3	1.09	4.3	5.3	-1.0	.51	.05	.16	.04	.04	.80

Profile 92

Soil Type: Dark red latosol (Latossolo vermelho escuro)
Typic Acrohumox, clayey, kaolinitic, thermic
Location: IPEACO Experiment Station, Sete Lagoas, Minas Gerais; pit located about 10 m S of an E-W access road in virgin cerradão on a slope about 100 m S from a fence and 700 m E from the road BR-040 in the northwest corner area of the station.
Physiography: dissected peneplain
Parent Material: Silurian schists and shales (Bambuí series)
Elevation: Approx. 750 meters
Topography and Slope: Gently rolling, 5% slope
Drainage: Well drained
Permeability: rapid
Vegetation: Cerradão with few grasses in the understory trees mostly Araticum sp.; undisturbed
Remarks: This description was made by Bernardo C. de Avelar for the reconnaisance (group level) soil survey of the experiment station. This description is a translation of his description plus added items from other sources (such as location, elevation, parent material, etc.)

Depth & Horizon	PROFILE DESCRIPTION
0-8 cm A1	Dusky red (2.5 YR 3/2) clay loam; weak medium granular structure; friable; slightly hard dry and friable moist, slightly plastic and slightly sticky wet; abundant roots; clear boundary.
8-24 A3	Dark reddish brown (2.5 YR 3/4) clay loam; massive structure; slightly hard dry and firm moist, slightly plastic and slightly sticky wet; many roots; diffuse boundary.
24-38 B1	Dark reddish brown (5 YR 3/4) sandy clay; crumb structure; slightly hard dry and friable moist, slightly plastic and slightly sticky wet; few roots; diffuse boundary.
38-61 B2	Dark reddish brown (2.5 YR 3/4) clay; crumb structure; slightly hard dry and friable moist, slightly plastic and slightly sticky wet; many roots; diffuse boundary.
61-97 B22	Dark red (2.5 YR 3/6) clay loam; crumb structure; slightly hard dry, friable moist, plastic and sticky wet; few roots.

Figure 6a. Soil Profile Description - Sete Lagoas 92

97-136 B3	Dark red (2.5 YR 3/6) sandy clay loam; crumb structure; slightly hard dry and friable moist, plastic and slightly sticky wet; few roots.

