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A Study on the Aquic Conditions of Two Natraqualfs in the Coastal Plain of Louisiana.

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A study on the aquic conditions of two Natraqualfs in the coastal plain of Louisiana

Szögi, Ariel Alejandro, Ph.D.

The Louisiana State University and Agricultural and Mechanical Col., 1992

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A STUDY ON THE AQUIC CONDITIONS OF TWO NATRAQUALFS IN THE COASTAL PLAIN OF LOUISIANA

A Dissertation

Submitted to the Graduate Faculty of the
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in partial fulfillment of the
requirements for the degree of
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in

The Department of Agronomy

by

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ABSTRACT

This study had the purposes of investigating the aquic conditions of two selected Natraqualfs to define the relationship between wetness and morphological properties and prediction of major soil processes. The proposed criteria for aquic conditions as defined by the International Committee on Aquic Conditions (ICOMAQ) were identified by: i) presence of redoximorphic features, and ii) measurement of saturation and reduction. They were used to locally verify morphological inferences used to predict the aquic conditions.

Morphological properties and laboratory analysis were used to predict the periodicity and duration of saturation and reduction. Soil and ground water analyses were used to understand the fate of electroactive species to predict reduction. Physical, chemical and mineralogical data were used to predict major soil enviromental processes relationship with aquic conditions.

Results indicate that: i) both soils supported aquic conditions with episaturation; ii) redoximorphic features found in both soils did not define uniquely soil episaturation or endosaturation; iii) episaturation produces long periods of stagnation when precipitation exceeds evapotranspiration, otherwise episaturation occurs for very short periods of less than 2 weeks; iv) the redox capacity factors OXC and AC predicted anaerobic conditions that correlated well with field Eh measurements; v) the strong horizon differentiation between

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E and B horizons is the product of dispersion and degradation of clay minerals. Dispersion and degradation occur by interaction of seasonally wet conditions and the presence of Na in the soil system.

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CHAPTER 1.

SOIL AQUIC CONDITIONS AND AQUIC MOISTURE REGIMES:
A LITERATURE REVIEW

1.1. INTRODUCTION

The demand by public and private clientele of soil resource information regarding soil wetness has soared in the last two decades. This demand has been greatly influenced by the public and private concerns on environmental issues related to the preservation of wetlands because of their important role in influencing ground and surface water quality.

Wetland and seasonally wet soils that traditionally were considered non-suitable or marginally suitable for agriculture or forestry became an important issue in the legislation. The focus of the legislation was to protect the environment. Congressional bills such as the Clean Water Act (1977), the Food Security Act (1985) and the Emergency Wetland Resource Act (1988) were enacted to achieve the desired protection.

An extensive listing of seasonally wet soils defined as hydric soils by the National Technical Committee for Hydric Soils or NTCHS (1987, 1991) was compiled to aid in the delineation of jurisdictional wetlands as defined by the Federal Interagency Committee for Wetland Delineation (1989). This database relies heavily on soil properties and soil classification documented in Soil Taxonomy, the Key to Soil Taxonomy and Soil Interpretation Records (Soil Survey Staff,

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1975, 1990, 1983). All the soils in this list have an aquic moisture regime such that they belong to an aquic suborder.

In Soil Taxonomy, the characteristics that define soils with stagnant or perched water tables appear at different taxonomic levels. However, they are not explicitly defined according to the definition of the aquic moisture regime. The difficulties in applying the definition of the aquic moisture regime for the taxonomic placement of these kinds of soils are related to the specification of the minimum duration of saturation and reduction, definition of the soil moisture control section, verification of low chroma colors and in situ reduction.

The recognition of the different problems that plagued the classification of wet and seasonally wet soils inspired the International Committee on Aquic Moisture Regime (ICOMAQ) to thoroughly revise the definition and criteria for the aquic moisture regime. Terminology to classify wet soils are defined and discussed by Bouma (1991). This revision proposes to use the term "aquic conditions" instead of "aquic regime". The aquic conditions are defined by three elements: i) presence of redoximorphic features, ii) duration and depth of saturation and iii) occurrence of reduction unless the soil is artificially drained. A distinction is made between soils with perched water tables (episaturation) and soils with true ground water table (endosaturation).

Two Natraqualfs, one located in Calcasieu Parish and another one located in Livingston Parish, are the objects of study in this research. These two soils as well as other Natraqualfs and associated soils in the Coastal Plain of Louisiana are seasonally wet soils with strong horizon differentiation, i.e. a light textured horizon overlies a heavy textured horizon rich in exchangeable sodium. These soils are reduced, seasonally saturated with a perched water table and have redoximorphic features in the profile. They are marginally suited for most uses due to their poor drainage, sodium content, poor structure and low fertility.

Investigations by Fleming (1984), Goh (1984), McQuaid et al. (1987) and Walthall et al. (1992) in other areas of Louisiana were undertaken to address the multiple problems on genesis, classification, reclamation and management of Natraqualfs and associated soils. However, the pedogenic processes have not been studied so far as directly influenced by aquic conditions.

The scope of this dissertation has an emphasis on investigating the aquic conditions and its effects on the morphology, classification and soil environmental processes of these soils.

The following are the objectives of this study:

i) Define the depth, frequency, and duration of saturation and reduction in two selected sodium affected soils of the Coastal Plain of Louisiana.

ii) Determine how morphological properties and laboratory analysis are useful to predict the periodicity and duration of saturation and reduction.

iii) Discuss and define the classification of the two soils selected with respect to the ICOMAQ definitions.

iv) Use the chemical analyses of the soil and ground water to understand the fate of electroactive species in order to predict anaerobic conditions.

v) Predict the major soil processes from physical, chemical and mineralogical data.

Objectives i), ii) and iii) are the subject of chapter 2, objective iv) is the subject of chapter 3 and objective v) is the subject of chapters 4 and 5.

The achievement of these objectives are not merely academic. The ultimate goal is to apply the acquired knowledge on aquic conditions and soil processes in the preservation, management and restoration of Natraqualfs and associated soils in Louisiana

1.2. PROBLEMS IN CHARACTERIZING AND CLASSIFYING WET SOILS

The "aquic moisture regime" was one of the six classes of soil moisture regimes in Soil Taxonomy (Soil Survey Staff, 1975). These six classes that defined the moisture regime from the driest to the wettest conditions were: aridic, xeric, ustic, udic, perudic and aquic. An aquic moisture regime characterized those soils as aquic when saturation with water

occurred for periods long enough to cause reducing conditions in the soil moisture control section. The soil moisture control section was defined by an upper boundary that "is the depth to which a dry (tension more than 1500 kPa but not air dry) soil will be moistened by 2.5 cm of water within 24 hours and a lower boundary that "is the depth to which a dry soil will be moistened by 7.5 cm of water within 48 hours" (Soil Survey Staff, 1975).

The "aquic moisture regime" as a diagnostic property failed to distinguish between perched versus true ground water tables, did not specified periods of saturation, did not recognized saturation without reduction and did not recognized paddy soils as a separate taxa. These limitations led to depend on the soil morphology to determine if soils were saturated and reduced (Moorman and Van de Wetering, 1985; Wilding and Rehage, 1985). The classifications from Germany (Blume and Schlichting, 1985), France (Duchaufour, 1982), England (Avery, 1973), and The Netherlands (de Bakker, 1973) handle several of these problems in their systems. For instance, they classify soils with perched water tables or by assigning water table depth classes, while Japanese pedologists (Kyuma, 1985) consider the classification of soils with controlled flooding (wetland rice) as an important variant in the classification of soils with perched water tables.

The Keys to Soil Taxonomy (Soil Survey Staff, 1990) underwent a significant revision in most of its orders. The "aquic moisture regimes" affected all the orders at the suborder or at the subgroup taxonomic levels, and also subjected to significative revision by the International Committee on Aquic Soil Moisture Regimes (Bouma, 1991).

1.3. THE DEFINITION OF NEW TERMS TO IMPROVE THE CLASSIFICATION OF WET SOILS IN THE USDA SOIL TAXONOMY

The recognition of the different problems that plagued the classification of wet soils and seasonally wet soils, inspired the ICOMAQ to thoroughly revise the definition and criteria for the aquic soil moisture regime. Terminology to classify wet soils are defined and discussed in ICOMAQ's Circular Letters (Bouma 1988, 1989, 1990, 1991).

The main modifications to aquic regime were:

i) The "aquic soil moisture" regime became: "aquic conditions". Aquic conditions means that the soil is currently experiencing periods of saturation and reduction to be identified by redoximorphic and measurements of saturation and reduction, unless artificially drained. This definition introduces the concept of diagnostic soil characteristic in Soil Taxonomy rather than diagnostic horizon in the particular case of the diagnosis of aquic conditions in wet soils.

ii) Definition of the three elements that define aquic conditions:

Saturation: defined by zero or positive pressure in the soil water and established by observing free water in an unlined borehole. Three types of saturation are defined:

i) Endosaturation, the soil is saturated in all layers from the upper boundary of saturation to a depth of 200 cm or more.

ii) Episaturation, the soil is saturated in one or more layers within a depth of 200 cm and also has one or more layers that are unsaturated below the saturated layer. The upper boundary of unsaturation must be within a depth of 200 cm.

iii) Anthric saturation, represents a variant of episaturation and is associated with controlled flooding for wetland rice, resulting in reduction processes in saturated, puddled surface soil and oxidation of reduced and mobilized iron and manganese in the unsaturated soil.

Reduction: characterized by direct measurement of redox potentials (Eh) or indirect measurements by staining tests. Only reduction that results in reduction of Fe is considered to represent the reduced state is considered as a diagnostic property.

Redoximorphic features: defined in terms of Munsell colors and color patterns defined in the keys. They are formed as a result of reduction and oxidation processes of iron and manganese compounds following saturation and desaturation of the soil.

1.4. DEPTH, PERIODICITY AND DURATION OF SATURATION AND REDUCTION IN WET SOILS

According to Wilding and Rehage (1985), the occurrence of soils with aquic conditions is not restricted geographically by any specific soil formation factor (climate, topography, parent material, biota, or time). The only requirement is that hydrologic and pedogenic processes were combined in such a way that they provide an excess of water for saturation, and enough time to produce reduction. Bouma (1983), pointed out that chemical and mineralogical transformations in soils with aquic moisture regimes are better known than the associated soil-moisture regimes. However, Daniels et al. (1967), Franzmeier et al. (1983), Pickering and Veneman (1984), Creemens and Mokma (1986), Evans and Franzmeier (1986), Ransom and Smeck (1986), Chase-Dunn and Veneman (1991) and Griffin (1991) provide useful information about the interaction of hydrologic and pedogenic processes in soils of the United States. The research of Faulkner and Patrick (1992) in Louisiana was also in the same context, and its objective was to provide data that would aid in delineating wetland from nonwetland in bottomland hardwood forests.

Soil saturation is controlled by the following edaphic and microclimate parameters (Wilding and Rehage, 1985):

    i) rainfall amount, intensity, and duration.

    ii) evaporation losses

    iii) surface structural and vegetative characteristics that affect interception and infiltration.

iv) vertical and horizontal hydraulic conductivities.

v) landscape position.

vi) antecedent soil moisture conditions.

The unconfined aquifers and semiconfined aquifers (aquifers with semipervious layers) are directly related to the above mentioned parameters and according to Van Breemen and Brinkman (1978), there are four general cases where soil saturation may occur which we interpreted according to ICOMAQ's definition for soils of Louisiana (Szögi and Hudnall, 1992):

i) moderately deep, fluctuating ground-water table, no flooding (endosaturation)

ii) shallow true ground-water table, periodic water saturation or flooding (endosaturation).

iii) moderately deep ground water table, periodic water saturation or flooding by a perched water table (epi- or anthric saturation).

iv) ground water at great depth, periodic water saturation or flooding by a perched water table (epi- or anthric saturation with simultaneous endosaturation).

The depth, duration, and periodicity of saturation can be measured during a long period of time (more than ten years) by piezometry and point wells (Zobeck and Ritchie, 1989). Alternatively they can be predicted by numerical simulation models properly calibrated with field data, like those developed by Boersma et al. (1972), Bouma (1973), Nelson et

al. (1973) and Carbon et al. (1979). The long term records of water table depths obtained by these methods can be utilized to generate statistical information in the form of water table probability diagrams describing the probability of observing water tables at a given depth.

Saturation produces the depletion of soil air, and soil reduction may be induced only if organic matter contents and soil temperature allow microbial activity (Bouma, 1983). According to Turner and Patrick (1968) waterlogging or saturation of soil with water causes drastic changes in the normal chemical and biological reaction in the soil. These changes are produced by the oxygen depletion by the microbes immediately after the soil is saturated. Facultative anaerobic organisms utilize oxidized compounds such as NO_3^-, MnO_2, Fe_2O_3, SO_4^- and assimilation products of organic matter converting these materials into their reduced forms.

The electron content and proton activity measured as electrode potential (Eh) and pH of an environment characterize this environment (Baas Becking et al.,1960). The soil reduction can be measured directly with platinum electrodes or indirectly by staining tests. In the case of direct measurements of redox potentials there is an abundant bibliography that agrees in the theoretical stepwise reduction of the various oxidized materials in a waterlogged soil in the following sequence: O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, CO_2, and H^+ (Turner and Patrick, 1968; Patrick and Delaune, 1972;

Ponnamperuma, 1972; Van Breemen and Brinkman, 1978; Patrick, 1980; De Datta, 1981; Bouma, 1983). Bohn (1971), states that redox potential is a mixed potential in most natural systems and is quantitatively unrelated to the theoretical Nernstian (thermodynamic) distribution of ion oxidation states. In oxidized systems, the low activity of redox couples reduces stability, reproducibility, and usefulness of redox measurements. However, in reduced systems, the higher activities of redox couples improves the stability and usefulness of redox potentials measurements and it must be complementary to other methods of measurements of reduced conditions.

Another method of determining reduction conditions in waterlogged soils is by a staining test. A staining test is a colorimetric method that indicates the presence of reduced iron in the soil. Several substances have strong affinity for reduced iron such as $\alpha - \alpha'$ dypridyl, potassium ferricyanide, and orthophenathroline. Benzidine is another dye that has strong affinity for Mn oxides.

The $\alpha - \alpha'$ dipyridyl was used by Mortimer (1941), Hutchinson (1941) and Gabe et al. (1965) in lake sediments. More recently Childs (1981) used this test in soils and describes the errors associated with the photochemical reduction of ferric-organic complexes. Both $\alpha - \alpha'$ dypiridyl and potassium ferricyanide were recommended by ICOMAQ Circular letter 11 (Bouma, 1991) to be used as a field test.

Orthophenatroline was mentioned by Wilding and Rehage (1985) as a field test for soil reduction. Limited information is available related to the use of potassium ferricyanide (Hoffer, 1945), and benzidine as staining tests in wet soils (Bartlett, 1981).

According to Faulkner et al. (1989), the interpretation of Fe^{2+} test is critical to properly assess the saturation and reduction status of a soil. The test of soil reduction in the Eh range where iron is reduced is consistent with the concept that iron is the most important element under reducing conditions. The works by Patrick (1964), Patrick and Mahapatra (1968), Collins and Buol (1970 a,b), Patrick et al. (1973), Gotoh and Patrick (1974) and Patrick and Henderson (1981) show that Fe^{2+} in complete anaerobic conditions contributes to neutralize the pH, overlaps and interacts with the reduction of manganese, and it intervenes in the release of occluded phosphorous. The higher Eh ranges where nitrogen reduction and denitrification occurs are not reliable to use as a reference of saturation-reduced state. For instance, it was demonstrated that the denitrification can occur in reduced microsites of the soils with simultaneous consumption of oxygen between -1.2 to -12 kPa. (Pilot and Patrick, 1972).

1.5. MORPHOLOGICAL PROPERTIES OF WET SOILS

The alternating reduction - oxidation cycles in soils can be traced by the "paints" left by characteristic segregations of Fe and Mn released from primary minerals and concretions (nodules) according to Fanning and Fanning (1989). These characteristic colors and patterns are associated with the seasonal changes in soil wetness.

Diers and Anderson (1984) give a good summary on how soil mottling is developed. Once Fe and Mn have been reduced by the bacterial activity they are carried by the soil water until an oxygen rich zone is encountered. They oxidize and precipitate, accumulating as coatings of reddish or yellowish Fe oxide or black Mn oxide on the faces of peds, walls of pores and voids or inside the peds. The areas from which Fe and Mn were removed become light grayish color and are called gleyed.

Soil Taxonomy (Soil Survey Staff, 1975) has defined the "gleyed" horizon as those horizons with "mottling" having chromas of two or less. Bouma (1983), found the following problems associated with this definition:

i) Mottling may not reflect a current, but a relict moisture regime.

ii) Mottling may not form as a result of saturation due to lack of energy sources.

iii) The definition in Soil Taxonomy does not identify the length of period of saturation, nor does it separates

perched from true water tables, which may have different mottling patterns.

According to the NC-109 Project Report (Mokma, 1988), these problems have been encountered in the classification of soils from Ohio, Indiana, Michigan, and Illinois, where the color criteria of Soil Taxonomy for degree of wetness tended to underestimate soil saturation. It was found that B horizons with 3 chroma colors and gray coatings were saturated during six months and some 4 chroma colors and grey mottles were saturated for 20 weeks during the year. In Nebraska and South Dakota many soil horizons that had mottles were not saturated. Gray mottles on ped exteriors only were more reliable indicators of soil saturation than ped interior mottles. However, in Minnesota, Iowa, and Missouri, the 2 chroma color criteria of Soil Taxonomy predicted satisfactorily the soil saturation in most soils. Vepraskas and Wilding (1983), found morphological features in reduced soils (Alfisols) with high chroma (>2). They recommended that 3 chroma or less be used as criteria to allow some soils in south east Texas to be included in the aquic taxa. These observations can also be applied to soils in Louisiana (B.A. Touchet, pers. comm.).

In order to have consistent information on morphological indicators the ICOMAQ devoted part of its efforts to propose a new terminology to avoid ambiguities in the description of mottles and low chroma colors. "Mottles" technically could

consist of carbonates or organic stains which are not indicative of saturation and reduction.

Mottles and low chroma colors will be described by redoximorphic features which are formed by the concentration or removal of Fe and Mn oxides. New terms were invented by ICOMAQ (Bouma, 1991) to describe the redoximorphic features that conformed to terms that were already in use in the new Soil Survey Manual (Soil Survey Staff, 1981).

According to ICOMAQ (Bouma, 1991), redoximorphic features will be defined as follows:

i) Redox concentrations, which are zones of apparent accumulation of Fe-Mn oxides. Three types of redox concentrations can be described:

a) Nodules and concretions; firm to extremely firm irregularly shaped bodies that have irregular boundaries. Concretions appear to be organized in concentric layers, whereas nodules have an uniform internal fabric when broken in half.

b) Masses; soft bodies, frequently within the matrix, whose shape is variable.

c) Pore linings; zones of accumulation along pores which may be either coatings on the pore surface, or impregnations of the matrix adjacent to the pore.

ii) Redox depletions, which are zones of low chroma (< 3) where Fe-Mn oxides alone have been stripped out called iron

depletions, or where both Fe-Mn oxides and clay have been stripped out called clay depletion.

iii) Reduced matrices, soil matrices that have low chroma in situ, but whose color increases in hue or chroma when exposed to air within 30 minutes.

1.6. GEOGRAPHICAL SETTING

Verdun Soil

The profile described in this study is located in Livingston Parish: latitude 30-27-15 N, longitude 90-44-44 W; Frost, LA 7.5' quadrant, UTM zone 15; 2 km south of I-12 Highway. The classification is fine-silty, mixed, thermic Glossic Natraqualfs. The narrative field description of the profile is found in appendix A. Fig. 1.1 shows the location of the site in Louisiana and the soil map with the location where the pit for the profile description was excavated. Verdun soils are formed over Coastal Plain alluvium on nearly level Pleistocene terraces. Slopes are slightly convex to level and generally less than 1 %. The mean annual air temperature is 19.7 °C and the average annual rainfall is 157 cm (Hudnall et al. 1990). The Verdun soil was described on the Dv (Deerford-Verdun silt loams) mapping unit. These soils are level, somewhat poorly drained, and contain high levels of sodium in the subsoil. The topsoil has low fertility and moderately high levels of exchangeable aluminum (Mc Daniel, 1991). Deerford and Verdun soils are so intermingled that
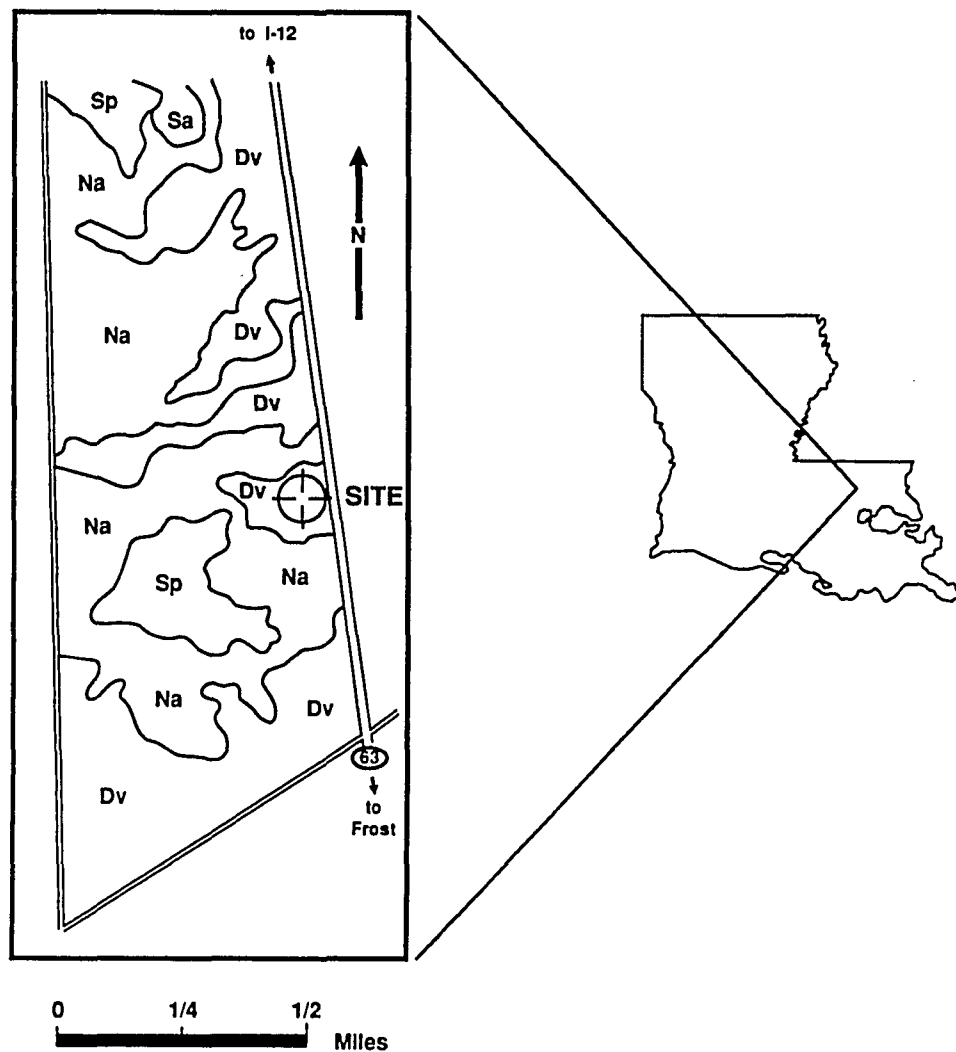
Fig. 1.1. Site location for the Verdun soil and soil map of the area adjacent to the site: Dv (Deerford - Verdun soils), Na (Natalbany soils), Sa (Satsuma soils), Sp (Springfield soils).

they cannot be mapped separately at the scale selected. Areas of this soil unit range from 8 to 405 ha. Included in the soil map of Fig. 1.1 are the Natalbany (Na), Springfield (Sp) and Satsuma (Sa) soils. The Natalbany soils (fine, montmorillonitic, thermic Vertic Ochraqualfs) are in lower positions than the Springfield and Deerford-Verdun soils and consists of very poorly drained, formed in clayey and loamy sediments of Holocene or late Pleistocene age. The Springfield soils (fine, mixed, thermic Aeric Albaqualfs) are in lower positions than the Deerford and Verdun soils and they have a clayey subsoil. The Satsuma soils (fine-silty, siliceous, thermic Glossaquic Hapludalfs) are somewhat poorly drained soils occupying higher positions than the Verdun and Deerford soils on stream or marine terraces of late Pleistocene age with slopes in the range of 1 to 3 %.

Brimstone Soil

The profile described in this study is located in Calcasieu Parish: latitude 30-22-22 N, longitude 93-10-55 W; Moss Bluff, LA 15' quad., UTM zone 15; 1 mile east of US 171 in Gillis. The classification is fine-silty, mixed, thermic Typic Ochraqualf. Fig. 1.2 shows the location of the site in Louisiana and the soil map with the location where the pit for the profile description was excavated. Brimstone soils are on broad flats of late Pleistocene age terraces. Slope ranges from 0 to 1 %. The soil formed in loamy alluvium.
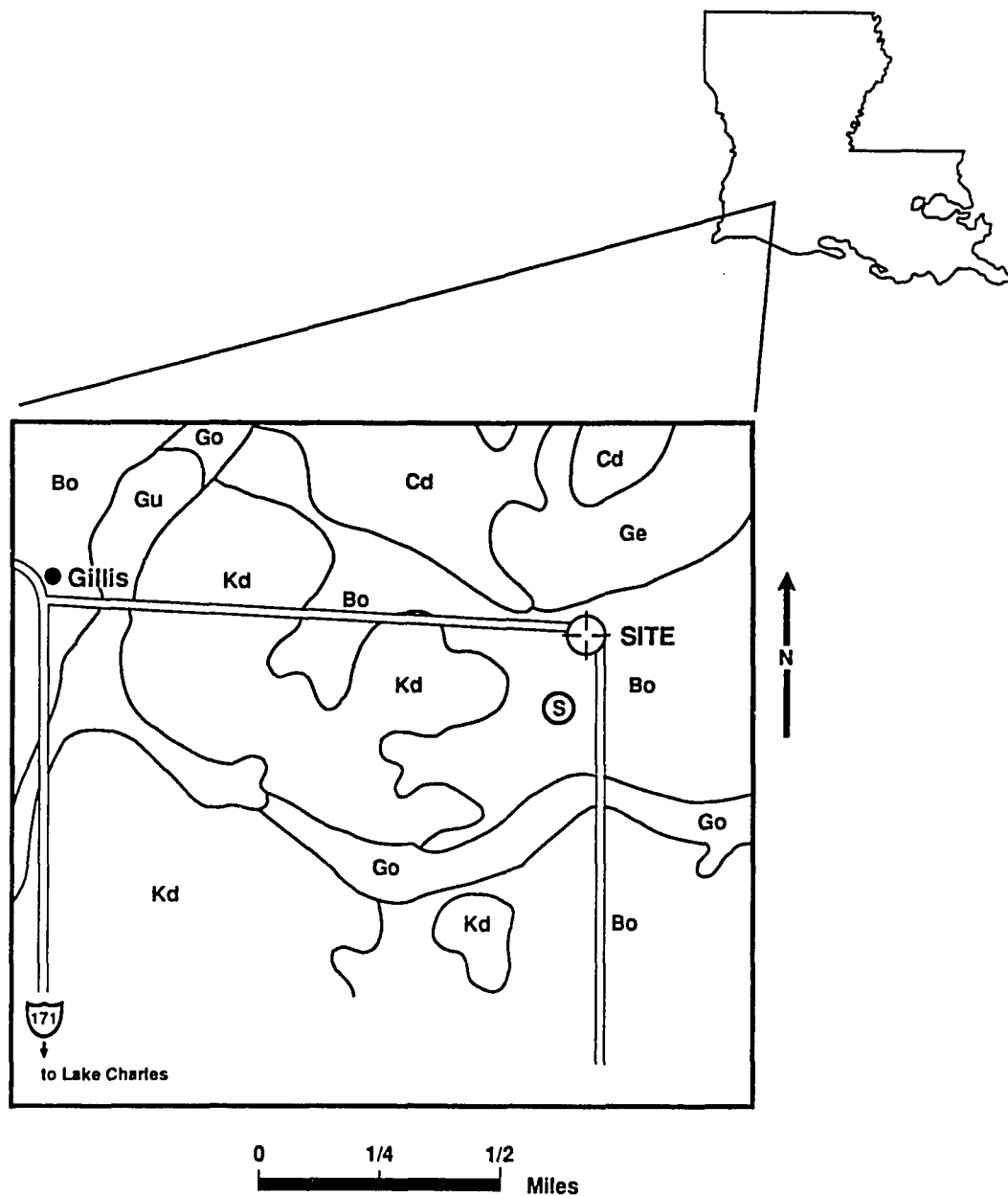
Fig. 1.2. Site location for the Brimstone soil and soil map
of the area adjacent to the site: Bo (Brimstone soils),
Cd (Caddo - Messer soils), Ge (Glenmora soils), Go
(Guyton occasionally flooded soils), Gu (Guyton
frequently flooded soils), Kd (Kinder - Messer soils).
The "S" indicates the place where Brimstone soil was
described by Roy and Midkiff (1988).

The mean annual air temperature is 20°C, and the mean annual rainfall is about 145 cm . The soil profile was described on the Bo (Brimstone silt loam) mapping unit (Fig. 1.2). This soil is level and poorly drained. The surface layer is acid silt loam (15 cm thick), the subsurface layer is mildly alkaline silt loam (18 cm thick). The subsoil is moderately alkaline silty clay loam (Hudnall et al., 1990). However, according to Roy and Midkiff (1988), the true Brimstone series consist of poorly drained, slowly permeable soils that are high in exchangeable sodium (fine-silty, siliceous, thermic, Glossic Natraqualfs) described by them a few meters from the site location (Fig. 1.2). Areas of this soil range from 4 to 608 ha. Included in the soil map of Fig. 1.2 are Caddo - Messer (Cd), Glenmora (Ge), Guyton occasionally flooded (Go), Guyton frequently flooded (Gu) and Kinder - Messer (Kd) soils. These soils contain less sodium in the subsoil than the Brimstone soil. The Caddo and Kinder soils (fine-silty, siliceous, thermic Typic Glossaqualfs) are in slightly higher positions than Brimstone soils on broad flats on terrace uplands. The Guyton soils (fine-silty, siliceous, thermic Typic Glossaqualfs) are in lower positions and are more acid in the subsurface and subsoil layers. The Glenmora (fine-silty, siliceous, thermic Glossaquic Paleudalfs) and Messer soils (coarse-silty, siliceous, thermic Haplic Glossudalfs) are in higher positions than Brimstone soils and moderately well drained.

CHAPTER 2.

TESTING THE AQUIC CONDITION CRITERIA IN TWO SOILS
WITH SEASONAL SURFICIAL SATURATION

2.1. INTRODUCTION

In Soil Taxonomy and Keys to Soil Taxonomy (Soil Survey Staff, 1975, 1990), the characteristics that define soils with stagnant or perched water tables appear at different taxonomic levels. However, they are not explicitly defined according to the definition of the aquic moisture regime. The difficulties in applying the definition of the aquic moisture regime for the taxonomic placement of these kinds of soils are the lack of: specification of minimum duration of saturation and reduction, precise definition of the soil moisture control section and verification of low chroma colors and in situ reduction in the field (Wilding and Rehage, 1985).

Aquic Conditions

The recognition of the different problems that plagued the classification of wet and seasonally wet soils (Moorman and van de Wetering, 1985), inspired the International Committee on Aquic Moisture Regime (ICOMAQ) to thoroughly revise the definition and criteria for the aquic soil moisture regime. Terminology to classify wet soils are defined and discussed in ICOMAQ's Circular Letters numbers 8, 9, 10 and 11 (Bouma, 1988, 1989, 1990, 1991). This terminology is

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incorporated at the appropiate category of all orders in the Keys to Soil Taxonomy.

"Aquic conditions" will be used instead of "aquic regime". Aquic conditions are identified by determining three soil properties: i) presence of redoximorphic features, ii) duration and depth of saturation and iii) occurrence of reduction unless the soil is artificially drained.

"Redoximorphic features" are the morphological expression of redox concentrations and depletions in the soil profile. They are an indicator of anaerobic conditions resulting from periodic or prolonged saturation. The term "redoximorphic features" replaces the word "mottling" to avoid misinterpretation of the kind of mottling that must be described to determine the aquic conditions. For example, mottles resulting from calcium carbonate or organic matter accumulation are not redoximorphic features.

Identification of Redoximorphic Features

Redoximorphic features are easily identified by their color patterns in the soil profile. These features must be described for every horizon. According to ICOMAQ (Bouma, 1991) the basic types of redoximorphic features are:

i) Redox concentrations, which are zones of apparent accumulation of Fe-Mn oxides. Three types of redox concentrations can be described:

a) Nodules and concretions; firm to extremely firm irregularly shaped bodies that have irregular boundaries. Concretions appear to be organized in concentric layers, whereas nodules have an uniform internal fabric when broken in half.

b) Masses; soft bodies, frequently within the matrix, whose shape is variable.

c) Pore linings; zones of accumulation along pores which may be either coatings on the pore surface, or impregnations of the matrix adjacent to the pore.

ii) Redox depletions, which are zones of low chroma (< 3) where Fe-Mn oxides alone have been stripped out called iron depletions, or where both Fe-Mn oxides and clay have been stripped out called clay depletion.

iii) Reduced matrices, soil matrices that have low chroma in situ, but whose color increases in hue or chroma when exposed to air within 30 minutes.

Redoxomorphic features may not be present in a profile with aquic conditions or redoximorphic features may be relicts of past aquic conditions in old landscapes. Sandy wet soils without Fe/Mn mottles and nodules, such as some Aquods, Humaquepts and Umbraquults cited by Fanning et al. (1992), are thought to have lost Fe and Mn after have been mobilized by reduction and slow leaching of water. A Wockley soil (fine-loamy, siliceous, thermic Plinthaquic Paleudalf) described in Texas did not have saturation (based on piezometer data) and

reduction but had redoximorphic features in the upper 2 m (Wilding and Griffin, 1990).

Formation of Redoximorphic Features

Pore linings are formed by diffusion of reduced Fe and Mn ions toward aerated macropores. Fe and Mn are oxidized adjacent to the wall of the macropores or on root surfaces in plants that have mechanisms of aeration of their roots in saturated soils (Fisher and Stone, 1991).

The formation of masses, nodules and concretions is not well understood yet. Ciric and Skoric (1973), consider that they are formed as a result of sudden changes of oxidizing and reducing conditions. Blume and Schlicting (1985), consider that masses are formed when air enters quickly into the soil while nodules and concretions are believed to form when air enters slowly into the reduced soil.

A reduced matrix is formed when Fe is reduced in the soil. The soil is reduced for long periods such that air is excluded so concentrations and depletion are not formed.

Fe depletions and Fe-clay depletions are formed by similar processes. These features have been described in detail in dense horizons by Vepraskas and Wilding (1983a). The process of formation occurs in stable macropores that have roots that provide the organic material for microbial decay. When saturation occurs in the pore and after O_2 is consumed, the microbes reduce Fe. This Fe is removed in its ferrous

form from the root channel (that also is part of a ped face) to the interior of the ped that is unsaturated and rich in oxygen. The Fe is reprecipitated in the interior of the ped forming redish rims. Fanning and Fanning (1989) generalized the formation of pore linnings and masses on peds by calling it Mottling Model I, and the formation of Fe and Fe-clay depletions Mottling Model II. Some soil scientists thought that Model I would be diagnostic for soils saturated by a true ground water table (endosaturation) and Model II for soils saturated by a perched water table (episaturation). However, it is not possible to define a set of redoximorphic features that is uniquely characteristic for endo- or episaturation, so that model generalizations are unrealistic (Bouma 1991)

Saturation

"Saturation" occurs when soil has zero or positive matric suction potentials.

"Episaturation" defines soils that are saturated in one or more layers within a depth of 2-m with one or more unsaturated layers between the saturated layer. The upper boundary of unsaturation must be within a depth of 2-m.

Perched water tables are peculiar of episaturation. They are supplied by rainfall water that is saturated with oxygen. This water rests in the upper part of the soil on top of a slowly permeable horizon. If the water saturates the horizon for enough time to become anoxic and to reduce manganese and

iron, then, these elements in their reduced forms will move vertically downward through cracks and macropores into lower unsaturated horizons or layers where they will precipitate upon oxidation, in response to an increase in pH, oxygen or both. In lack of macroporosity the precipitation occurs throughout the soil matrix.

"Endosaturation" defines soils that are saturated in all layers from the upper boundary of saturation to a depth of 2-m or more. The endosaturation conditions are associated to the occurrence of horizons with oxidizing conditions above reduced horizons.

"Epi-" and "endosaturation" are distinguished in Soil Taxonomy because of the different nature and duration of perched and ground water tables.

Reduction

"Reduction" is characterized by the soil redox potential at a given pH determined with a platinum electrode or estimated indirectly by a staining test. A soil is considered reduced when O_2 is depleted by microbial activity and Fe is reduced to its ferrous form. The reduction of Fe is chosen as an indication of reducing conditions because it is carried out by microbes that are facultative anaerobs (Alexander, 1977). The main limitation of most methods to measure O_2 such as oxygen probes is their inability to measure trace concentrations (White et al., 1990).

Objectives

A preliminary testing of the ICOMAQ approach has been made in soils of Louisiana by Szögi and Hudnall (1992). They showed that soil aquic conditions are able to be characterized by describing redoximorphic features, and measurements of saturation and soil redox potential.

The objective of this study was to test the aquic conditions criteria in two soils with episaturation. This was accomplished by: i) to define the depth, frequency, and duration of saturation and reduction in the soils; ii) to identify "aquic conditions" via the presence of redoximorphic features, duration and depth of saturation and occurrence of reduction by using morphological properties, field measurements and laboratory analyses as diagnostic tools; iii) to classify the two soils with respect to the ICOMAQ definitions.

2.2. MATERIALS AND METHODS

Site Characterization

The investigation was based on two series: Verdun silt loam (fine-silty, mixed, thermic Glossic Natraqualfs) located in Livingston Parish and Brimstone silt loam (fine-silty, siliceous, thermic Typic Natraqualfs) located in Calcasieu Parish (Hudnall et al. 1990). The profile that was described for this study is morphologically similar to Brimstone Series,

however it does not have a natric horizon. It was classified as fine-silty, siliceous, thermic Typic Ochraqualf.

Verdun soils are formed in loess over Coastal Plain alluvium on nearly level Pleistocene terraces. Verdun soils form complex mapping units with Deerford soils at 1:20,000 scale. Slopes are slightly convex to level and less than 1 percent. The mean annual air temperature is 19.7 °C and the mean annual rainfall is 1570 mm.

Brimstone soils are formed on broad flats of late Pleistocene age terraces from loamy alluvium materials. Brimstone soils form complex mapping units with soils with similar morphology without natric horizons. Slopes range from 0 to 1 percent. The mean annual air temperature is 20 °C, and the mean annual rainfall is 1450 mm.

The land use for the Verdun silt loam is forestry (pine trees). The management has been thinning at 17 and 22 years, clearcut at 27 years and burn every 3 years. The land use for Brimstone is cropland or forestry. The past soil management has been paddy rice, rotated with pastures or wheat, and fallow followed by winter wheat for the last two years.

The pedons were described and sampled by the Soil Conservation Service (SCS) in concert with Louisiana Agricultural Experiment Station (LAES). The characterization analyses were completed at the National Soil Survey Laboratory (NSSL), Lincoln, Nebraska following the methods described by Soil Survey Investigations Staff (1991). The profile

descriptions and characterization analyses were taken from Hudnall et al. (1990) and they appear in Appendix A.

Redoximorphic features were described and quantified for every horizon according to the definitions of ICOMAQ (Bouma, 1991). Definitions and criteria employed for their description are presented in Appendix B. The criteria were elaborated following the Soil Survey Manual (Soil Survey Staff, 1981) complemented by descriptive elements from Bullock et al. (1985) and Vepraskas and Wilding (1983 a,b).

Site Instrumentation and Measurements

Each site was fenced with galvanized wire that enclosed a 9.12- x 9.12-m square plot next to the place where the pit for soil characterization was excavated. The rainfall was measured with a rain gauge. The accumulated rainfall records as well as the other measurements were taken every two weeks, or whenever required. The rainfall data was complemented by daily rainfall records from Livingston (Livingston Parish) and Moss Bluff (Calcasieu Parish) meteorological stations.

The water table depths were determined with piezometers. The piezometers were constructed from 1.9-cm O.D. PVC pipe and installed as described by Szögi and Hudnall (1992). The water level in the piezometers was measured by the "hot air method" (Reeve, 1986).

The water tension was measured in triplicate with jet-filled tensiometers (Soil Moisture Corp, Santa Barbara,CA)

placed in the soils at three different depths (0.25, 0.50 and 1.00 m). The original gauges were substituted by a swagelok brass fitting (Swagelok Co., Solon, OH) connected to a rubber septum by a 1.5-cm piece of nylon tubing. The soil suction was measured through the septum with a tensimeter (Soil Measurement Systems, Tucson, AZ).

The reduction was characterized by measuring the redox potentials directly with permanently installed platinum electrodes and indirectly by the presence of reduced iron tested with dyes in the field. The platinum electrodes were fabricated according to Szögi and Hudnall (1992). The electrodes were tested in the lab in a pH-buffered quinhydrone solution (Jones, 1966). The electrodes were installed in the field at 0.50- and 1.00-m depth in triplicate, in order to monitor the redox potential in the soil moisture control section.

Redox potentials taken in the field were adjusted by adding +244 mV to them in order to base redox potentials on the standard hydrogen reference electrode (SHE) or Eh readings. A few redox measurements were taken at the topsoil of every soil when they were saturated for several weeks with platinum electrodes to complement the information on soil reduction. A soil was considered reduced when reduction was below 150 mV. The interpretation is made without pH correction (Bohn et al. 1985) and based on redox ranges given by Patrick and Mahapatra (1968) and Turner and Patrick (1968).

Two staining tests were performed: i) a 0.2% $\alpha - \alpha'$ dipyridyl solution in 10% acetic (Bouma, 1989), and ii) a 0.2% $\alpha - \alpha'$ dipyridyl solution in 10% acetic acid buffered with 1 M ammonium acetate (Childs, 1981). This dye was droppered onto freshly broken surfaces of field samples taken at 0.25- 0.50- and 1.00-m depth. A positive reaction indicating the presence of reduced iron is obtained when a strong pink color develops almost immediately.

The water from each piezometer was pumped out and the pH of the water samples were measured immediately with a pH meter. The pH of the water was considered to be the soil pH, since near equilibrium was assumed between the soil solution and the solid phase according to Brinkman (1978).

The soil temperature was measured at 0.50- and 1.00-m depth from samples taken with a push probe and measured inmediately in the field with a stem thermometer.

2.3. RESULTS
Soil Morphology and Characterization Analyses

The selected analytical data relevant for this study are found in Table 2.1 for Verdun and Brimstone soils. The description of redoximorphic features are presented for the Verdun soil in Table 2.2 and for the Brimstone soil in Table 2.3. These descriptions are the result of the reexamination of the profile in the field and the descriptions presented in Appendix A. Only concentrations and depletions were described

from the Verdun profile. Reduced matrices in the Brimstone are described in Cg1, Cg2 and Cg3 horizons in addition to the concentrations and depletions found in the overlying horizons. The depletions in both soils have colors with chromas less than 3. Silt pockets have a characteristic light gray and white (10YR 7-8/1-2) colors and were classified as iron and clay depletions. Very few concentrations in the form of black (10YR 2/1) soft masses were found in both profiles.

A characteristic redoximorphic feature in both profiles is the presence of very small orange concentrations. They were more abundant in the Brimstone soil than in the Verdun soil. These orange concentrations may be lepidocrocite, a characteristic oxihydroxide in wet soils with episaturation (Fitzpatrick et al., 1985; Schwertmann and Taylor, 1989). Other concentrations with brownish or yellowish colors were also present in larger amounts. These redox concentrations (brownish pore linings) may be formed by ferrihydrite in the Ap horizon of both soils. Ferrihydrite is known to be formed in the presence of organics and silica (Scwertmann and Taylor, 1989) wich are abundant in the Ap horizons of the two soils. Goethite is the other Fe oxide present in both profiles (Self, pers. comm.). Goethite is an ubiquitous Fe oxide in hydromorphic soils according to Schwertmann (1985) and Schwertmann and Taylor (1989). Goethite in the Ap horizon is probably formed by alteration of ferrihydrite and lepidocrocite. Goethite is more concentrated in those soil

Table 2.1. Selected analytical data for Verdun and Brimstone soils (Hudnall et al. 1990).