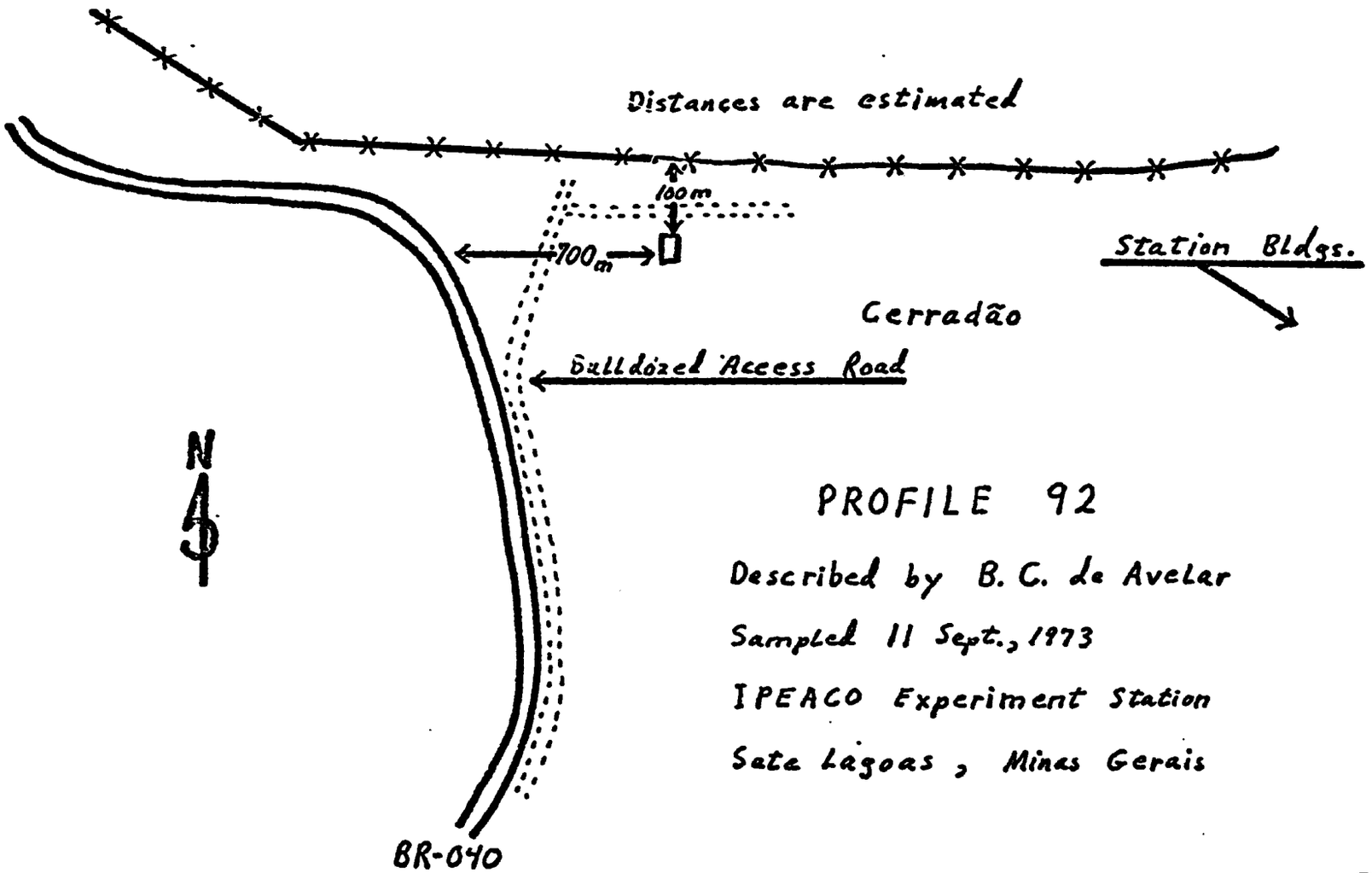


Figure 6b. Profile Location - Sete Lagoas 92

Table 5a. Particle size distribution of Sete Lagoas soil 92

Horizon	%SAND very coarse	coarse	medium	fine	very fine	total	%SILT fine	coarse	total	%CLAY fine	coarse	total	texture
	mm 1-2	.5-1	.25-.5	.1-.25	.05-.1	.05-2	2-20	20-50	2-50μ	< .2	.2-2	<2μ	
A1	1.3	6.6	6.0	9.5	1.8	25.2	9.0	19.9	28.9	23.5	22.4	45.9	clay
A3	1.8	2.8	2.4	6.2	1.8	15.0	10.0	1.1	11.1	37.3	36.6	73.9	clay
B1	2.8	2.5	1.8	5.2	2.3	14.6	7.2	0	7.2	42.3	35.9	78.2	clay
B21	1.6	2.4	1.5	5.1	2.3	12.9	9.4	1.2	10.6	42.9	33.6	76.5	clay
B22	1.8	2.0	1.5	4.2	2.3	11.8	7.0	0.5	7.5	77.7	3.0	80.7	clay
B3	2.2	2.2	1.2	4.0	2.3	11.9	6.2	13.1	19.3	78.5	2.2	80.7	clay

Table 5b. Chemical properties of Sete Lagoas soil 92

Horizon	Organic C %	1:2 pH KCl	1:2 pH water	ΔpH	Exch. cations as me/100 gm soil Al^{3+}	Ca^{2+}	Fe^{3+}	K^{+}	Mg^{2+}	Σ
A1	4.02	4.2	5.0	-0.8	1.16	2.44	1.99	1.86	.65	8.10
A3	3.34	4.0	4.6	-0.6	1.29	.17	3.38	.12	.08	5.04
B1	2.81	4.0	4.6	-0.6	1.18	.07	2.90	.05	.06	4.26
B21	1.94	4.0	4.7	-0.7	.81	.02	1.34	.02	.04	2.23
B22	1.82	4.1	4.7	-0.6	.88	.11	.64	.02	.04	1.69
B3	1.65	4.1	4.8	-0.7	.88	.01	.54	.02	.04	1.49

Profile P-2

Soil Type: Dark red latosol (Latosol Vermelho Escuro-orto) or Typic Haplorthox, clayey, oxidic, isothermic

Location: In the municipality of Piracicaba in São Paulo state, about 1.5 km NW of Iracemópolis road on Piracicaba-Rio Claro road, in the Santo Antonio Refinery farm, about 1 km SE of Piracicaba-Rio Claro road on a farm road situated in a block of forest about 10 m E of a large tree on the NW edge of the forest.

Physiography: dissected peneplain

Parent Material: Shales

Elevation: 714 meters

Topography and slope: Gently rolling, 1-2% slope

Drainage: Well drained

Permeability: Rapid

Vegetation: Broadleaf forest (mata latifoliada)

Remarks: This description is a translation of that made by S.S. de Andrade in a study for his MSc thesis at ESALQ (1971). The area near this profile is often used by soil classification students of ESALQ for field trips. Many of these pits are located along the margin of the NW edge of the forest.

Depth & Horizon	PROFILE DESCRIPTION
0-12 cm A1	Dark reddish brown (2.5 YR 3/4) clay; moderate medium, granular structure; hard dry and friable moist, very plastic and very sticky wet.
12-55 B1	Dark red (2.5 YR 3/6) clay; moderate, small subangular blocky structure; slightly hard dry, friable moist, plastic and sticky wet.
55-90 B21	Red (2.5 YR 4/6) clay; weak, small granular structure; friable moist, plastic and sticky wet.
90-240 B22	Red (2.5 YR 4/6) clay; weak, small granular structure; friable moist, plastic and sticky wet.