Soil	Horizon	Depth cm	pH	Texture	Org.C %	Tot.N %	Exch.Na %	Fe %	Bulk dens. kg/m³	EC dS/m
VERDUN	Ap	0-13	4.2	SiL	1.73	0.092	2	0.2	1.36	0.87
	Eg1	13-24	4.6	SiL	0.48	0.019	6	0.1	1.58	1.22
	Eg2	24-45	4.4	SiL	0.41	0.015	8	0.2	1.54	2.13
	Eg/Btg	45-71	4.7	SiL	0.21	0.015	12	0.5	1.61	2.20
	Btng/Eg	71-103	6.5	SiCL	0.07	0.033	14	0.9	1.78	2.59
	Btkng1	103-128	7.6	SiCL	0.04		19	1.0	1.85	1.81
	Btkng2	128-170	7.5	SiCL	0.03		15	0.6	1.87	1.67
	Btng1	170-215	7.5	SiC	0.02		16	0.6	1.84	1.46
	Btng2	215-280	7.3	C	—		15	0.4		0.92
	BCg	280-380	7.9	SL	0.01		13	0.2		1.04
BRIMSTONE	Ap	0-15	4.6	SiL	0.80	0.071	4	0.1	1.54	0.81
	Eg	15-33	6.6	SiL	0.20	0.017	6	0.1	1.76	1.11
	E/Btng	33-60	6.6	SiL	0.16	0.024	8	0.1	1.73	1.16
	Btng/E	60-81	6.4	SiCL	0.09	0.011	8	0.1	1.74	1.03
	Btng1	81-147	6.9	SiCL	0.05		7	0.3	1.73	0.41
	Btng2	147-190	6.6	SiCL	0.02		7	0.2	1.78	0.20
	BCg	190-264	6.8	SiCL	0.02		6	0.1	1.96	0.18
	Cg1	264-314	6.7	SiL	0.02		7	0.2		0.15
	Cg2	314-325	6.8	SiCL	0.02		5	0.3		0.12
	Cg3	325-360	6.9	SL	0.01		6	0.1		0.06
	2C	380-400	7.6	SL	0.02		12	0.1		1.19

Table 2.2.   Description of redoximorphic features for the Verdun soil profile

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Horizon

Ap   Many fine continuous vertical and oblique tubular inped pores lined with brownish yellow (10YR 6/8) ferruginous coatings.

Eg1   Few medium distinct black (10YR 2/1) clear iron-manganese masses. Few medium faint light gray (10YR 7/2) inped clay depletions. Many fine constricted random tubular inped pores lined with prominent yellowish brown (10YR 5/8) iron coatings.

Eg2   Common coarse prominent yellowish brown (10YR 5/8) and strong brown (7.5YR 5/8) clear to diffuse iron mass. Common medium faint white (10YR 8/2) inped clay depletions. Common fine constricted random tubular inped pores lined with prominent strong brown (7.5YR 5/8) iron coatings. Few constricted random tubular inped pores lined with prominent yellowish brown (10YR 5/8) iron coatings.

Eg/Btg   Many coarse distinct yellowish brown (10YR 5/6) clear ferruginous masses in spots. Few fine distinct black (10YR 2/1) clear iron-manganese masses.

Btng/Eg   Many coarse distinct yellowish brown (10YR 5/6) clear to diffuse ferruginous masses. Common fine faint yellowish brown (10YR 5/8) clear ferruginous masses. Comon fine prominent black (10YR 2/1) clear iron-manganese masses. Common coarse faint to distinct yellowish brown (2.5YR 6/2) sharp exped clay depletions in tongues.

Btkng1   Many coarse distinct light yellowish brown (10YR 6/4) diffuse ferruginous masses Common medium distinct yellowish brown (10YR 5/8) clear ferruginous masses in spots. Few fine prominent black (10YR 2/1) clear iron-manganese masses. Common coarse light brownish gray (2.5Y 6/2) clear exped iron depletions.

Btkng2   Many coarse distinct light yellowish brown (2.5Y 6/4) diffuse ferruginous masses. Common medium distinct yellowish brown (10YR 5/6) clear ferruginous masses. Few coarse prominent black (10YR 2/1) sharp manganese or iron-manganese masses. Common coarse light brownish gray (2.5Y 6/2) clear exped iron depletions.

Btng1   Common coarse distinct yellowish brown (10YR 5/8) diffuse ferruginous masses. Few medium prominent black (10YR 2/1) sharp manganese or iron-manganese masses on vertical faces of peds. Many coarse distinct light brownish gray (2.5Y 6/2) clear iron depletions.

Btng2   Common medium distinct olive yellow (2.5Y 6/6) diffuse ferruginous masses in. Few medium prominent black (10YR 2/1) sharp masses on vertical and horizontal faces of peds. Many coarse distinct light brownish gray (2.5Y 6/2) clear iron depletions.

BCg   Common medium distinct yellowish brown (10 YR 5/8) clear ferruginous massses. Many coarse distinct light gray (10 YR 7/2) clear clay depletions.

2C   Few medium distinct strong brown (7.5 YR 5/6) clear ferruginous masses. Many coarse distinct light gray (10 YR 7/2) clear clay depletions.

Table 2.3. Description of redoximorphic features for Brimstone soil profile.

Horizon

Ap — Many fine and medium continuous vertical tubular inped pres, lined with prominent reddish yellow (7.5YR 6/8) iron coatings; a few with prominent brownish yellow (10YR 6/8) ferruginous coatings. Few fine light gray (10YR 7/2) clear inped clay depletions.

Eg — Common fine vesicular inped pores lined with distict dark yellowish brown (10YR 4/6) iron coatings. Common fine light gray (10YR 7/2) clear inped clay depletions. Common fine continuous vertical tubular inped pores, lined with prominent reddish yellow (7.5YR 6/8) iron coatings; a few os them lined with distinct dark yellowish brown (10YR 4/6) iron coatings.

E/Btng — Many fine vesicular imped pores and common fine random constricted tubular inped pores, few of these poes lined with prominent strong brown (7.5YR 5/8) iron coatings and few distinct dark yellowish brown (10YR 4/6) iron coatings. Few fine constricted irregular exped pores lined with black (10YR 2/1) patchy iron-manganese coatings. Common fine light gray (10YR 7/2) clear inped clay depletions. Many fine dark grayish brown (10YR 4/2) exped iron depletions (continuous clay films on faces of peds).

Btng/E — Few fine tubular inped pores and few fine and medium vesicular pores, lined with strong brown (7.5YR 5/8) iron coatings. Few fine constricted tubular or irregular exped pores lined with black (10YR 2/1) patchy iron-manganese coatings. Many fine light gray (10YR 7/1) clear exped clay depletions. Many coarse vertical and few oblique krotovinas, lined with dark grayish brown (10YR 4/2) clay, many horizontal and concentric bands of light brownish gray (10YR 6/2).

Btng1 — Many coarse faint light olive brown (2.5Y 5/6) ferruginous masses. Few coarse distinct black (10YR 2/1) clear iron-manganese rounded masses. Many coarse light brownish gray (2.5Y 6/2) clear clay depletions. Few coarse prominent (10YR 7/1) clear exped clay depletions in pockets. Many fine dark grayish brown (10YR 4/2) exped iron-manganese depletions (continuous clay films on faces of peds).

Btng2 — Many coarse faint light brownish gray (2.5Y 6/2) and fine distinct yellowish brown (10YR 5/8) masses. Many fine and medium light gray (10YR 7/2) clear clay inped silt depletions. Many fine dark grayish brown (10YR 4/2) exped iron-manganese depletions (continuous clay films on faces of peds).

BCg — Common fine distinct light olive brown (2.5Y 5/6) clear ferrouginous masses common fine faint light brownish gray (2.5Y 6/2) diffuse exped iron depletions.

Cg1 — Reduced matrix, pale yellow (5Y 7/3) oxidized.

Cg2 — Reduced matrix, pale yellow (5Y 7/3) oxidized and few fine prominent yellowish brown (10YR 5/8) clear soft masses.

Cg3 — Reduced matrix, light gray (5Y 7/1) oxidized.

horizons where the content in percentage of free Fe oxides is higher (Table 2.1). It correlates well with the abundance, kind and color of the Fe concentrations described in Tables 2.2 and 2.3.

Crawfish krotovinas are found in the narrative description of the Brimstone soil. The characteristic concentric streaks of the krotovinas were formed by crawfish pedoturbation. These features are stratified soil materials with different textures and low chroma colors that fill the crawfish burrows. Crawfish krotovinas also exist in the Verdun soil but they were not thoroughly described since they were difficult to distinguish from glossic features and pedoturbation caused by the coarse roots of the trees. Fresh crawfish burrows are also present in both profiles. They can be considered as very large macropores.

Saturation

The three measured hydrological variables related to soil saturation, rainfall, water table depth (WTD) and soil matric potential (ψ_m) are presented in the graphs A, B and C of Fig. 2.1 for Verdun soil and in Fig. 2.2 for Brimstone soil. The graphs of these two figures show the variation in time (Date) of the three hydrological variables and soil redox potential (graph D). They are plotted with the same x-axis in order to compare the different variables for a given date. In both figures, the precipitation every two weeks was plotted for a
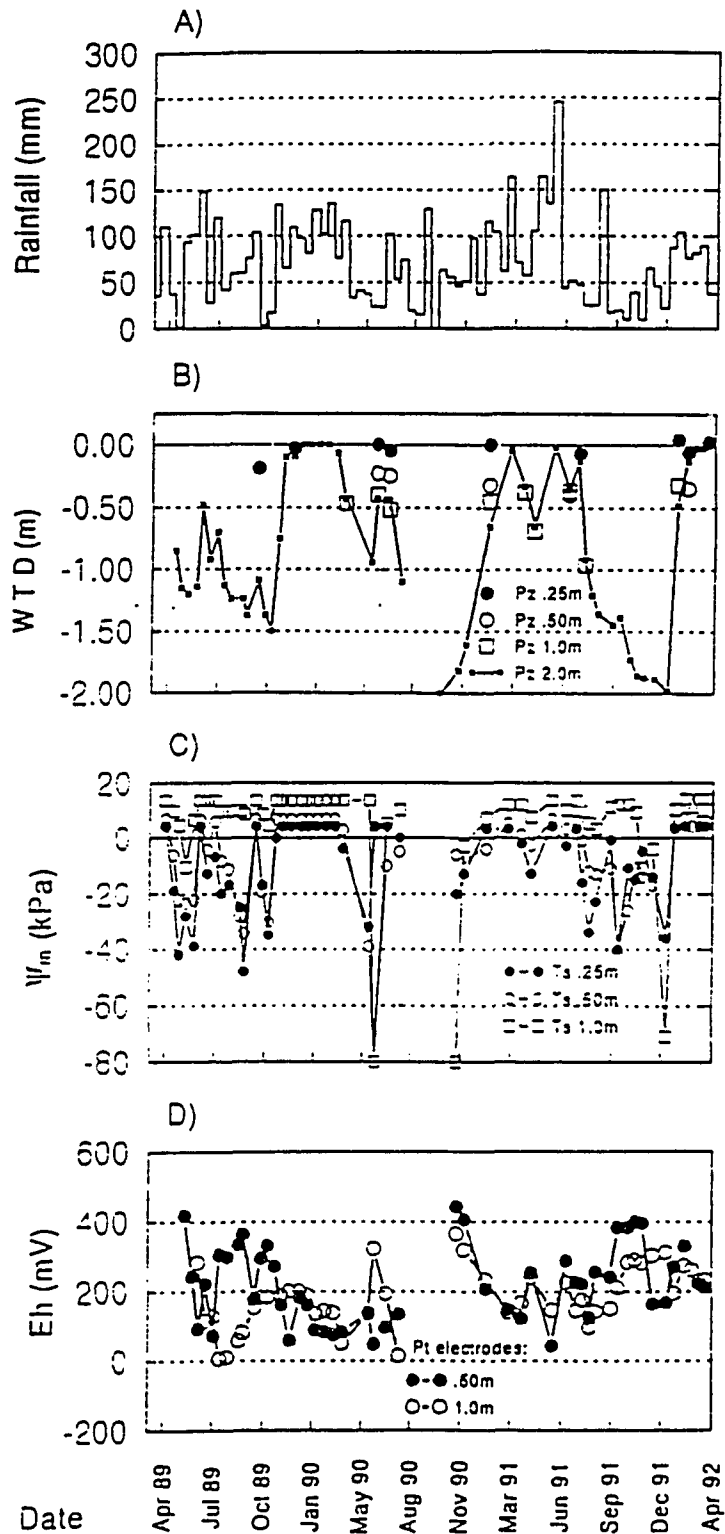
Fig. 2.1. A) Rainfall distribution, B) water table depth (WTD), C) soil matric suction (ψ_m), D) redox potential (Eh) for Verdun soil from April 1989 to April 1992.
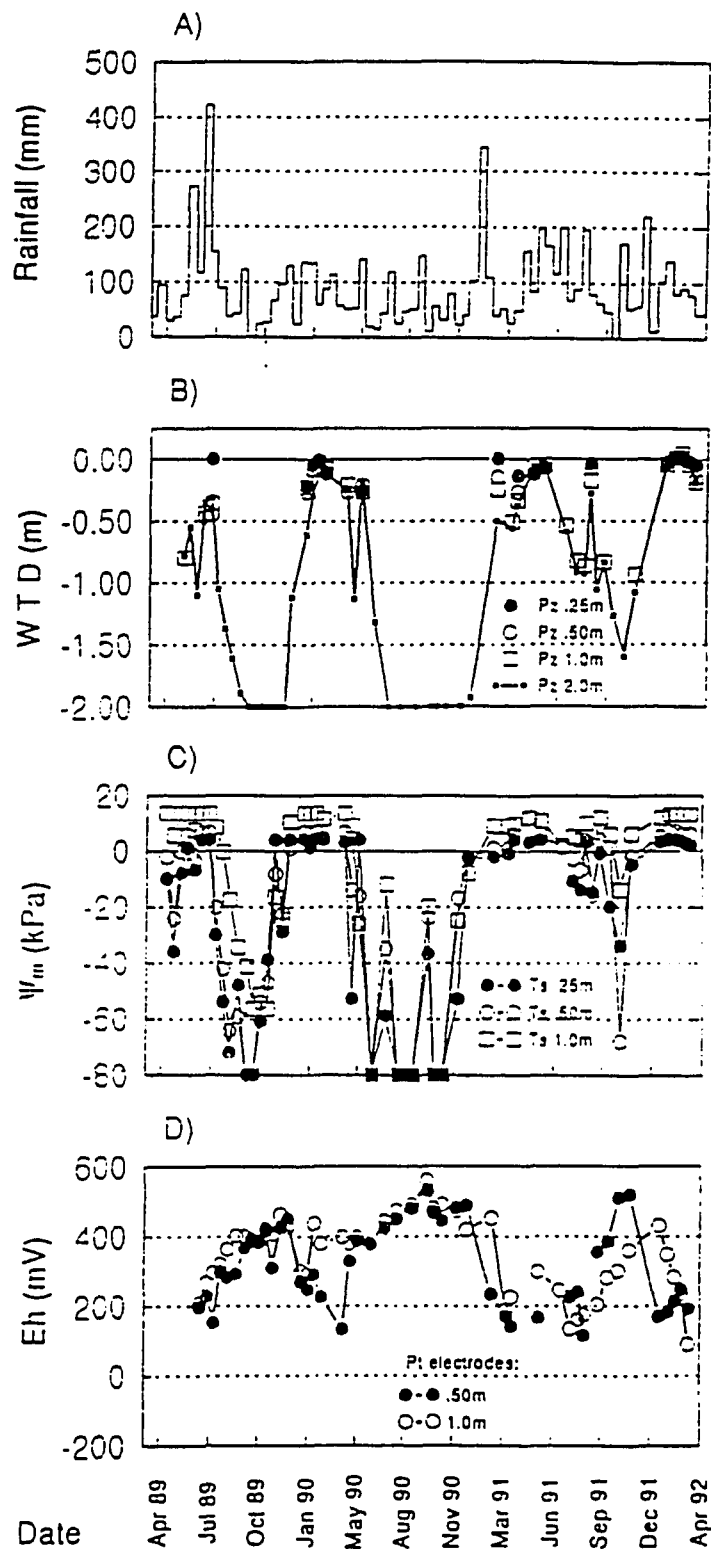
Fig. 2.2. A) Rainfall distribution, B) water table depth
(WTD), C) soil matric suction (ψ_m), D) redox potential
(Eh) for Brimstone soil from April 1989 to April 1992.

period of 36 months (April 1989 to March 1992). The WTD and ψ_m were plotted for the same period of time but the number of observations are lower than for the rainfall.

Since WTD records were taken from nested piezometers, the piezometers at 2.00-m depth were the only ones that were plotted with a continuous line. WTD values of -2.00 m with respect to the soil surface indicate that the average water level dropped below this depth and no water level was recorded in the piezometer. Large differences in WTD were measured among the piezometers in both soils at times. These occurred after a period of unsaturation (relatively dry) followed by abundant rainfall.

The soil saturation is represented by the zero or positive ψ_m in Figs. 2.1 and 2.2. Data show that these two soils were completely saturated for two to three months in late fall and winter seasons. Marked fluctuations in ψ_m (saturation - unsaturation cycles) occurred in the first 0.25-m depth in both soils. A potential of -80 kPa was assumed as the limit the tensiometer could measure the soil matric suction (Cassell and Klute, 1986). The changes in volumetric water content (θ) with time (Date) within the working range of the tensiometer are shown in the Figs. 2.3 and 2.4. The values of (θ) were obtained from the soil moisture characteristic curve for each soil suction value observed in the field and for the respective depths of 0.25-, 0.50- and 1.00-m in both soils.
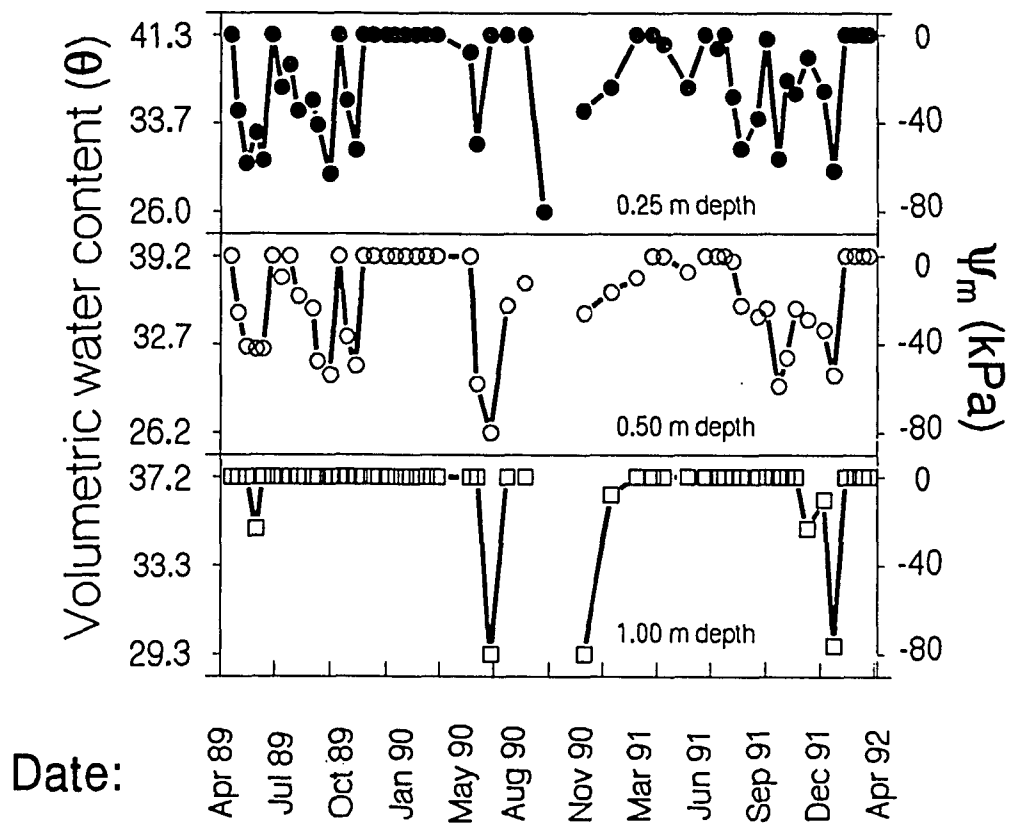
Fig. 2.3. Volumetric water content changes in time (Date) for Verdun soil at three different depths 0.25, 0.50 and 1.00 m.
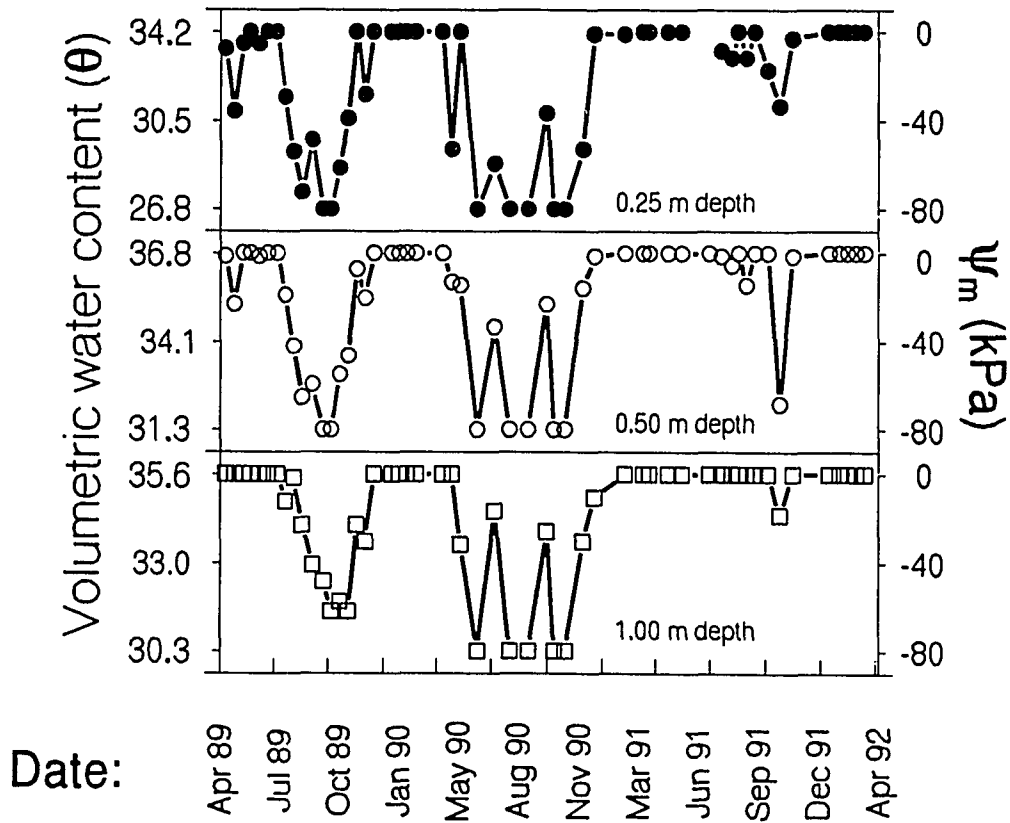
Fig. 2.4. Volumetric water content changes in time (Date) for Brimstone soil at three different depths 0.25, 0.50 and 1.00 m.

The two graphs show that changes in ψ_m give relatively small changes in θ.

The Verdun soil remained saturated for three and a half months (middle December 1989 to March) in 1990 and for two months (February to March) in 1991 and 1992 because rainfall exceeds evapotranspiration and the soil infiltration capacity (Fig. 2.1 C) at this time of the year. Large amount of rains occured during these periods (Fig. 2.1 A).

Episaturation during the rest of the year (late spring, summer and fall season) had a low frequency in the Verdun soil, since the water stayed perched or ponded for short periods (less than two weeks) on the topsoil after a rainstorm preceded by a period where the soil was unsaturated. This is indicated in Fig. 2.1 B by the large differences in WTD between the nested piezometers in October 1989, June 1990, December 1990, and July 1991. Prolonged saturation occurred in the summer (May-June) of 1991 due to rainfall exceeding 200 mm in two weeks period.

The Brimstone soil was saturated for three months every year (middle January to middle April) in 1990, 1991 and, 1992. After the winter-early spring discharge, the soil began to drain and dry from the top downwards (Fig. 2.2 C) during drought periods. Water remained perched or ponded for short periods on the top soil after a rainstorm in July 1989, December 1990, and August 1991. The same effect of large differences between WTD of the nested piezometers can be

oberved in Fig 2.2 B. Prolonged saturation occurred in the summer (May to July) of 1989.

Redox Potential

Gaph D of Fig. 2.1 for Verdun soil and graph D in Fig. 2.2 for Brimstone soil show the fluctuation of redox potential (Eh) with time (Date) for two soil depths (0.50- and 1.00-m). The redox potential depends upon the pH of the soil. The average pH and coefficient of variation (C.V.) for every depth are presented in Table 2.4.

Table 2.4. Average pH of the ground water and coefficient of variation (C.V.) measured from samples taken from nested piezometers at two depths for Verdun amd Brimstone soils.

SOIL	DEPTH	pH	C.V.
	(m)		(%)
VERDUN	0.50	6.9	4.3
	1.00	6.7	2.3
BRIMSTONE	0.50	7.1	5.4
	1.00	7.0	4.0

The frequency of reduction determined by the staining test is presented in Table 2.5. The frequency of positive reaction of the two staining tests with the two $\alpha - \alpha'$ dipyridyl solutions can be compared with: i) the frequency of saturation and ii) the frequency of occurrence of water tables above a given depth. These data in Table 2.5 show that for the two staining tests in both soils there was not very much

difference in the % of positive reaction at the 0.25-m depth.
Large differences in the frequency of positive dye reaction
were recorded at 0.50- and 1.00-m depth. When the positive
reaction is compared to saturation, the frequency of positive
test was higher for both tests than for saturation in both
soils at the 0.25-m depth. At 0.50-m and 1.00-m depth, the
frequency of a positive test is always lower than the
saturation frequency.

Table 2.5. Reduction and saturation frequency (expressed as %
of total number of observations) measured by staining
tests, Pt-electrodes, tensiometry and piezometry for
Verdun and Brimstone soils.

Depth		Verdun	Brimstone
(m)	(*)	%	%
0.25	R a.	59.2	54.5
	b.	51.8	39.2
	S	43.1	38.4
	PZ	35.2	31.3
0.50	R a.	54.0	29.4
	b.	34.6	22.7
	Pt	31.2	8.9
	S	44.2	43.4
	PZ	40.7	35.2
1.00	R a.	60.0	25.5
	b.	27.0	18.2
	Pt	39.1	3.3
	S	86.5	62.2
	PZ	55.6	51.0

(*) R = positive test to α-α dipyridyl: a) acid soution, b)
buffer solution, Pt) Eh < 150 mV. S = saturated, zero or
positive tension. PZ = free water in piezometer above a given
depth.

Table 2.6 presents data for the reduction potentials and pH attained on the top soil of Verdun and Brimstone soils when they were saturated for four consecutive weeks in January 1992. These values are the average of 10 observations at each depth. In the same table is included the redox potential and pH measured from crawfish burrows on the Ap horizon. The acid reaction and low redox potential indicate that the soil was reduced.

Table 2.6. Average redox potential and pH in Ap horizons of the Verdun and Brimstone soils after 4 weeks of saturation and positive staining test (early spring 1992).

Soil	Depth	Eh	pH
	(m)	(mV)	
VERDUN	0.10	84	5.0
	0.20	275	5.3
BRIMSTONE	0.10	64	5.8
	0.20	110	5.8
Crawfish burrows	0.15	89	5.8

Temperatures

Soil temperatures recorded at 0.50- and 1.00-m depth are presented in Fig. 2.5 for the Verdun soil and in Fig. 2.6 for the Brimstone soil. Both figures show that the temperature never drop below 5°C. At temperatures below 5°C most soil microbial activity stops (Alexander, 1977). The maximum summer soil temperatures for Verdun forest soil were lower than for the Brimstone prairie soil.

For both soils temperature taken at 0.50-m depth were generally one or two degrees Celsius higher than at 1.00-m. During winter the reverse phenomena was observed a few times: temperatures at 1.00-m depth were higher than temperatures at 0.50-m depth by one or two degrees Celsius.

Verdun soil is thermic with an annual average soil temperature of 19.5 °C and Brimstone soil is hyperthermic with an annual average soil temperature of 22°C.
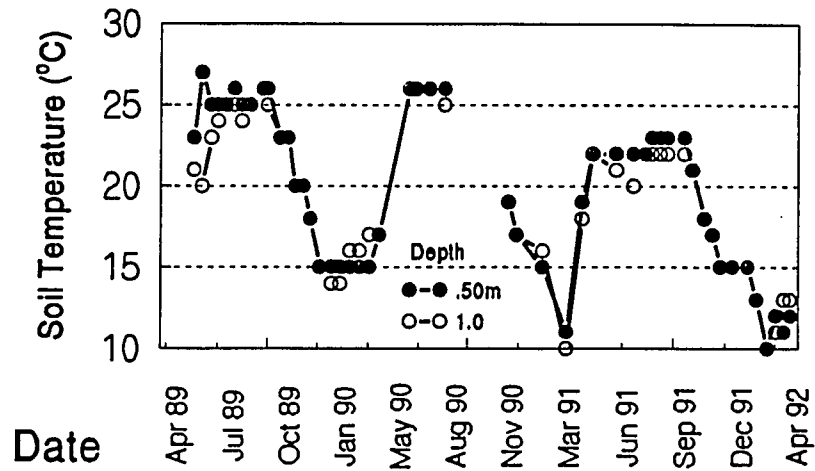
Fig. 2.5. Soil temperatures for Verdun soil.
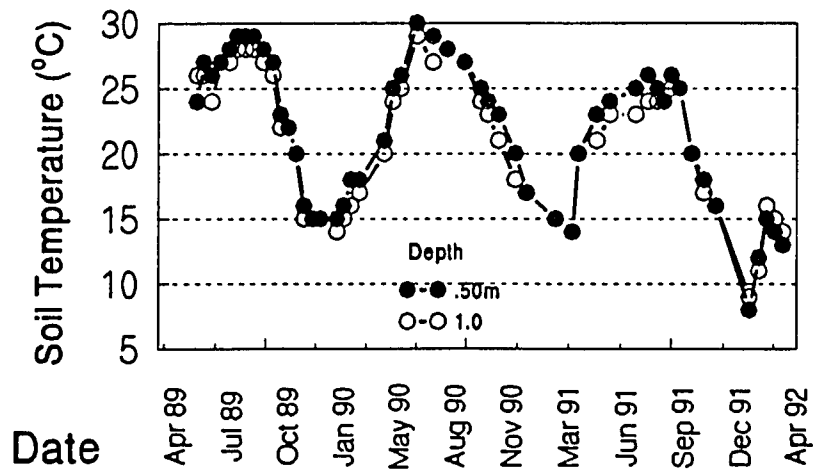
Fig. 2.6. Soil temperatures for Brimstone soil.

2.4. DISCUSSION

Identification of "Aquic Conditions"

Results from Tables 2.2 and 2.3 indicate that Verdun and Brimstone soils have redoximorphic features in every horizon. Redoximorphic features similar to the ones we observed in the field are well documented by Vepraskas and Bouma (1976) and Fisher and Stone (1991). These features are the primary clue that these soils may have aquic conditions. Saturation and reduction results must be examined in detail to reach the taxonomic placement of the soil. The problems related to the consideration of morphological properties, lab analysis data and field monitoring data as predictive tools to identify aquic conditions were thoroughly discussed by Hudnall and Wilding (1992). We will make a brief reference of some of these problems during our discussion.

A soil will be placed in an aquic suborder if aquic conditions are identified within 50 cm of the mineral soil surface (Witty, 1991) seven out of ten years. The minimum period required for saturation is 30 days each year. They are not consecutive days but cumulative. Reduction must be observed at least once a year.

Verdun Soil

As noted by Szögi and Hudnall (1992), the Verdun soil has a perched and a true ground water table that coexist for short periods of time. During the winter-early spring season the

two water tables merge (Fig. 2.1 B and C). The merging of the two water tables is possible by artesian flow from the true ground water table and preferential downward flow of rain water through fresh crawfish burrows and glossic features. Diab et al. (1988) illustrated the relationship between the morphology of Glossaqualfs and its water movement. They found by using two different tracer techniques, that tongues are preferential paths of water flow, and that the soil matrix is nearly short circuited under saturated conditions.

Hudnall and Wilding (1992), indicate that sometimes it is difficult to differentiate a moving water front from true water tables. The rainfall may be so frequent that the soil is saturated from top downward with free water present throughout the profile that epiaquic or endoaquic saturation cannot be differentiated.

According to Fig. 2.1 B, episaturation was found only in 10 % of the observations from piezometers. Perched water tables were not observed with a higher frequency because of their short duration (less than two weeks). These observations are correlated to previous periods of low rainfall (< 75 mm / 2 weeks) as shown in Fig. 2.1 A. This ephemeral character of perched water tables was also observed in Alfisols by Baize (1989).

The tensiometric data at 1.00-m depth reveals that the soil is saturated most of the time at this depth by effect of the slow downward movement of water or the capillary fringe of

the true groundwater table that can range from 35 to 55 cm above the water table for silty clay loam textures according to Mausbach (1992). Table 2.5 indicates that saturation is more frequent than the observation of free water at a given depth, probably because of the capillary fringe effect. However, Hudnall and Wilding (1992) interpreted these differences as differing responses from tensiometers and piezometers. This is found in the field when there is a lag of time between when the tensiometer indicates saturation and when free water occurs in the piezometer at the same depth.

Results indicate that abundant rainfall, shallow water tables and saturation in all soil layers relate well to reduction (< 150 mV) and positive dye tests, at 0.50- and 1.00-m depth. The Eh was in the oxidizing to moderately reduced ranges (> 150 mV) when the soil was not saturated (ψ_m < 0 kPa) at 0.50- and 1.00-m depth.

In summary, the data for the Verdun soil support aquic conditions. Redoximorphic features, saturation and reduction occurred within 0.50 m to below 2.00 m. This soil has both epiaquic and endoaquic saturation. Alfisols with aquic conditions are considered always episaturated. However, Witty (1991) considered the classification of endoaquic Alfisols in the Keys to Soil Taxonomy. The Verdun soil is keyed first as an episaturated Alfisol with a natric horizon (ESP > 15, Table 2.1). Therefore, the classification according to the Keys to

Soil Taxonomy (Witty, 1991) is: Fine-silty, mixed thermic Glossic Natraqualf.

Brimstone Soil

The Brimstone soil has a BCg horizon with a very high dry bulk density of 1.96 kgm^{-3} (Table 1.1). This layer, is probably the most restrictive layer to water flow. The soil saturates from the top downwards and water perches on this layer. The water perching on these layer has the characteristic of a shallow unconfined aquifer.

Another layer that slows down the downward movement of water is the Eg horizon. A plow pan with subangular to platty structure perches water on top of this horizon. When rainfall exceeds the storage capacity of the Ap horizon it remains stagnant or episaturated because this layer impedes percolation of water deeper into the soil profile.

Redox potential results indicate that the Brimstone soil was reduced on few occasions (Eh < 150 mV) at 1.00-m depth. It had a higher frequency of reduction at 0.50-m depth. Dye reaction and redox measurements (Tables 2.5 and 2.6) indicate that reduction occurs when the topsoil is saturated. When the soil reaches saturation at 0.50-m depth, the transport in solution of the reduction products from the topsoil (Mn^{2+} and Fe^{2+}) to this depth produces the drop of Eh to the reducing range.

Summarizing, the Brimstone data supports aquic conditions. The redoximorphic features, saturation and reduction occurred within 0.50-m to below 2.00-m depth. The classification according to the new Keys to Soil Taxonomy (Witty, 1991) is: Fine-silty, siliceous, hyperthermic Typic Epiaqualf.

Relationship of Redoximorphic Features to Wetness Conditions

The Verdun and Brimstone soil become reduced initially in the topsoil. The reduction is intense and more frequent in the topsoil (Tables 2.5 and 2.6) than in underlaying horizon because energy sources in the form of organic C are available for the microbes (Table 2.1). Also it is important to consider that redox potential depends on soil pH. Redox reactions in natural systems involve the transfer of electrons (Eh) and protons (pH) according to Baas Becking et al. (1960). The pH of most soils tends to change toward the neutral point after flooding (Patrick et al., 1985). For instance, Tables 2.1 and 2.4 show the large differences in pH measured in dry samples (acidic) and in the field (close to neutrality) for the Eg/Btg (0.50-m depth). However, Bouma (1983) concluded that several factors must be present at the same time in order to have optimum conditions for intense reduction besides the presence of soil organic matter and optimum pH. These include: i) absence of oxygen supply due to waterlogging

conditions, ii) presence of anaerobic organisms, iii) optimum temperature, iv) presence of iron and manganese oxides.

The description of redoximorphic features for the Ap horizon in Table 2.2 for the Verdun soil and Table 2.3 for the Brimstone soil shows the occurrence of iron coatings on macropores. These features correlate with the observation of higher frequency of reduction in the Ap horizon than in other horizons (Table 2.5). The reduced Fe moves from the soil matrix into the macropores. If the soil becomes aerated, Fe^{2+} will precipitate from solution when it comes in contact with O_2 as coatings of reddish iron oxyhydroxides on the walls of pores and the surface of roots.

Hudnall and Wilding (1992), discussed the accuracy of reduction data obtained with dyes and Pt-electrodes. They concluded that in Louisiana the buffered solution of $\alpha - \alpha'$ dipyridyl had better agreement with Pt-electrodes measurements than the acidic one. This conclusion is illustrated in Table 2.5 by the higher percentage of observed positive test of reduction with the acidic staining test than with the buffered one. Childs (1981), also noted the interference of organic complexes giving a positive test when the soil was not reduced. This effect probably explain the higher observed frequencies of reduction with respect to saturation in the first 25 cm.

The Verdun soil is more frequently reduced at 0.50- and 1.00-m depth than the Brimstone soil (Table 1.5). This

probably is due to: i) a higher availability of organic C sources and free iron oxides in the Verdun soil at those depths (Table 2.1); ii) a longer duration of saturation in the Verdun than in the Brimstone soil (Figs. 2.3 and 2.4); iii) the presence of a plow pan as a result of cultivation in the Brimstone soil that enhances stagnation and probably hinders the downward movement of dissolved organic carbon and reduced substances.

These differences between the Verdun and the Brimstone soil are expressed in the abundance and size of the ferruginous masses for the Verdun soil in the Eg/Btg and Btng/Eg horizons (Table 2.2) versus the few fine vesicular and constricted pores lined with iron coatings in the E/Btng and Btng/E horizons for the Brimstone (Table 2.3).

In the Verdun soil, the reduced Fe and Mn move downward through macropores and tongues. If the lower soil horizons become unsaturated Fe^{2+} and Mn^{2+} will precipitate from solution and accumulating as coatings of reddish or yellowish iron or black manganese oxihydroxides on the faces of peds, walls of pores, at the surface of roots or inside peds, while in the Brimstone soil the transport of reduced Fe is impeded by the plowpan. The effect of plowpans and soil compaction that impedes percolation of water deeper into the soil profile and creating an anaerobic environment above the compacted layer is documented by Lal and Fausey (1990).

An important morphological feature that complicates the interpretation of the relationship between wetness and redoximorphic features are the crawfish krotovinas that appear in both profiles. The profile description for the Brimstone soil has a good description of them. While for the Verdun, krotovinas were not described because it was difficult to separate them from the glossic features (Appendix A). Table 2.6 shows that reduction can occur in crawfish burrows. The reaction is acidic and redox potentials are < 150 mV when the topsoil is stagnated for several weeks. Huner and Barr (1984), observed that water collected in crawfish burrows is slightly acidic, O_2 levels are low (< 1 gL^{-1}), and that CO_2 concentrations are high (60 to 110 gL^{-1}) compared with surface waters. We conclude that the open crawfish burrow is a reducing environment when it is saturated. The low chroma colors of the krotovina are a result of the reduction of the materials that plugged the burrows. Krotovinas are the result of physical and chemical pedoturbation of the profile by the crawfish. For this reason we proposed to describe the crawfish krotovinas as associated redoximorphic features (Appendix B).

Reduction patterns are not uniform for a given horizon. The soil sometimes can be close to saturation and still is reduced in microzones as cited by Anderson (1984). This fact probably explains the higher frequency of positive staining tests with respect to saturation at 0.25-m depth. We

observed, in underlaying horizons that reduction occurred along macropores or roots where organic matter is present when using staining tests. Therefore, the placement of Pt electrodes or where the staining tests are performed are crucial for a good interpretation of the reduction patterns with respect to saturation and the presence of redoximorphic features.

In soils with episaturation, the Eh measurements and staining tests must be performed in the mineral horizon with the highest organic C percentage. This is generally the A horizon. Other tests or measurements must be done within 0.50 m and below this depth to define the taxonomic placement.

2.5. CONCLUSIONS

Aquic conditions were recognized for Verdun and Brimstone soils. Since saturation and reduction occur within the 50 cm depth these soils belong to an aquic suborder. Redoximorphic features found on both soil profiles follow the different models proposed by Fanning and Fanning (1989). However, they do not define uniquely episaturation or endosaturation of the soil. The kind of saturation was discerned from tensiometric and piezometric field data. The origin of reduction is not in the control section but in the horizon with higher % of organic C content (Ap horizon). The products of reduction (Mn^{2+}, Fe^{2+}) eventually are detected in lower horizons whith a staining test or Pt-electrodes when they flow in their reduced

form from the topsoil into underlaying horizons. If the lower soil horizons are unsaturated Fe^{2+} and Mn^{2+} will precipitate from solution and accumulating as coatings of reddish or yellowish iron or black manganese oxihydroxides on the faces of peds, walls of pores, at the surface of roots or inside peds. Episaturation as a result of perched water tables has an ephemeral character. A minimum of one week monitoring period is needed in order for it to be detected precisely. In winter, when precipitation exceeds largely evapotranspiration rates, the episaturation is expressed as stagnation that may last two to three months.

CHAPTER 3.

PREDICTION OF FIELD ANAEROBIC CONDITIONS
BY SOIL REDOX CAPACITY FACTORS

3.1. INTRODUCTION

The different terrestrial environments have been characterized in terms of hydrogen ion activity (pH) and oxidation-reduction potential (Eh) by Baas Becking et al. (1960). Eh is also expressed as electron activity or pe (Sposito, 1989). These parameters have been very useful to characterizing the stability of minerals by Eh-pH diagrams (Garrels and Christ, 1965) and pe-pH diagrams (Lindsay, 1979).

Eh or pe and pH are also used to classify wet soils. Eh-pH field measurements (Bohn et al. 1985) and Eh-pH diagrams (Collins and Buol, 1970) are diagnostic tools in determining the redox status of a soil. In two cases, the inference of the soil redox status is of utmost interest for classifying the soil: i) the definition of aquic conditions in the Keys to Soil Taxonomy, and ii) the determination of hydric soils. Soil reduction is one of the three properties in addition to soil saturation and the presence of redoximorphic features required to define the aquic conditions and the taxonomic placement of a soil in the aquic suborder in Soil Taxonomy according to the International Committee on Aquic Moisture Regimes or ICOMAQ (Bouma, 1991). Hydric soils are defined by the National Technical Committee for Hydric Soils (NTCHS) as soils that are saturated, flooded, or ponded long enough

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during the growing season to develop anaerobic conditions in the upper part (NTCHS, 1992).

The in situ characterization of the redox status of a soil is made either with Pt electrodes placed permanently in the soil or by a staining test (Faulkner et al., 1989). The redox staining tests methods are not very reliable indicators of redox conditions as discussed by Childs (1981) and Hudnall and Wilding (1992). On the other hand, Eh measurements with Pt electrodes are inaccurate because of the heterogeneity of soil materials and the characteristic inequilibrium of soil redox reactions. Redox reactions in soil systems generally are not in equilibrium because of the continuous addition of electrons, usually by oxidizable organic compounds (Bohn, 1971).