Figure 7a. Soil Profile Description - Piracicaba P-2

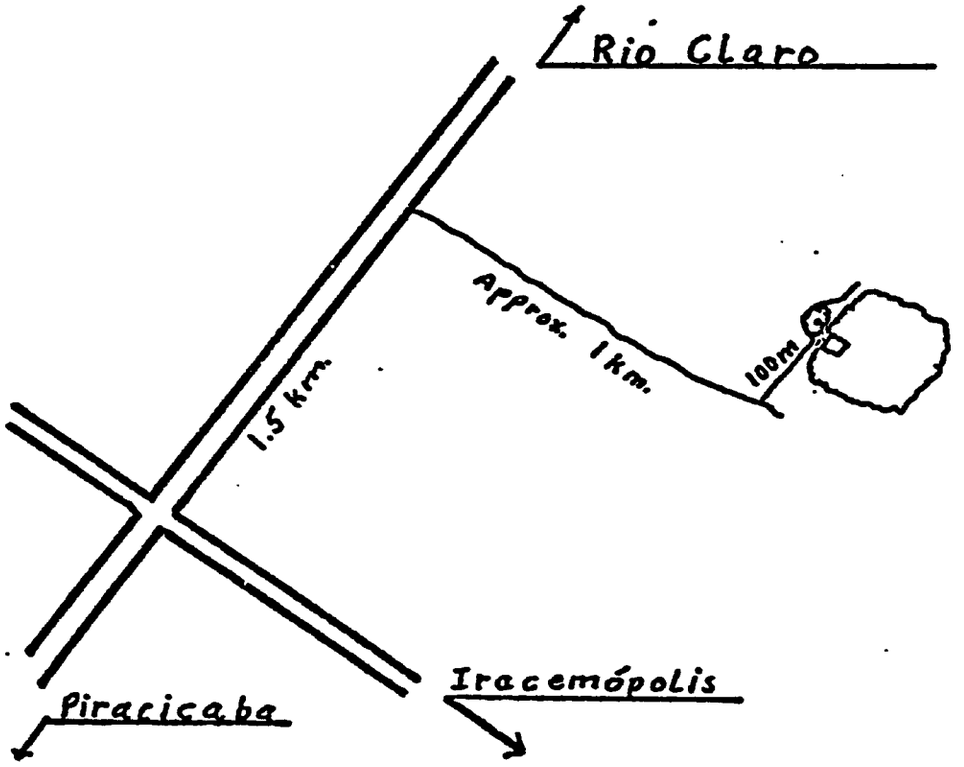


Figure 7b. Profile Location - Piracicaba P-2

PROFILE P-2

Described By. S.S. de Andrade

Sampled 14 Sept. 1973

Santo Antonio Refinery Farm

Piracicaba, São Paulo

Table 6a. Particle size distribution of Piracicaba soil P-2

Horizon	%SAND very coarse	coarse	medium	fine	very fine	total	%SILT fine	coarse	total	%CLAY fine	coarse	total	texture
mm	1-2	.5-1	.25-.5	.1-.25	.05-.1	.05-2	2-20	20-50	2-50μ	<.2	.2-2	<2μ	
A1	0.5	2.2	3.2	7.3	3.9	17.1	10.9	15.0	25.9	29.6	27.4	57.0	clay
B1	0.2	1.0	2.1	6.8	4.9	15.0	8.8	3.9	12.7	46.4	25.9	72.3	clay
B21	0	0.9	1.8	5.7	4.7	13.1	6.1	5.4	11.5	46.3	29.1	75.4	clay
B22	0	0.9	1.9	6.1	4.7	13.6	5.9	5.4	11.3	47.8	27.3	75.1	clay

Table 6b. Chemical properties of Piracicaba soil P-2

Horizon	Organic C %	1:2 pH KCl	1:2 pH water	ΔpH	Exch. cations as me/100 gm soil Al^{3+}	Ca^{2+}	Fe^{3+}	K^{+}	Mg^{2+}	Σ
A1	4.19	4.4	5.1	-0.7	.49	5.98	1.13	51.61	3.21	62.42
B1	1.66	3.9	4.5	-0.6	.60	.09	.86	.13	.13	1.81
B21	1.56	4.1	4.6	-0.5	.72	.07	.27	.09	.10	1.25
B22	.68	4.2	4.6	-0.4	.68	.05	.21	.07	.13	1.14

Table 7. Mineralogy of upper Horizons

Brasilia 1

Horizons A1 and A2

Kaolinite, Gibbsite, Amorphous, Haemitite
Moderately crystalline Gibbsite
Relatively low Haemitite content

Brasilia 2

Horizons A1 and B1

Kaolinite, Gibbsite, Amorphous
Moderately crystalline Gibbsite
Gibbsite peak slightly low

Piracicaba P-2

Horizons A1 and B1

Kaolinite, Gibbsite, Amorphous, Haemitite
Strongly crystalline Gibbsite

Sete Lagoas IP-01

Horizons A1P and A3P

Kaolinite, Gibbsite, Amorphous, Haemitite
Moderately crystalline Gibbsite

Sete Lagoas 92

Horizons A1 and A3

Kaolinite, Gibbsite, Amorphous, Haemitite
Moderately crystalline Gibbsite

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