An alternative method, reviewed by Stolzy and Flühler (1978), is the use of a polarographic sensor or oxygen probe to measure dissolved oxygen (DO). According to Berner (1981), the distinction between an oxic and anoxic environment is an oxygen concentration < 1 μmol kg^{-1}. This represents 0.5 percent of its concentration in fully aerated water in equilibrium with the atmosphere at 25 °C (10 mg kg^{-1}). This oxygen concentration is the detection limit of conventional oxygen probes. The main limitation of most methods to measure dissolved oxygen is their inability to measure trace concentrations of DO as reported by White et al. (1990). These researchers managed to measure very low concentrations

of DO by spectrophotometry using the Rhodazine-D colorimetric technique in shallow ground water tables.

Daniels and Buol (1992) considered some other problems in the determination of reducing conditions related to the biogeochemical characteristics of the saturated zone. Soil microbes, either under aerobic or anaerobic respiration need an energy source in form of organic carbon (OC) to maintain their metabolic activity. After O_2 is depleted by microbial aerobic respiration, other species are used in anaerobic respiration as electron acceptors, such as NO_3^-, Mn^{4+}, Fe^{3+} and SO_4^{2-} (Bouma, 1983). Anaerobic conditions may be difficult to determine in saturated soils if one or more of the following situations occur: i) the water is rich in DO, ii) low concentration of OC, iii) low soil temperatures.

Several studies give evidence of these problems. Low chroma colors are diagnostic of reducing conditions, however Vepraskas and Wilding (1983 a,b) described a toposequence of seasonally wet Alfisols in the coastal plain of Texas where some of them had high chroma colors (> 2). This feature can be attributed to a low soil organic matter content (< 1 %) and/or to the presence of an oxygenated water table. Reducing conditions are not easily detected in sandy wet soils low in Fe or Mn oxides. Sandy soils without redoximorphic features like some Aquods, Humaquepts and Umbraquults cited by Fanning et al. (1973, 1992), probably become anaerobic only when the depletion of oxygen occurs if enough OC is available.

Seasonally wet Oxisols with a lack of energy sources for microbial reduction do not develop redoximorphic features and never became reduced with a high water table during long periods of saturation (Couto et al. 1985; Buol and Camargo, 1992). Soil temperatures below the biological zero (5 °C) inhibit microbial activity and reduction in saturated soils (Daniels et al. 1971; Gilliam and Gambrell, 1978). However, evidence presented by Ping et al. (1992) indicate that microbial activity persists in permafrost soils of Alaska below this limit.

Bouma (1991) concluded in his final report for ICOMAQ, that we do not have yet an adequate technique to measure anaerobic conditions in soils. The objective of this study is to examine and evaluate an alternative methodology to predict anaerobic conditions in soils. The approach is based on the energetics and conservative properties of redox systems described by Scott and Morgan (1990). These authors consider that a natural system must be characterized by both intensity and capacity factors. According to Patrick (1980), intensity factors (e.g. pH and Eh) reflect the activities of free species and the relative ease of reduction. Capacity factors are the expression of the total concentration of relevant species (e.g. total acidity and total concentration of reducible species). Capacity factors are conservative properties of the system that depend indirectly on temperature

and pressure while intensity factors depend directly on temperature and pressure.

We applied the oxidative capacity (OXC) concept described below combined with Berner's geochemical classification (Berner, 1981) as conceived by Scott and Morgan (1990) to wet soil environments in order to predict anaerobic and reductive conditions in the field.

3.2. THEORY

According to Scott and Morgan (1990), the oxidative capacity (OXC) system represents the total number of transferable electrons in a redox system per unit mass of the system. It is a conservative property of the system that can be defined regardless of the system's equilibrium. OXC is determined as the equivalent sum of all oxidants that can be reduced with a strong reductant to an equivalence point. By analogy, the reductive capacity (RDC) is determined as the oxidation of reductants by a strong oxidant to a preselected equivalent point. OXC is defined mathematically as:

$$OXC = \Sigma n_i \, [Ox]_i - \Sigma n_i \, [Red]_i = - RDC \qquad (1)$$

Where $[Ox]_i$ and $[Red]_i$ are the molal concentrations of the individual oxidants and reductants of the system and n_i is the number of moles of electrons that are transferred. OXC is expressed in moles of charge (or equivalents) per kilogram of solution $(mol_c \, kg^{-1})$. According to Scott and Morgan (1990), for solid phases, concentrations are expressed as the mean

number of moles of solid per volume of contacting water. In other words, this is the surface molal concentration of the solid, which is equal to the product of the total solid concentration (g kg^{-1}), the mean surface area of the solid (m^2 g^{-1}), and the mean mole number of surface sites per unit area (mol m^{-2}).

Equation (1) is expressed in a simplified form by equation (2):

$$OXC = OX_T - RD_T \qquad\qquad (2)$$

Where OX_T are total oxidants and RD_T are total reductants.

A system consists of several initial oxidants and potential reductants. Microbes will use first the most energetically favored species to reduce. For instance, O_2 is generally the first to be consumed by aerobic cell respiration processes. Next, the following strongest oxidant (NO_3^-) is used when oxygen is depleted. This step-by-step order of redox reactions from the most energetically efficient to the least efficient constitute a "redox sequence".

The evidence for the sequential reduction was presented by Connell and Patrick (1968), Patrick and Mahapatra (1968), Turner and Patrick (1968) and Martens and Berner (1974) among others. A redox sequence is a series of electron free energy steps whose limits are the strongest oxidant (O_2) and the strongest reductant (OC).

The redox sequence represented by selected reactions in soils and their thermodynamic data (log K^0 and E_H^0) taken from

Sposito (1989) are presented in Table 3.1. Log K^0 is the equilibrium constant for the half cell reaction at standard pressure and temperature and E_h^0 is the standard half cell potential.

Table 3.1. Selected half reactions in soil solutions, thermodynamic equilibrium constants (log K^0 and E_h^0) and equilibrium potential at pH 7 (Eh_7 and pe).

Half reaction	$\log K^0$	E_h^0 (V)	Eh_7 (V)	pe
$1/4O_2(g)+H^++e^-=1/2H_2O$	20.75	1.23	0.82	13.9
$1/5NO_3^-+6/5H^++e^-=1/10N_2 + 3/5H_2O$	21.05	1.25	0.75	12.7
$1/2MnO_2(s)+2H^++e^-=1/2Mn^{2+}+H_2O$	20.42	1.21	0.40	6.8
$Fe(OH)_3(s)+3H^++e^-=Fe^{2+}+3H_2O$	16.00	0.95	-0.30	-5.1
$1/8SO_4^{2-}+9/8H^++e^-=1/8HS^-+1/2H_2O$	4.25	0.25	-0.22	-3.7
$1/4CO_2(g)+H^++e^-=1/4CH_2O+1/4H_2O$	-1.20	-0.07	-0.49	-8.3

High cell potentials (E_h^0) indicate that the elements or ions on the left side of the corresponding half reaction would accept electrons (Bohn et al. 1985). The equilibrium potentials at pH 7, expressed as Eh_7 and pe, were calculated from the thermodynamic data for each half reaction. The electron reference level (ERL) defined by Scott and Morgan (1990) is a relative electron level on the redox sequence

chosen according to the case under study. ERL represents an arbitrary equilibrium point to be reached. If HS⁻ is chosen as the ERL, the species on its left and above sulfate in Table 3.1 are considered oxidants. HS⁻ is neither oxidant nor reductant, while all species below HS⁻ are reductants (in this particular case, only OC).

By choosing HS⁻ as the ERL, the OXC can be introduced in Berner's classification system using the following equations:

$$OXC = (o\text{-}OXC) + (p\text{-}OXC) + (s\text{-}OXC) - (m\text{-}RDC) \qquad (3)$$

$$(o\text{-}OXC) = 4[O_2] \qquad (4)$$

$$(p\text{-}OXC) = 5[NO_3^-] + 2[MnO_2] + [FeOOH] \qquad (5)$$

$$(s\text{-}OXC) = 8[SO_4^{2-}] \qquad (6)$$

$$(m\text{-}RDC) = 4[CH_2O] = RDC \qquad (7)$$

$$(op\text{-}OXC) = (o\text{-}OXC) + (p\text{-}OXC) \qquad (8)$$

$$(ops\text{-}OXC) = (op\text{-}OXC) + (s\text{-}OXC) = OX_T \qquad (9)$$

The letters o, p, s and m represent a class of environment: oxic, post oxic, sulfidic and methanic respectively. The concentration of every species is expressed in molality (mol kg^{-1}). A system is initially oxic if $[O_2] > 1$ μmol kg^{-1} (Berner, 1981). The geochemical classification system is listed in Table 3.2. The classification has two classes: a) oxic and b) anoxic. The anoxic class is divided in three subclasses: i) post-oxic, ii) sulfidic and iii) methanic.

Table 3.2.   Berner's geochemical classification of natural
environments (after Scott and Morgan, 1990)

----

a)   oxic

        if (o-OXC) - (m-RDC) > 0.0

        or (o-OXC) > (m-RDC)

b)   anoxic

        if (m-RDC) ≥ (o-OXC) then:

        i)   post-oxic

                if (op-OXC) > (m-RDC)

        ii) sulfidic

                if (m-RDC) ≥ (op-OXC)

                and OX_T > RD_T

        iii) methanic

                if RD_T > OX_T

                or OXC < 0.0

3.3 MATERIALS AND METHODS

The investigation was based on two soil series: Verdun silt loam (fine-silty, mixed, thermic Glossic Natraqualfs) and Brimstone silt loam (fine-silty, mixed, thermic Typic Natraqualfs) both described by Hudnall et al. (1990). Both soils belong to an extensive network of monitoring sites to test the aquic conditions in the Coastal Plain of Louisiana, and to the list of hydric soils of the United States (NTCHS, 1987, 1992). The Verdun soil is identified in this list as Deerford Series because these two series are associated in a complex mapping unit.

The field measurements comprised: pH, DO, Fe^{2+} in the water samples and in situ Eh. The pH was measured with a portable pH-meter (Beckman Instruments Inc., Fullerton, CA, Model 11Φ) with a combination electrode. The DO was measured by the Rhodazine-D colorimetric method (CHEmetrics Inc., VA, kit Model K-7501). The Fe^{2+} was measured with an orthophenanthroline colorimetric method (CHEmetrics Inc., VA, Model K-6201). The water samples for DO and Fe^{2+} were obtained with a syringe device for water sampling described by Gillham (1982). The syringe was connected to the sampler cup provided with the DO kit. Immediately after the sample was injected in the cup, an ampoule containing Rhodazine-D solution under vacuum was broken at its capillary tip inside the sampling cup permiting a small amount of water to be drawn into the ampoule. The same procedure is followed to determine Fe^{2+}

using an orthophenanthroline solution ampoule with another water sample. The DO or Fe^{2+} concentration was estimated by comparing the color developed in the ampoule against a standard. Soil redox potentials were measured with permanently installed Pt electrodes at 0.25-, 0.50- and 1.00-m depth as described by Szögi and Hudnall (1992).

Water samples were taken with a pump from triplicate nested piezometers at four different depths (0.25-, 0.50-, 1.00- and 2.00-m) at the beginning of the growing season in early spring of 1992. An aliquot of each water sample was filtered though 0.45 μm milipore filter. Dissolved organic carbon (DOC) was calculated from absorbance at 360 nm (4 cm cells) with a spectrophotomer with a light filter (Hitachi Ltd., Tokyo, Japan, Model 100-20) according to the method of Lewis and Canfield (1977). The concentration of NO_3 and SO_4 was measured by ion chromatography (IC) for water samples of the Brimstone soil. The IC method was not used for the measurement of anions in the ground water of the Verdun soil because of the large interference peaks of Cl in the chromatograms. The concentration of NO_3 in water samples from the Verdun soil was determined with an ammonium-total nitrogen autoanalyzer (Wescan Instrument Inc., Model 360, Santa Barbara, CA), while SO_4 was calculated using a correction factor for total sulfur analysis (S. Feagley, pers. comm.) obtained by inductively coupled plasma - atomic emission spectrometry (ICP).

The concentration of Fe and Mn oxihydroxides were obtained by ammonium oxalate - oxalic acid (Fe_o) extraction (Schwertmann, 1964) and by sodium dithionite - citrate - bicarbonate (CBD or Fe_d) extraction (Mehra and Jackson, 1960) and analyzed by ICP.

3.4. RESULTS AND DISCUSSION

Prediction of Anaerobic Conditions

The analytical data in Table 3.3, were used to calculate the OXC for Verdun and Brimstone soils presented in Table 3.4. Ferrous iron (Fe^{2+}) concentrations in Table 3.3 were not used in the calculation of OXC, but as an indicator of the presence of reduced iron. Concentrations > 1 mg kg^{-1} indicate the presence of Fe^{2+} and reducing conditions, however, iron-organo complexes may affect the accuracy of the staining test (Childs, 1981).

The class, subclass of environment and dominant redox species included in Table 3.4, were calculatd for each soil depth by using equations 4, 7 and 8 with verification for the anoxic and postoxic conditions according to the inequalities defined in Table 3.2. The dominant redox species at each depth, was calculated as the species that contributed more than 50 % to the OXC.

For the Verdun soil, OXC increases with depth. The OXC is approximately 2.5 times larger at 0.5-m depth than at 0.25-m, below 1.00-m depth the OXC is almost 5 times larger than at

Table 3.3. Analytical data for Verdun and Brimstone soils.

Soil	Depth	DO	NO_3^-	Mn_d	Fe^{2+}	Fe_o	Fe_d	SO_4^{2-}	DOC
	(m)				mg kg^{-1}				
Verdun	0.25	0.5	0.9	9	>1	598	733	111	12.0
	0.50	0.9	<0.1	2	0.2	1774	4012	180	4.5
	1.00	0.6	<0.1	579	0.1	807	3558	255	2.7
	2.00	0.05	<0.1	190	0.1	381	2968	330	3.4
Brim-	0.25	0.4	18.9	115	>1	532	1004	37	8.8
stone	0.50	0.3	18.8	100	0.3	244	731	4	7.5
	1.00	0.3	20.0	47	0.1	220	1236	16	3.0
	2.00	0.6	18.8	<1	0.3	257	1950	6	2.0

Dissolved oxygen (DO), nitrate NO_3^-, ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), dissolved organic carbon (DOC) in mg kg^{-1} solution. CBD extracted manganese (Mn_d), oxalate extracted iron (Fe_o), CBD iron extracted (Fe_d) in mg kg^{-1} soil.

CBD = sodium dithionite - citrate - bicarbonate extraction (Mehra and Jackson, 1960).
oxalate = Ammonium - oxalate - oxalic acid extraction (Schwertmann, 1964).

Table 3.4. Total oxidants (OX_T), total reductants (RD_T) and oxidative capacity (OXC) concentrations by depth calculated from the analytical data in Table 3.3, class and subclass of redox evironment and dominant redox species in the ground water of Verdun and Brimstone soils.

Soil	Depth	OX_T	RD_T	OXC	Class (*)	Sub-class	Dominant sp.
	(m)	---- $\mu mol_c kg^{-1}$ -----					
Verdun	0.25	11048	4000	7048	An-ox	P-ox	SO_4^{2-}
	0.50	19588	1500	18088	An-ox	P-ox	SO_4^{2-}
	1.00	33886	900	32986	An-ox	P-ox	SO_4^{2-}
	2.00	35410	1133	34277	An-ox	P-ox	SO_4^{2-}
Brimstone	0.25	8028	2933	5095	An-ox	P-ox	---
	0.50	5742	2512	3230	An-ox	P-ox	NO_3^-
	1.00	5907	1000	4907	An-ox	P-ox	NO_3^-
	2.00	4184	667	3517	An-ox	P-ox	NO_3^-

(*) An-ox = anoxic; P-ox = postoxic.

0.25-m depth. For the Brimstone soil, OXC decreases from 0.25- to 0.50-m depth, increases between 0.50- and 1.00-m, and decreases again between 1.00 and 2.00-m.

The different OXC trends for the two soils are explained by the different OX_T, RD_T and the dominant ion species. RD_T decreases in both soils as a function of depth (Table 3.4). DOC is the only contributor to RDC and therefore is equivalent to RD_T, so changes in DOC (Table 3.3) is equivalent to a change in the soil RD_T. The decrease in DOC with depth in both soils is probably caused by some combination of microbial decomposition, adsorption and precipitation as a solid (Stevenson, 1985; Thurman, 1985; Dunnivant et al., 1992 and Qualls and Haines, 1992). The changes in OX_T will depend on the total sum and on the individual concentrations of the different species in this fraction. Microbes use the oxidized forms of redox couples as final acceptors of electrons in the process of cell respiration (Alexander, 1977). The microbial reduction proceeds by using the different electron acceptors according to the energy efficiency of the redox sequence given in Table 3.1.

In the Verdun soil, the DO, NO_3^- and Mn^{+4} concentrations are low (Table 3.3). Upon the successive reduction of these three species, Fe^{3+} is reduced next, until all the reductant (OC) is consumed by microbial activity. Sulfates are the dominant redox species in the Verdun soil and the next in the sequence to be reduced after Fe. To reduce SO_4^{2-}, a large

amount of organic C is required to take the soil from a postoxic to a sulfidic environment. Probably most of the reductant (OC) is consumed in the reduction of O_2 and Fe^{3+}, according to the OX_T and RD_T concentrations for the four soil depths (Table 3.4).

In the Brimstone soil, the same redox sequence takes place. However, the dominant species is NO_3^- except for the 0.25-m depth where NO_3^- accounts for 30 % of the OX_T. Since NO_3^- reduction (denitrification) follows in the sequence after O_2 reduction (Patrick and Mikkelsen, 1985), the anoxic environment in the Brimstone soil is different from the anoxic environment of the Verdun soil because most of the RD_T is consumed in the reduction of NO_3^-.

Ottow (1973), investigated the mechanism of iron reduction by bacteria. He found that NO_3^- inhibited the reducing capacity of iron reducing bacteria (obligate iron reducing anaerobes) and that other microbes (facultative iron reducing anaerobes) were able to use the NO_3^- instead of Fe^{3+} when a NO_3^- source was added to the culture. According to Ottow and Glathe (1971), the iron reducing obligate bacteria responsible for most of the reduction of Fe^{3+} in soils lack an enzyme (nitrate reductase) or lost it by mutation, so they are able to reduce iron only when NO_3^- is not present in the system.

These facts could explain the higher values of the Fe_o/Fe_d ratio for the Verdun soil, for 0.25- and 0.50-m with respect

to the same depths of the Brimstone soil in Fig. 3.1. The ratio Fe_o/Fe_d is an index of the relative degree of aging or crystallinity of free iron oxides (Blume and Schwertmann, 1969). A high Fe_o/Fe_d ratio (> 0.5), indicates the formation of highly disordered Fe oxides (ferrihydrite) as compared to other Fe oxides (goethite or lepidocrocite) with better crystallinity in hydromorphic soils. The short range order Fe oxides are formed by quick oxidation of waters in the presence of substances which impede nucleation and growth (organics, silicates or phosphates) according to Schwertmann (1985). The higher Fe_o/Fe_d ratio is probably also indicating a higher activity of Fe reducing bacteria in the Verdun soil at 0.25- and 0.50-m depth because of the very low contents of NO_3 and higher RD_T.

The same may also occur at the 0.25-m depth in the Brimstone soil where NO_3^- concentration is lower than at the other depths and RD_T is the highest. When any of these two soils becomes unsaturated, a rapid oxidation of Fe^{2+} to Fe^{3+} occurs with the formation of short range order Fe oxihydroxides in the presence of organics in the Ap and Eg horizons of both soils.

Soil Spatial Variability and OXC

One of the problems in the application of the concept of OXC to soils is that in the sequential reduction of O_2, NO_3^-, Mn^{4+}, Fe^{3+} and SO_4^{2-} in a saturated soil, usually one component
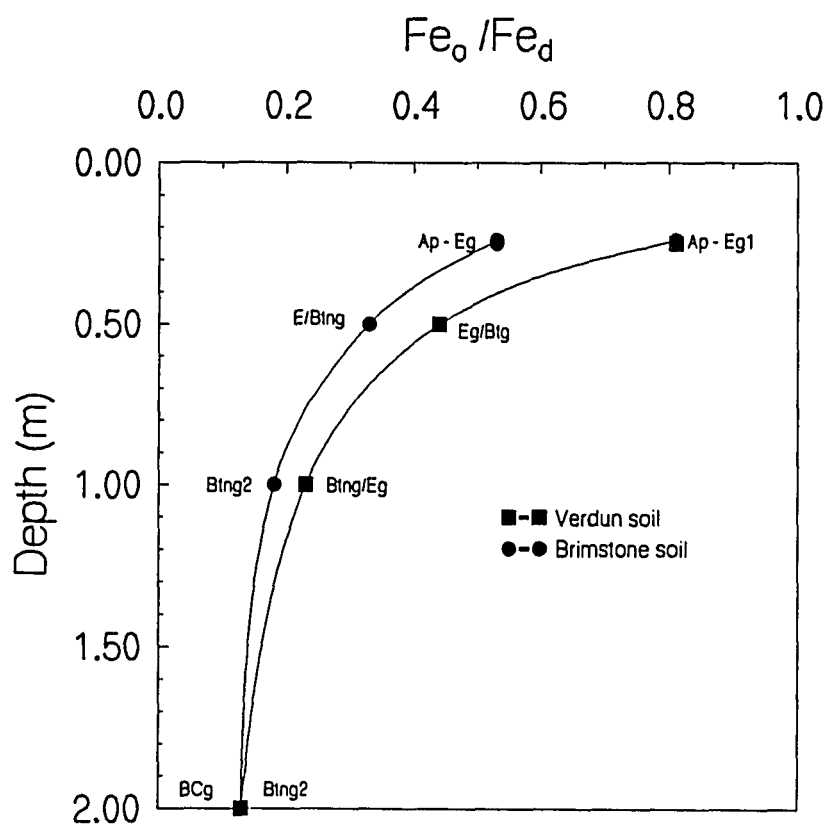
Fig. 3.1. Fe_o/Fe_d ratio as function of soil depth.

is not completely reduced before the next in the sequence begins to be reduced (Patrick and Mahapatra, 1968). Nitrate reduction starts before complete removal of O_2 (Pilot and Patrick, 1972) while manganese reduction starts before all nitrate has disappeared (Turner and Patrick, 1968 and Gotoh and Patrick, 1972). However, Fe^{3+} reduction will not take place before O_2 is completely removed. This is the reason why the detection of Fe^{2+} by staining tests or by the Eh measurement in the range of iron reduction has been considered the most reliable method so far to determine anaerobiosis in soils (Bouma, 1991).

The overlapping of reactions are due to spatial variability expressed as soil microsite diffrences which are a source of noise in attempts to obtain in situ measurements (Daniels and Buol, 1992). According to Stolzy and Flühler (1978) anaerobic microsites in well aerated soils are much more frequent in space and time than one would expect as documented by Currie (1961), Greenwood (1961) and Greenwood and Goodman (1967).

Analytical Data Limitations

Another limitation of OXC as a method to characterize the redox status of soils is the analytical data required to calculate it. Scott and Morgan (1990) arrived at the same conclusion when they calculated OXC for a ground water system from existing field data.

In our case, we assumed that the DOC has an average oxidation state of zero and that four electrons are transferred upon oxidation. According to Stumm and Morgan (1981), the average oxidation state can be calculated for OC if chemical oxygen demand (COD) and total organic carbon (TOC) are determined. The nominal oxidation state of OC ranges from -IV methane to III in formic acid. The use of DOC instead of TOC may underestimate the RDC because DOC is obtained by filtration of the water sample through 0.45 μm milipore filter and therefore it is not equivalent to TOC. However, filtration not only separates dissolved and suspended organic C, but also isolates DOC from suspended clay minerals in the sample (Aiken, 1985), that otherwise may induce analytical errors.

The measurement of low concentrations of O_2 is another analytical limitation of OXC. We adopted the colorimetric version of the method of White et al. (1990) instead of the spectrometric method because we considered the possibility of using a simple field method that may complement the DO probe method in the range of low DO contents. Since Rhodazine-D is highly reactive with atmospheric O_2, sampling is the crucial factor in obtaining accurate measurements with this technique. The use of pressure for taking water samples, as we did with a syringe sampling device, may be subject to errors due to oxygen dissolution during sampling and application of the test solution. Litaor (1988), reviewed these kind of errors with

respect to sampling of redox species from soil solution samplers. These samplers are analogous to our piezometers when the soil is saturated. This remark is also extended to the sampling of Fe^{2+}. Following the general rate law for Fe^{2+} oxidation (Pankow and Morgan, 1981) with the concentration of DO measured in the field the oxidation of Fe^{2+} to Fe^{3+} close to neutral pH is a matter of seconds. Fe^{2+} concentrations in Table 3.3 were considered as qualitative for this reason. A sampling device that breaks the capillary tip of the ampoule under the ground water level such as the one designed by White et al. (1990) is advisable to avoid the interference of atmospheric O_2. Otherwise, for O_2 and Fe^{2+} determinations, the water samples must be purged with N_2 and acidified to avoid oxidation (Ransom and Smeck, 1987).

The determination of the amount of reducible iron and manganese oxides poses another problem in the calculation of OXC. The total amount of iron oxides is fairly well estimated by the CBD extraction of iron (Blume and Schwertmann, 1969). However, not all iron oxides have the same solubility under reducing conditions. Gotoh and Patrick (1974) concluded from their experiments that the redox pair Fe^{2+} - $Fe(OH)_3$ governed the solubility of Fe under reducing conditions. A positive high correlation was found between the rate of bacterial reduction (the rate of iron oxide dissolution) and the oxalate solubility of Fe (Fischer and Pfanneberg, 1983). The Fe_o dissolves poorly crystallized oxides predominately

ferrihydrite, while goethite, hematite and well ordered lepidocrocite are not solubilized by the oxalate extraction (Schwertmann and Taylor, 1989). For our study, the total concentration of reactive iron oxides was considered to be the Fe_o fraction in Table 3.3.

The mean surface area of ferrihydrite was estimated as 350 m^2g^{-1} from measurements made by Eggelton and Fitzpatrick (1988). The mole number of surface sites per unit area was calculated from the surface structure of hematite (Breeuwsma, 1973). According to Schwertmann and Taylor (1989), ferrihydrite resembles hematite structurally. The difference between the two oxides is that one half of the Fe positions in ferrihydrite are vacant and replaced by O_2 and H_2O (Eggelton and Fitzpatrick, 1988). We estimated the average moles of surface sites per unit area for ferrihydrite as half of hematite (3.7 μmol m^{-2}). To be consistent with the half reaction for iron reduction listed in Table 3.1, the molecular formula $Fe_4(OH)_{12}$ was selected. It is one of the two possible formulas suggested by Eggelton and Fitzpatrick (1988) for ferrihydrite.

In the case of Mn oxides, a good estimation of their content is the amount extracted by the CBD method (Blume and Schwertmann, 1969). Jarvis (1984), investigated diverse extractants and found that the CBD extraction was well correlated with reducible Mn, while oxalate extractions overestimated this amount by dissolving a variety of primary

and secondary soil minerals containing Mn besides Mn oxides. The amount of reactive Mn oxides was calculated from Mn_d in Table 3.3. The most common Mn oxides in soils are birnessite and vernadite (McKenzie, 1989). Vernadite has a relatively large surface area. Loganathan and Burau (1973) reported a surface area of 350 m^2g^{-1} for vernadite, and Norvell (1988) reported a range of 50 to 300 m^2g^{-1} for Mn oxides of the birnessite group. Vernadite (δ-MnO_2) was chosen to maintain consistency with the half reaction for Mn reduction listed in Table 3.1. The mole number of surface sites per unit area were estimated from surface charge at pH 7 from Gilkes and McKenzie (1988) as 17 μmol m^{-2}.

Aerobic Capacity

A simpler way to estimate if a soil will be oxic or anoxic is by computing the difference between o-OXC (eq. 4) and m-RDC (eq. 7). This difference is defined as the "aerobic capacity" (AC) of the system:

$$AC = (o\text{-}OXC) - (m\text{-}RD) \qquad (10)$$

If AC is positive, the soil will be oxic; if AC is zero or negative the soil will be anoxic as defined in Table 3.2. When the AC is negative, it can have large negative values or small negative values. Large negative AC values indicate that the RDC is very large and reduction of other species in the redox sequence is expected. The large negative AC values are a result of DOC concentrations. Daniels and Buol (1992)

estimated from various sources that a DOC concentration of 10 mg L^{-1} (RDC = 3300 μmol_c kg^{-1}) or more provides enough energy for reduction of nitrate, manganese and iron in soils. On the other hand, DOC concentrations lower than 4 mg L^{-1} (RDC = 1300 $\mu mol_c kg^{-1}$) prevented reduction in saturated systems (Obenhuber and Lowrance, 1991).

The AC further explains in Fig. 3.2 what we already discussed about OXC. It demonstrates that the surficial horizons (Ap and Eg in the soils studied with episaturation) are anaerobic - postoxic with large negative AC. The subhorizons are slightly anaerobic (postoxic - oxic limit) with smaller negative AC (close to zero) than the surficial horizons (Table 3.4). The AC follows also the reduction pattern of the soil. Large negative AC values (Fig. 3.2) in the surface horizons (Ap and E) correspond well with the Eh (reduction) measurements in Fig. 3.3.

Small negative AC values in the subhorizons (Fig. 3.2) correspond to redox potentials in the moderately reduced range presented in Fig. 3.3 for the same depth.

Oxic - Anoxic Limit Determination

The colorimetric version of the Rhodazine-D method that we used can measure DO concentrations close to 1 μmol kg^{-1}. This limit (1 μmol kg^{-1}) between oxic and anoxic sedimentary environments proposed by Berner (1981) seems to be acceptable for soil systems regarding the limited accuracy of the methods

AC (μmol_c kg^{-1})

-2.5   -2.0   -1.5   -1.0   -0.5   0.0   x 10^3

Ap - Eg1   Ap - Eg

E/Btng   Eg/Btg

Btng2   Btng/Eg

■ Verdun soil
□ Brimstone soil

BCg   Btng2
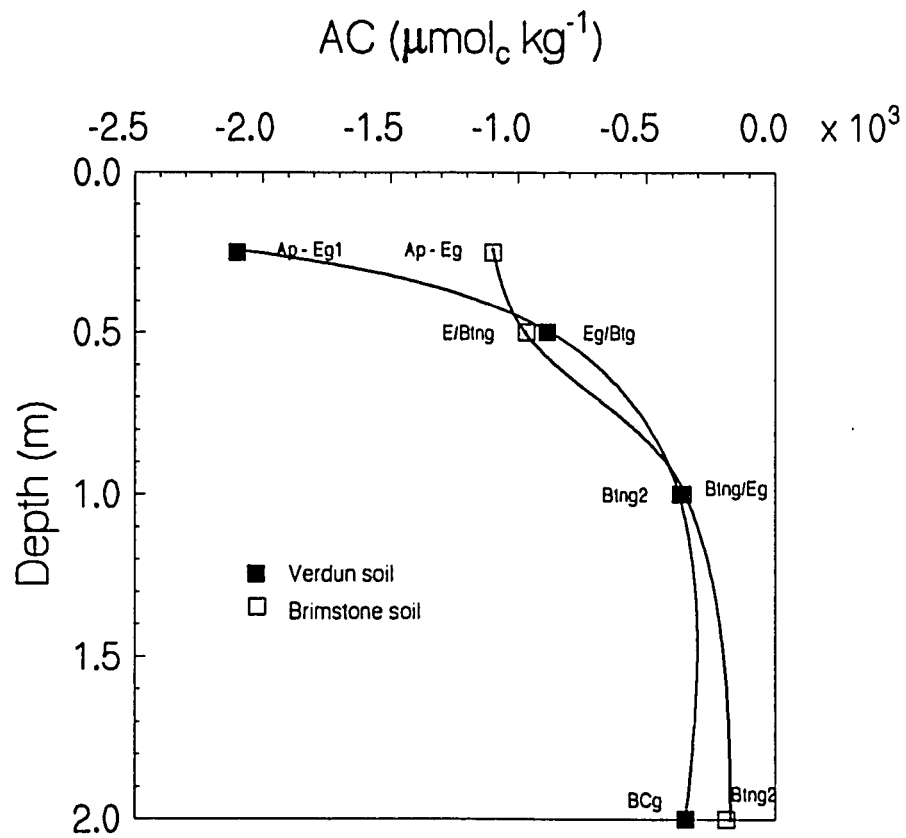
Depth (m)

Fig. 3.2.   Depth function for soil aerobic capacity [AC=(o-OXC)-(m-RD)]
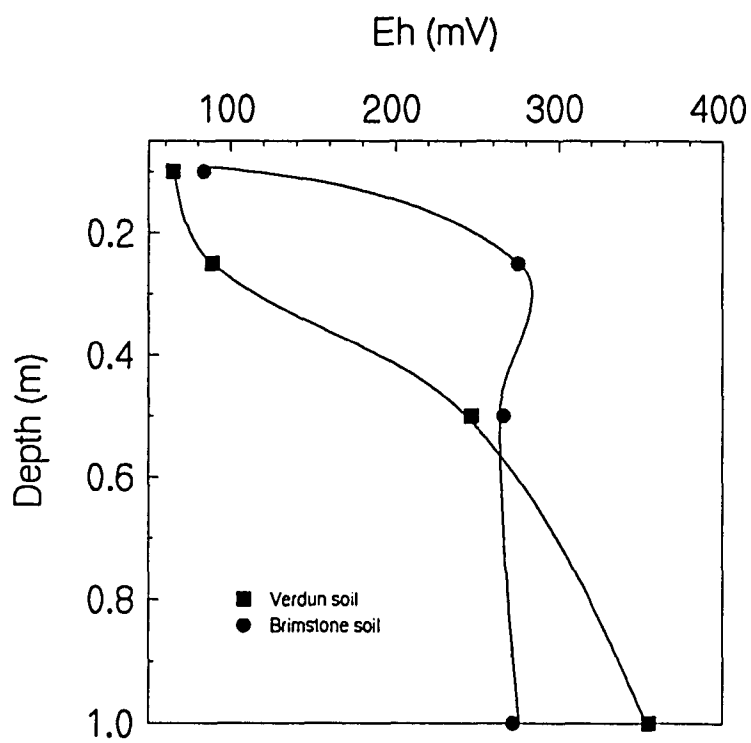
Fig. 3.3. Soil redox potentials as a function of depth.

used for the measurement of DO in the field. Greenwood (1961) reported that aerobic respiration was not inhibited unless the DO concentration was < 1 μmol kg^{-1} and that anaerobic metabolism of organic materials started at a DO concentration below 3 μmol kg^{-1} in widely different soils. Scott and Evans (1955) reported a limit of 5 μm kg^{-1} after which O_2 concentration fell rapidly to zero and Eh dropped to the reduced range. Daniels et al. (1973) found that once the DO concentration measured with an oxygen probe was < 6 μmol kg^{-1} (0.2 ppm) the Eh decreased rapidly in the ground water of some North Carolina Aquults and Udults and interpreted these results as Fe reducing conditions. Similar trends between DO and Eh were found in Louisiana for soils in the bottomland hardwood wetland-nonwetland transition zones in the lower Mississippi River valley by Faulkner and Patrick (1992). They delimited the oxic from anoxic environments when the O_2 content was < 5 %, which is very close to 1 μmol kg^{-1}. We can conclude that the limit ([O_2] < 1μmol kg^{-1}) given by Greenwood (1961) for soils and Berner (1981) for sediments is reasonable to separate aerobic and anaerobic environments. According to Callebaut et al. (1982), there is little or no diffusion of O_2 at this concentration. This limit is used to confirm the predictions made by the OXC and AC.

3.5. CONCLUSIONS

The estimation of OXC is an useful method to predict the redox status in soils. Conceptually, OXC is a balance between the equivalent sum of all oxidants and reductants and; therefore, a conservative property of the soil system. The advantage of estimating OXC in soils is that it can be defined whether the system is in equilibrium or not.

The disadvantages of OXC as a predictive tool are: i) the need of comprehensive analytical data to compute it, ii) the uncertainty of the number of electrons transferred in every step of the redox sequence, iii) soil spatial variability, such as the occurrence of reduction in microsites.

From the study of the OXC for the Verdun and Brimstone soils, we can conclude that soils with episaturation are reduced in the topsoil (OXC is low) when saturated, and moderately reduced to oxidized in the underlying horizons. However, at the class level all soil depths were anoxic-postoxic with no distinction between topsoil and subsurface soil layers. The prediction of anaerobiosis depends very much on the dominant redox species and its inherent ease of reduction as demonstrated by the OXC of the Verdun soil dominated by SO_4^{2-} and the OXC of the Brimstone soil dominated by NO_3^- except in the Ap horizon. This different dominance of redox species influences the field Eh measurements because nitrates are reduced first and at higher potentials than sulfates.

The decrease of RD_T as a function of depth also helped to explain the decrease in the Fe_o/Fe_d ratio due to a decrease in OC with depth. The reduction of iron only occurs extensively when the topsoil is saturated. Fe^{2+} diffuses to underlaying horizons and oxidizes to form better crystallized oxyhydroxides (goethite) in the absence of crystallization inhibitors (organics and silicates).

An alternative, simpler method to predict soil anaerobiosis was derived from the OXC. The aerobic capacity (AC) is used only to predict oxic and anoxic conditions by computing the difference between the oxidative capacity of oxygen and the reductive capacity of OC. If the difference is positive or zero, the environment is predicted oxic. This estimation must be confirmed by DO measurements in the field to test the prediction of soil anaerobiosis ($[O_2] < 1 \; \mu$mol kg^{-1}).

CHAPTER 4.

SOIL SALINITY AND SODICITY RELATIONSHIP WITH
AQUIC CONDITIONS

4.1. INTRODUCTION

Soils with natric horizons occur in the Coastal Plain of Louisiana. They are represented by the Deerford-Verdun Series (fine-silty, mixed, thermic Glossic Natraqualfs) in Livingston Parish (McDaniel, 1991) and the Brimstone Series (fine-silty, mixed, thermic Typic Natraqualfs) in Calcasieu Parish (Roy and Midkiff, 1988), which have also been correlated and mapped across other Parishes in the Coastal Plain (Amacher et al., 1988). A natric horizon is defined by its exchangeable sodium percentage or ESP. It requires an increase in clay as an argillic horizon and a ESP of $\geq$ 15 % or sodium absorption ratio (SAR) of $\geq$ 13 in some subhorizon within a depth of 40 cm of the upper boundary of the argillic horizon (Soil Survey Staff, 1990). High ESP in soils affect some soil properties such as fertility, soil water availability for plants, permeability and workability. Verdun and Brimstone soils have low fertility, limited effective rooting depth, limited soil water availability and very slow permeability, and therefore they are poorly suited for most crops, recreational and urban development (Hudnall et al., 1990).

High ESP is a major factor affecting important soil properties. Several studies by Pettry et al. (1981), Fleming (1984), Goh (1984) and Walthall et al. (1992) were performed to determine the source of exchangeable Na in loess-derived

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soils in the Lower Mississippi Valley that are far from the Gulf Coast. The hypothesis that the exchangeable Na was the product of weathering of Na-rich minerals in the loess was proposed by all these authors except Walthall et al. (1992). This hypothesis was probably based on an earlier study by Wilding et al. (1963) in loessic soils of Illinois.

Walthall et al. (1992), have demonstrated that the source of Na in soils with natric horizons in the Macon Ridge in Louisiana is the ground water and not the dissolution of Na-rich minerals in the loess. They found that the variation of the thickness of the loess mantle overlying a sandy alluvium controls the upward movement of dissolved NaCl. The upward movement of NaCl is due to the discharge from a regional Tertiary aquifer containing saline water to the locally connected alluvium aquifer that underlies the loess mantle. This regional hydrologic system occupies much of the area beneath the Mississippi River floodplain (Payne, 1968). In their study, Walthall et al. (1992) also found that soils in swale positions had a thinner loess mantle than soils in ridge positions, natric horizons and aquic conditions (Natraqualfs). These results, interpreted according to the recharge and discharge hydrologic systems for aquic conditions described by Richardson et al. (1992), would indicate that Natraqualfs in the Macon Ridge are an example of a discharge wetland soils with addition of NaCl to the soil system by the ground water.

Other soils that have appreciable ESP but do not fulfill the requirements of a natric horizon were investigated by McQuaid et al. (1987). They proposed a modification in the classification of those soils that had a deeper occurrence of exchangeable Na in their profiles by defining a solodic subgroup. The criteria proposed to recognize solodic subgroups are: i) an ESP $\geq$ 15 (SAR $\geq$ 13) in some subhorizon within 1.25 m below the soil surface or ii) an ESP $\geq$ 6 (SAR $\geq$ 5) and < 15 (SAR < 13) within the upper 40 cm of the argillic horizon.

Fanning and Fanning (1989) cited Gedroiz (1927) to illustrate the solodic process as the continued leaching of the upper part of a sodic soil (solonetz), the soil becomes more acid with the development of A and E horizons, with a natric horizon moving deeper into the soil by elluviation-illuviation. Most Natraqualfs and associated soils in Louisiana have this morphology. According to Szabolcs (1989) this is the typical development of a solodized - solonetz when the ground water is rarely or not at all linked with the upper soil layers, however secondary salinization may occur by upward movement of saline ground water.

A possible source of Na is salt water intrusion into the soil parent materials. Deerford - Verdun and Brimstone soils were formed on deposits of the Prairie Formation or Terrace. It is an extensive regional coast-trending terrace that extends across Louisiana (Snead and McCulloh, 1984). The

origin of the sediment is fluviatile to deltaic of late-Pleistocene age. The sediment is blanketed by loess of variable thickness. Most radiocarbon dates on the Prairie Formation are older than 40,000 years, possibly falling within a high sea level episode of the Wisconsin and Illinoian glacial stages (Miller et al., 1986). In my opinion, salt water intrusion probably occurred locally in those areas where fluvial and coastal environment merged. Following the deposition of the Prairie Formation, the sea level dropped and the local major streams widened and deepened their channels 22,000 to 9,000 years ago (Miller et al., 1986; Autin, 1989). The glacial maximum occurred about 18,000 years ago with a drop of 120 to 130 m of the sea level below that of the present (Suter et al., 1987). As a consequence of these climatic and base level changes, drier conditions during glaciation set the environment for development of salt affected soils (solonization). During the Holocene in a humid climate documented by studies in Louisiana on changes of the sea level by Coleman and Smith (1964) and Curray (1965), salt affected soils were leached out (solodization) and evolved into the actual Natraqualfs and associated soils in the Coastal Plain.

The potential source of salt spray from the Gulf Coast is not taken into account in this study as an actual source of salinization. The reasons for this are: i) our study sites are located 40 and 60 miles from the coast line in Calcasieu

and Livingston Parish respectively. ii) The annual precipitation-weighted mean Cl ion concentrations for 1991 are 0.48 and 0.50 mg L^{-1}, while Na ion concentrations are 0.27 and 0.19 mg L^{-1} for New Iberia and Franklinton respectively, the two closest localities to our sites with records of atmospheric deposition (S. Feagley, pers comm.). These values are similar to those reported for the Macon Ridge by Walthall et al. (1992).

The objective of this study is to investigate the relationship between the variation of the ground water composition and the occurrence of saline and sodic soils as a consequence of the aquic conditions and the direction of water flow. We make use of the hypothesis of Walthall et al. (1992) that the source of sodium is the ground water and that the geochemistry of the wetland soils is a function of water movement through them according to the hydrological models of Richardson et al. (1992).

4.2. MATERIALS AND METHODS

Soils

The investigation was based on two soils series: Verdun silt loam (fine-silty, mixed, thermic Glossic Natraqualfs) and Brimstone silt loam (fine-silty, mixed, thermic Typic Natraqualfs) described by Hudnall et al. (1990). Both soils are part of an extensive network of monitoring sites constructed to investigate aquic conditions in the Coastal

Plain of Louisiana and to the list of hydric soils of the United States (National Technical Committee on Hydric Soils, 1992).

The Verdun soil is identified in this list as Deerford Series because these two series are associated in a complex mapping unit. They were formed in silty deposits of Pleistocene age. These soils are level, somewhat poorly drained, occupying broad flats on the terrace uplands in intermediate positions of the landscape.

The profile that was described for this study is morphologically similar to Brimstone Series, however it does not have a natric horizon. It was classified as fine-silty, siliceous, thermic Typic Ochraqualfs (Hudnall et al. 1990). Brimstone soils are poorly drained, slowly permeable soils that formed in loamy sediments of Pleistocene age. They are on nearly level to slightly depressional, broad flats on stream or marine terraces, with intermediate positions in the landscape.

Sampling of the Groundwater

Ground water samples were sampled from nested piezometers at 0.25, 0.50, 0.68 or 0.78, 1.00 and 2.00 m depth at least once a month from March 1991 to March 1992.

Analysis of Water

The pH of the water was measured in the field with a combination electrode. Electrical conductivity was measured in the laboratory at 25 °C. Concentrations of Na, Mg, Ca and K were measured by inductively coupled plasma (ICP). Total alkalinity was measured titrimetrically (CHemetrics, VA, alkalinity field kit). Concentrations of Cl were measured with a Cl selective electrode. The SO_4 concentrations were estimated by multiplying S measurements by ICP by an empiric conversion factor, and NO_3 was measured with an autoanalyser (Wescan Instruments Inc., Santa barbara, CA) for the Verdun soil water samples. Concentrations of Cl, SO_4, and NO_3 were determined by ion chromatography (IC) for the Brimstone soil ground water samples.

The overall reliability of the analyses was tested by charge balance calculations, following procedures in Bresler et al. (1982).

Analysis of Soils

Particle size analysis was determined by the pipette method. SAR was calculated from analysis of saturated paste solution extract (Ca, Mg and Na measured by ICP) as $SAR=Na/[(Ca+Mg/2)]^{0.5}$. ESP was calculated by subtracting water soluble Na from extractable Na (extracted by displacement with 1N ammonium acetate) divided by the soil CEC (pH 7).

4.3. RESULTS AND DISCUSSION

Ground Water Chemistry

The ground water composition expressed on percentage of its major constituents is shown in Fig. 4.1 for Verdun soil and Fig. 4.2 for Brimstone soil. In both ground waters the dominant cation is Na and the dominant anion is Cl. The percentage of Na with respect to Ca and Mg increases with depth as well as Cl with respect to the other anions for both soils. Potassium was not taken into account because of its low concentration (Tables 4.1 and 4.2). The percentage composition is a common way to express water quality (Fetter, 1988). However, this is a relative measurement that indicates that the ground waters are dominated in Na and Cl.

The ionic composition of the two ground waters are found in Table 4.1 for the Brimstone site and Table 4.2 for the Verdun site expressed the mean ionic constituent, EC and pH. In the same tables an indication of the variability of the water composition is illustrated by the coefficient of variation (CV) for each component. With the exception of pH, the components have large coefficients of variation (CV > 20 %). Some components, such as K and NO_3, have very skewed distributions with values of zero or close to zero, which explains their CV > 100 %. According to Pettijohn (1982), large variations in water quality can be expected in shallow and surficial aquifers due to chemical changes brought about by natural events occurring on the soil surface (e.g.,

wetting-drying cycles, development of cracks, etc.) or from man induced pollution (e.g., use of fertilizers).

The mean concentrations of every major constituent are different between the two groundwaters. When comparing values of tables 4.1 and 4.2, the mean concentration of Cl, SO4, Ca, Mg and Na are significantly different (P > 0.01) at any depth with the exception of pH and at 0.25 m depth where EC, NO_3 and Cl are the only ones significantly different.

The difference between the ionic concentrations of both soils is also expressed through their different EC. Since the EC has positive correlation with total dissolved solids (TDS) it is used as a simplified index to the total concentration of dissolved salts through the approximate relationship (Bresler et al., 1982): TDS (mgL^{-1}) $\approx$ 640 * $EC(dSm^{-1})$. Ground water from Verdun soil has a higher content of dissolved salts at any depth than Brimstone soil according to the EC (Table 4.1). The estimation of TDS indicates that Verdun soil water is brackish (1,000 to 10,000 mgL^{-1}) while Brimstone soil water is fresh to slightly brackish (< 1,000 mgL^{-1}) according to the classification of water based on TDS given by Fetter (1988).

Total alkalinity concentrations are similar in both ground waters. They are in the range of concentrations (10^{-3} to 10^{-2} mol_cL^{-1}) given by van Beek and van Breemen (1973) at pH 7 for a poorly aerated subsoil.

a)

Cations (%)

b)
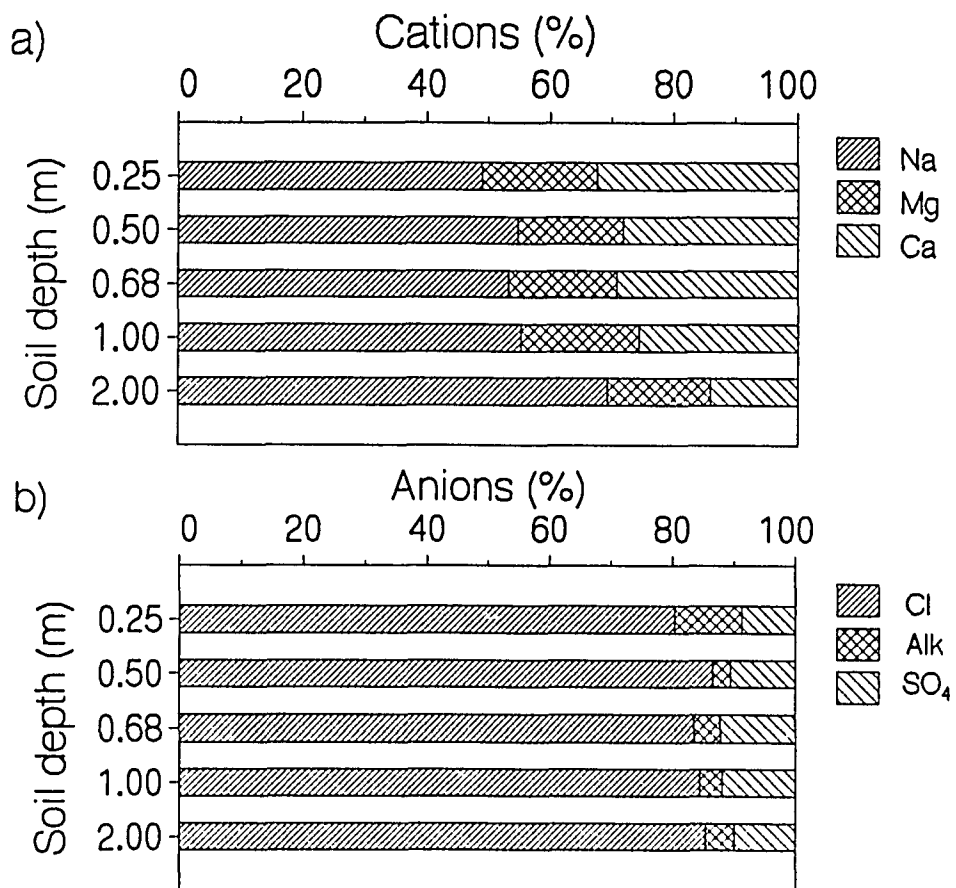
Anions (%)

Fig. 4.1. Ground water compositions for Verdun soil.
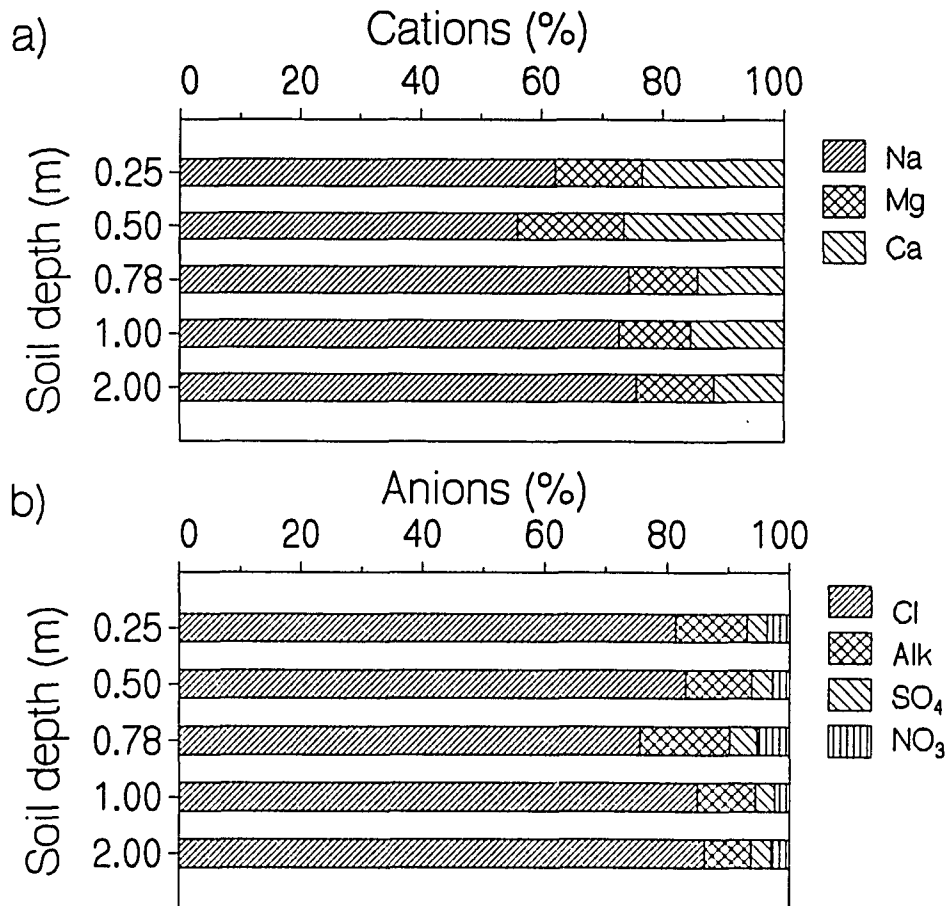
Fig. 4.2. Ground water compositions for Brimstone soil.

Table 4.1. Mean ionic composition, electrical conductivity (EC), pH and coefficient of variation (CV) between parenthesis of the groundwater at the Verdun soil site.

Depth (m)		0.25	0.50	0.68	1.00	2.00
Ca^{2+}	mg/L	91	247	217	225	83
CV	%	(45)	(32)	(40)	(32)	(59)
Mg^{2+}	mg/L	31	90	79	101	60
CV	%	(44)	(37)	(43)	(35)	(60)
Na^+	mg/L	155	544	450	516	440
CV	%	(65)	(21)	(47)	(47)	(49)
K^+	mg/L	1.9	7.0	3.5	9.4	3.1
CV	%	(240)	(264)	(283)	(143)	(274)
Cl^-	mg/L	461	1344	1105	1332	848
CV	%	(73)	(28)	(49)	(31)	(42)
SO_4^{2-}	mg/L	58	219	219	251	132
CV	%	(35)	(45)	(25)	(37)	(39)
NO_3^{-}[*]	mg/L	0.1	0.1	0.1	0.1	0.1
CV	%	(96)	(129)	(98)	(182)	(148)
Alk[**]	mg/L	63	65	54	75	49
CV	%	(34)	(45)	(31)	(32)	(39)
EC	dS/m	2.3	3.9	4.0	4.5	2.9
CV	%	(34)	(32)	(44)	(21)	(25)
pH		7.1	6.9	6.9	6.8	6.9
CV	%	(3)	(3)	(3)	(4)	(4)

(*) NO_3 expressed as $N-NO_3$
(**) Alk is total alkalinity

Table 4.2. Mean ionic composition, electrical conductivity
(EC), pH and coefficient of variation (CV) between
parenthesis of the ground water at the Brimstone soil
site.

Depth (m)		0.25	0.50	0.78	1.00	2.00
Ca^{2+}	mg/L	76	66	30	59	48
CV	%	(54)	(53)	(54)	(46)	(52)
Mg^{2+}	mg/L	28	28	14	27	28
CV	%	(62)	(68)	(55)	(46)	(48)
Na^+	mg/L	116	107	77	140	153
CV	%	(68)	(68)	(50)	(60)	(45)
K^+	mg/L	3.5	1.2	0.4	1.2	5.9
CV	%	(136)	(134)	(142)	(116)	(339)
Cl^+	mg/L	341	304	168	341	318
CV	%	(68)	(61)	(42)	(59)	(61)
SO_4^{2-}	mg/L	8.7	7.7	6.7	10.1	8.2
CV	%	(60)	(95)	(53)	(59)	(80)
NO_3^{-*}	mg/L	4.8	3.9	4.5	4.5	4.4
CV	%	(18)	(34)	(7)	(12)	(4)
Alk^{**}	mg/L	63	65	54	75	49
CV	%	(43)	(53)	(25)	(19)	(44)
EC	dS/m	1.3	1.2	0.76	1.1	1.1
CV	%	(75)	(60)	(43)	(50)	(45)
pH		7.1	7.1	7.0	7.0	7.0
CV	%	(7)	(4)	(5)	(4)	(5)

(*) NO_3 expressed as $N-NO_3$
(**) Alk is total alkalinity

Large differences exist between concentrations of NO_3 of the two ground waters. The higher concentration of NO_3 (Table 4.1) for Brimstone soil is the result of the fertilization of this agricultural soil with N sources. These concentrations do not surpass the safety limit of 10 ppm NO_3-N (US Environmental Protection Agency, 1976) but they are high enough to render a poor water quality. The high concentration of this anion at any depth suggests that the ground water flows laterally from higher parts of the landscape. For the Verdun site we found very low concentrations of NO_3 because it is a forest land where N fertilizers probably were never applied. The small amounts of NO_3 may rapidly be uptaken by plants or dinitrified when the soil is in anaerobic conditions.

Soil and Parent Materials

The particle size distribution with depth for Verdun and Brimstone soils is shown in Fig. 4.3. These two soils developed in loess and are underlain by sandy braided stream deposits (Schumacher et al., 1988). Processes operative during and after loess deposition have resulted in a diffuse, gradational contact between the loess and the underlying unit called basal mixing zone (BMZ) according to Miller et al. (1986). The BMZ is mainly determined by changes in texture and color (Schumacher et al. 1988). The thickness of the BMZ is inversely related to loess thickness (Rehage, 1980).

Walthall et al. (1992) found that Natraqualfs affected by saline groundwater occurred in thin loess. The BMZ is observed in Fig. 4.3 for Verdun and Brimstone soils at the depth where a particle size change occurs. The particle size distribution indicates that the loess has almost the same thickness in both soils (about 2 m). However, the BMZ are different. The Verdun soil has a characteristic BMZ with an steady increase in sand below 2.15 m depth. The loess and the BMZ overlying the sandy alluvium serve as a confining barrier to the upward flow of saline ground water when the thickness of the loess is 3 to 4 m (Walthall et al., 1992).

For a thinner loess mantle, as in the case of the Verdun, salinization occurs by upward saturated flow. The Brimstone soil has an irregular BMZ because of the presence of maximum content of clay with an oven dry bulk density reported by Hudnall et al. (1990) of 1.96 kg m^{-3} at the top of the BMZ between 1.90 and 2.30 m depth and a deeper clay layer between 3.15 and 3.25 m depth. These dense impermeable layers may confine the ground water to the underlying deeper sandy aquifer and prevent its upward flow. The soil water must then be supplied by rainwater or lateral flow. Fig. 4.4 shows the depth functions of the SAR and ESP. The ESP and SAR for Verdun soil meets the natric horizons criteria. The same does not apply for Brimstone soil because it does not reach the values the minimum SAR or ESP to qualify as Natraqualf. However, its morphology indicates that this soil as well as
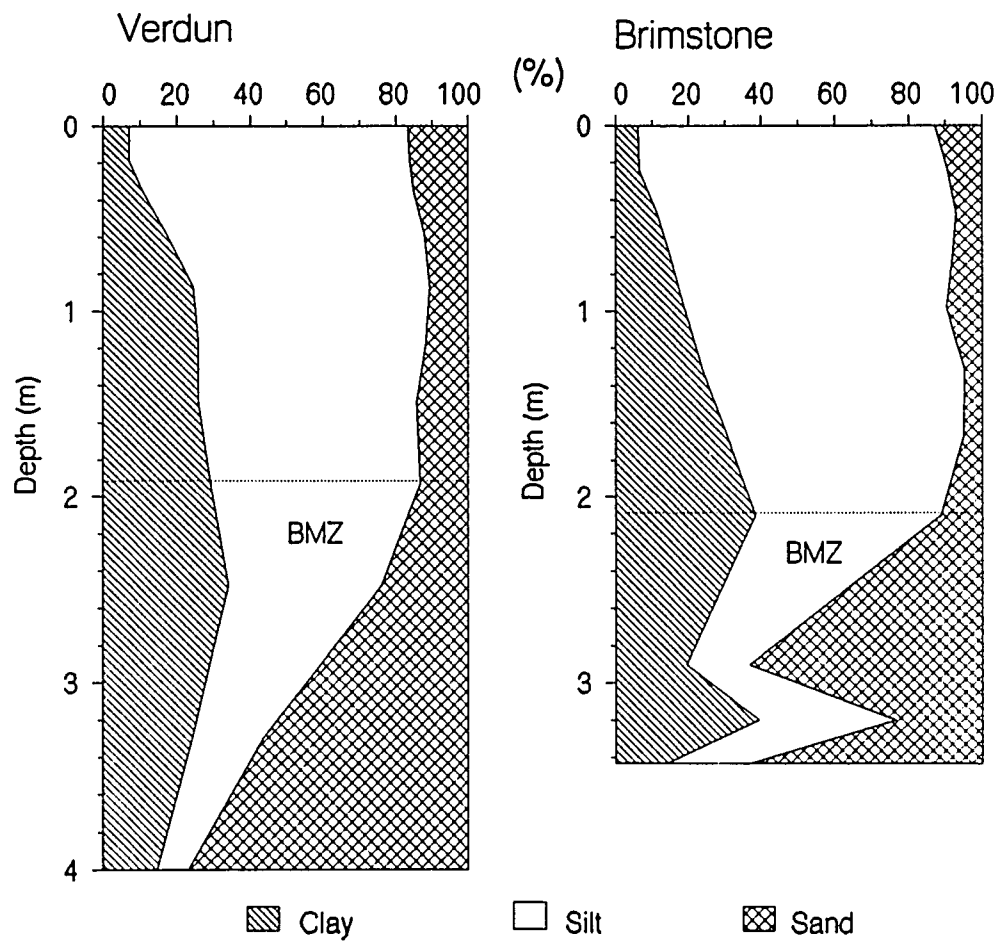
Fig. 4.3. Particle size distribution depth function for Verdun and Brimstone soil. BMZ indicates the basal mixing zone.
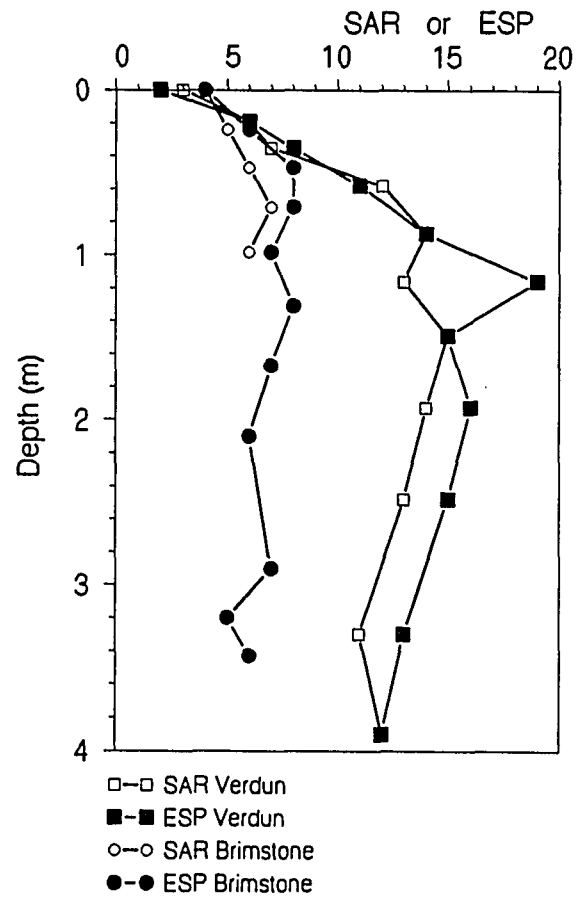
Fig. 4.4. SAR and ESP depth functions for Verdun and Brimstone soils.

the Verdun soil are or were under solodization processes. The Brimstone soil would be classified in the solodic subgroup as proposed by McQuaid et al. (1987).

Sources of Na

A strong relationship was found for Verdun soil between Cl and Na in the ground water (r^2 = 0.75, slope = 0.58, n = 45, P > 0.01). It indicates a limited removal of Cl due to the very poor drainage conditions of this soil. The correlation between Cl and Na in the ground water of Brimstone soil was much weaker than for Verdun (r^2 = 0.44, slope = 0.32, n = 50, P > 0.01). It indicates that additions of NaCl are not made by the ground water of Brimstone soil and probably Cl is being leached out. The trend between Na and Cl is shown in Fig. 4.5. Generally the lowest concentrations in Cl and Na comes from samples taken at 0.25 m depth and affected by the dilution effect of rain water. An even stronger relationship was found when Cl and Na+Mg in the ground water were correlated for the Verdun soil (r^2 = 0.89, slope = 0.88, n = 40, P > 0.01) while the same relationship is extremely weak for the Brimstone soil (r^2 = 0.12, slope = 0.61, n = 46, P < 0.01). The trend between Cl and Na+Mg is found in Fig. 4.6, with data plotted only for the Verdun soil. This significant correlation reinforces the hypothesis of the marine origin of the ground water.

Na and Cl had the same origin in the Brimstone soil but under continuous leaching by fresh water moved out of the profile. However, we have evidence that Na and Cl moved laterally over short distances. The EC, and concentrations of Na and Cl were consistently higher in water samples taken from one of the three 1.00-m depth piezometers placed of the plot in the Brimstone site than for the rest of the samples taken from other piezometers. The concentration were within the range observed for the ground water of Verdun soil. The causes of accumulation of salts at short distances is explained by: i) The pedoturbation produced by crawfish activity. The crawfish produces mixing of soil materials and preferential flow of water through freshly open burrows which induces large spatial variability and accumulation of salts in microsites. ii) The local low relief. According to Tóth (1963), under extended flat areas topographically driven groundwater movement is retarded, and the ground water system is not well defined with characteristic discharge and recharge areas. Under these circumstances groundwater is discharged by evapotranspiration. Discharge of this type results in waterlogged areas. Salts move to and accumulate in these areas which usually are depressions as a cosequence of the microrelief of the terrain as described by Richardson et al. (1992) for the mound-intermound system in soils of Coastal Plain of Texas. The horizontal mound-intermound distances can be short (15 m) and the difference in elevation as much as 0.5
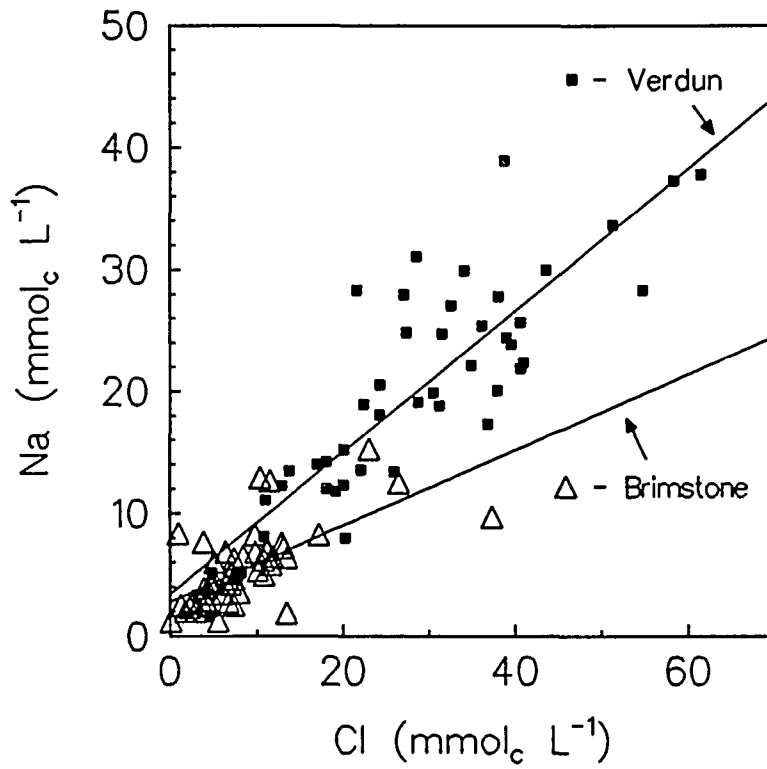
Fig. 4.5. Relationship between Na and Cl in the ground water of Verdun and Brimstone soils.
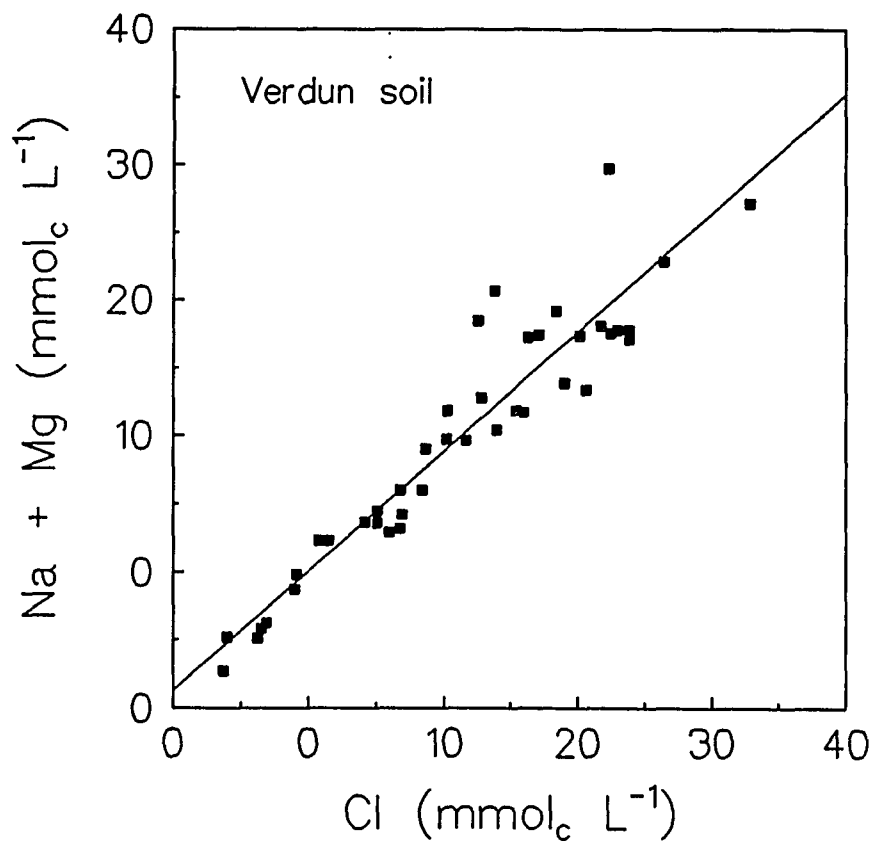
Fig. 4.6. Relationship between (Na + Mg) and Cl in the ground water of Verdun soil.

m (Carty et al., 1988). The Typic Ochraqualf that was sampled as the Brimstone Series in one side of the monitoring plot occupies microhigh areas of the landscape where recharge occurs. The true Brimstone Series is probably in the center of the monitoring plot which is also the center of a microdepression where we placed the piezometers that yielded samples with higher salt concentrations.

4.4. CONCLUSIONS

The Verdun soil has a well developed natric profile. Its morphology would indicate that leaching of Na was sometime a predominant process in the soil. However, presently the soil is undergoing secondary salinization. The discharging ground water is brackish, of probable marine origin as indicated by the strong relationship Cl - Na and Cl - Na+Mg. According to models of Richardson et al. (1992) we describe this case as a seasonal discharge wetland with addition of materials to the soil.

The particle size distribution of Brimstone soil suggests that the water flows very slowly laterally. The irregular BMZ with high oven dry bulk density influences the direction of the flow locally, by creating a perched water table. The origin of the water is not saline ground water but infiltrating rain water as demonstrated by the weak relationship between Cl and Na. According to the models of Richardson et al. (1992), the Brimstone site could be the case

of a seasonal flowthrough wetland. It receives water from the adjacent landscape with addition of NO_3, as well as it yields water to the ground water system. Na and Cl are leached out by this means and accumulated at short distances in microdepressions.

CHAPTER 5.

PROCESSES OF CLAY DIFFERENTIATION BETWEEN E AND B HORIZONS

5.1. INTRODUCTION

Natraqualfs in Louisiana are seasonally wet soils with a strong horizon differentiation. The E horizons are bleached, poorly structured, acid and have low clay content. They overlay blocky to prismatic, clay-rich, natric B horizons. These soils are reduced, seasonally saturated with a perched water table and have redoximorphic features in the profile. Consequently, they have aquic conditions as defined by the International Committee on Aquic Moisture regime or ICOMAQ and tested by Szögi and Hudnall (1992) for soils in Louisiana.

According to ICOMAQ (Bouma, 1991), the epiaquic conditions describe soils with perched water tables. In many classification systems other than the Soil Taxonomy (Soil Survey Staff, 1975), they are recognized as pseudogley or surficial gleys. Soils with epiaquic conditions have episaturation. This type of saturation is product of the impedance of saturated or unsaturated flow at the interface between a coarse-textured and a fine-textured one layer. Wilding and Rehage (1985) stated that there are many types of pedogenic, lithogenic or artificially induced layers capable of restricting the downward water flow. In Natraqualfs, the episaturation is caused by the presence of dense, textural natric horizons.

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The clay differentiation between the E and B horizons is not originated by a single process. Wilding and Rehage (1985) reviewed the different processes leading to textural differentiation between surface and subsoil horizons. They cite illuviation of clay into finer textured subsoils, sedimentary discontinuities, ferrolysis, in situ weathering of primary minerals and lithorelicts, neoformation of clay, and differential transport of eroded sediments as the contributing processes.

Natraqualfs are texturally differentiated by solodization. Gedroiz (1927) cited by Fanning and Fanning (1989), described this process as the continued leaching of the upper part of a sodic soil or Solonetz. The soil becomes more acid and A and E horizons develop while the natric horizon moves deeper into the soil by eluviation-illuviation. However, it seems that soils morphologically and chemically similar to the Solodized-solonetz may occur without ever having been through the stages of Solonchak and Solonetz (Hallsworth and Waring, 1964).

Szabolcs et al. (1980) concluded that solodization is a complex process of degradation of clay and accumulation of crystalline and amorphous silica in the E horizon as well as high concentrations of dissolved silica in the soil solution. Van Breemen and Brinkman (1978) explained the formation of many acid hydromorphic soils Aqualfs, Aquults and Albolls (including Natraqualfs or Solodic soils) by the process of

ferrolysis. Szabolcs (1989) recognized that ferrolysis is similar to certain processes occurring during the formation of solod soils.

Seasonally wet soils like the Natraqualfs undergo changes in redox conditions. Under these seasonal changes the process of ferrolysis may occur (Brinkman, 1970, 1977). This leads to clay decomposition or degradation in the E horizon. Brinkman et al. (1973) and Brinkman (1979) presented the different processes of desilication, cheluviation and ferrolysis that lead to the formation of bleached E horizons. They explained how to distinguish them by chemical, mineralogical and micromorphological methods. Ferrolysis, in particular, explains the acidification of the topsoil and the formation of eluvial horizons with a corresponding underlaying clay pan. In the wet season, the soil becomes reduced and yields Fe^{2+} with a corresponding pH increase. It displaces some of the exchangeable bases and aluminum. These bases and part of the aluminum are leached. The remaining aluminum becomes exchangeable, trapped in interlayers or is incorporated into the structure of pedogenic clays. In the dry season, the oxidation of exchangeable Fe^{2+} produces exchangeable hydrogen resulting in a lower pH. The H^+ may attack clay minerals and the system is neutralized by liberation of ions from the clay structure. The silica remaining from the clay structure may be leached during the next wet season or may accumulate in the

amorphous form. This process is very similar to hydrolysis by H_2CO_3.

Aurousseau (1990) tested through micromorphological and mineralogical analyses the origin of clay differentiation between E and B horizons under two alternative hypothesis: i) clay translocation from the E horizon to B horizon, and ii) clay degradation under three pathways. They were primary degradation, secondary degradation and ferrolysis. He stated that clay degradation occurs when we have both, low pH (< 5.0) and reducing conditions. Clay degradation is called primary if this process has been operating since the beginning of the pedogenesis. Clay degradation occurs secondary to clay translocation when acid conditions are due to progressive base desaturation in the E horizon and development of reducing conditions due to the incremental impermeabilization of the B horizon. The difference of ferrolysis from these other two mechanisms is that the soil is neutral to slightly basic under reducing conditions. When the soil is oxidized, iron hydrolysis induce the soil acidity.

The objective of this chapter is to investigate the processes of clay differentiation between E and B horizons under the condition that clay differentiation is not of lithogenic origin. The hypothesis to be tested are that E and B horizons have been differentiated by: i) translocation, ii) clay degradation, iii) a combination of both. To achieve our

objective we will use the characterization data (physical, chemical and mineralogical) of a Natraqualf in Louisiana.

5.2. MATERIALS AND METHODS

The Verdun silt loam (fine-silty, mixed, thermic Glossic Natraqualfs) was described and sampled by the Soil Conservation Service (SCS) in concert with Louisiana Agricultural Experiment Station (LAES). The characterization analyses were completed at the National Soil Survey Laboratory (NSSL), Lincoln, Nebraska following the methods described by Soil Survey Investigations Staff (1991). The complete profile description, chemical, physical and mineralogical analysis can be found in Appendix A.

Equivalent pore size distribution was calculated according to Bathke et al. (1991) from water retention characteristic curves that can be found Appendix A.

Total alkalinity was measured titrimetrically from ground water samples in the field (Chemetrics, VA, alkalinity field kit). Silicon concentration in the ground water was measured by inductively coupled plasma (ICP). The method of Bernas (1968) for the dissolution of the whole soil was followed and total analysis of the different elements was made by ICP.

X-ray diffractograms obtained from X-ray diffraction analysis (XRD) were furnished by the NSSL. A Phillips diffractometer with a copper tube (CuKα radiation) was used. The XRD's were obtained from oriented clay samples that were

saturated with Mg^{2+} (room temperature and glycerated) or saturated with K^+ and heated at 300° and 500° C.

Samples for transmission electron microscopy (TEM) were scrapped from fresh samples of the Ap and Btng1 horizons. The clay fraction was suspended and atomized onto carbon coated 400 mesh copper grids. Transmission electron micrographs were obtained by a Hitachi EM operated at 100 kV with an emission current of less than 20 Ma. Elemental composition of clay were obtained by energy dispersive X-ray analysis (EDAX).

5.3. RESULTS AND DISCUSSION

Lithological Discontinuities

Soils in the Coastal Plain of Louisiana may be formed on parent materials with different sedimentary facies. Lithological discontinuities are detected by changes in the vertical direction by examining the function depth of the clay-free particle size distribution and the distribution of weathering resistant minerals (Buol et al., 1989). Zircon is one of the most resistant minerals to weathering in soils (Marshall and Haseman, 1942). Changes in zircon content in the profile with an uniform clay-free particle size distribution provides information on losses or gains of materials by the different soil layers. A lithological discontinuity is probable to occur when the clay-free particle size distribution and zircon distribution change (Oertel and Blackburn, 1970).

Clay-free particle size distribution (%)
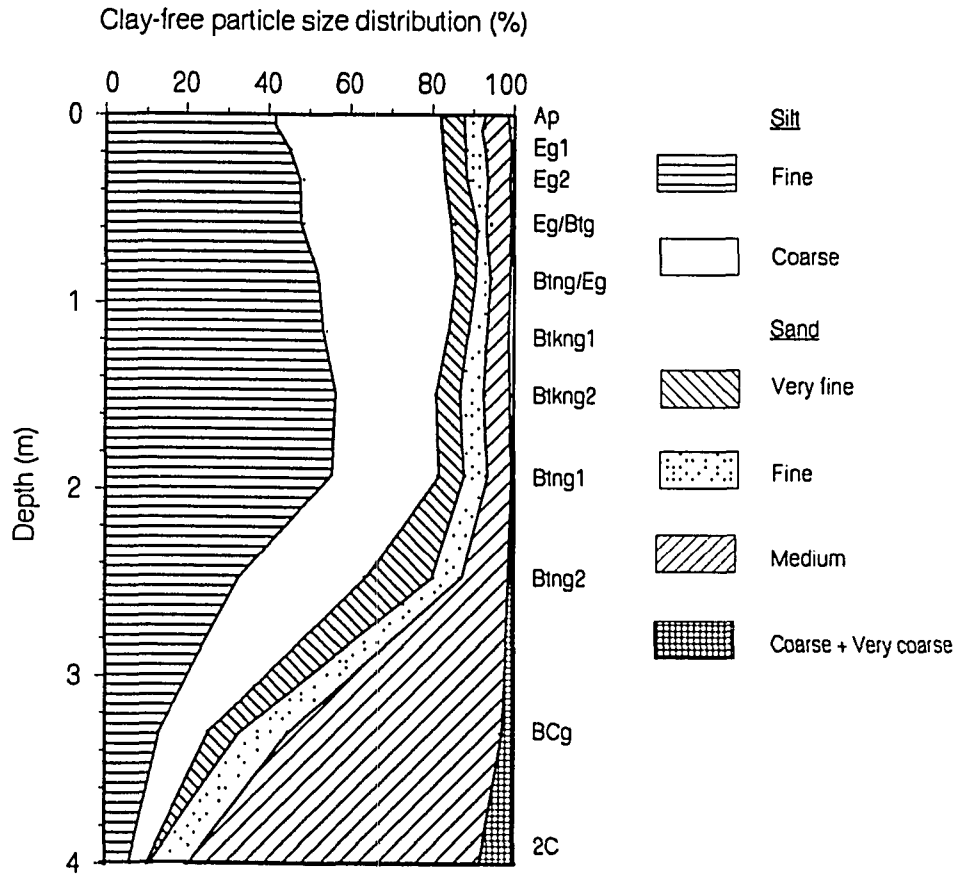
Fig. 5.1. Depth function of the clay-free particle size distribution for Verdun soil.
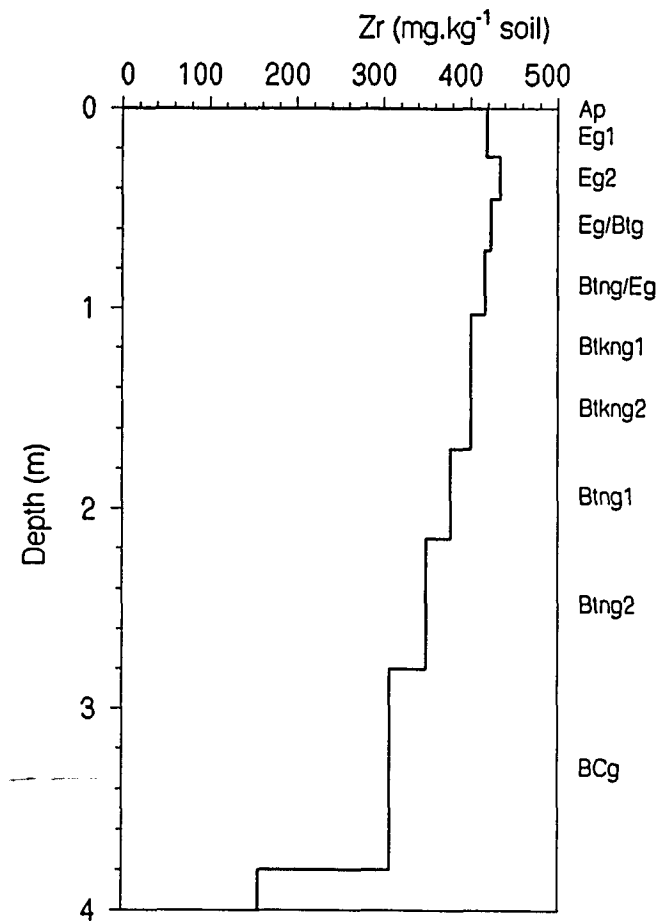
Fig. 5.2. Depth function of Zr distribution in Verdun soil.

Table 5.1. Selected analytical data for Verdun Soil (after Hudnall et al. 1990).

Soil	Horizon	Depth	pH	Clay content	Org.C	CEC	Exch. Na	Fe	Bulk dens.	COLE
		m		%	%	cmol/kg	%	%	kg/m^3	cm/cm
VERDUN	Ap	0.00-0.13	4.2	7.0	1.73	6.6	2	0.2	1.36	0.005
	Eg1	0.13-0.24	4.6	6.9	0.48	4.1	6	0.1	1.58	0.006
	Eg2	0.24-0.45	4.4	10.6	0.41	6.8	8	0.2	1.54	0.007
	Eg/Btg	0.45-0.71	4.7	17.2	0.21	10.6	12	0.5	1.61	0.006
	Btng/Eg	0.71-1.03	6.5	24.6	0.07	16.3	14	0.9	1.78	0.012
	Btkng1	1.03-1.28	7.6	25.8	0.04	15.3	19	1.0	1.85	0.010
	Btkng2	1.28-1.70	7.5	25.8	0.03	14.3	15	0.6	1.87	0.012
	Btng1	1.70-2.15	7.5	29.2	0.02	17.1	16	0.6	1.84	0.014
	Btng2	2.15-2.80	7.3	34.0	—	19.9	15	0.4		
	BCg	2.80-3.80	7.9	24.2	0.01	15.2	13	0.2		
	2C	3.80-4.00	7.6	14.6	0.02	9.6	12	0.1		

The Zr distribution determined chemically can be used instead of a mineralogical analysis assuming that Zr is present only in the mineral zircon (Barshad, 1964).

The depth function of the clay-free particle size distribution is presented in Fig. 5.1. The depth function for Zr is shown in Fig. 5.2. Both figures indicate an uniform distribution of sand and Zr between 0 and 2.15 m depth. Two lithological discontinuities exist below this depth. One between 2.15 and 3.80 m and the second between 3.80 and 4.00 m. The first discontinuity is not indicated as such in the soil horizonation (Table 5.1). The second discontinuity (2C) is similar to the basal mixing zone (BMZ) described by Schumacher et al. (1988) for loesses in Louisiana.

Evidence of Translocation and Degradation of Clay

According to Brinkman (1979), evidence for ferrolysis in a profile containing translocated clay is based on a combination of criteria resulting from a clay balance and the clay CEC depth function. Decomposition or interlayering mechanism, may be suggested by: i) a low CEC of the clay fractions in the upper horizons and ii) a higher CEC of the clay in the lower horizons that is constant or continually increasing with depth.

The Btng1 horizon (1.70 to 2.25 m depth) of Verdun soil was substituted to calculate a clay balance. It was replaced by a C' horizon. It had a clay content of 12% and an oven dry

bulk density of 1.45 kgm^{-3}. Results of the balance are presented in Table 5.2.

The balance was calculated for that part of the profile with uniform stratigraphy (Marshall and Haseman, 1942). The Zr analysis was used to calculate the index mineral (IM). The problem encountered before using the substitution was that there was not C horizon which could be used as the reference parent material because of the deep weathering of this profile. The loess parent material was defined by calculating the original clay content of the inexistent C' horizon by the method of Van Wambeke (1972). An homogeneous parent material and a closed profile was assumed. The weighted average clay content for the eluvial (Ap, Eg1, Eg2, Eg/Btg) was equal to 11.8%. That of the illuvial horizons (Btng/Eg, Btkng1, Btkng2, Btng1) was 26.6%. This gives an illuvial/eluvial clay ratio of 2.03. The computations by Van Wambeke's method yielded a clay content of 12% for the C'. This result is acceptable compared to the clay content in the C horizons (11 to 12 %) of a Memphis Soil (fine-silty, mixed, thermic Typic Hapludalf) described by Miller et al. (1986) where the loess is considered unweathered. However, the comparison is only valid with respect to the clay content and not for the loessic material per se. Verdun soil sand fraction contains much more fine, medium and coarse sand than the loess described in Prairie Terrace Formation by Miller et al. (1986). The parent material of Verdun soil is probably a loess locally

Table 5.2. Balance of total weight, clay and non-clay for Verdun Soil with a simulated C' horizon.

Horizon	Thick-ness	BD (*)	Present total weight	IM (**)	--Present--clay	non-clay	----Original----total	clay	non-clay	--Change--clay	non-clay	Net trans-loc.
	m	kg/m³	kg/m²		kg/m²			kg/m²				
Ap	0.13	1.36	0.18	1.20	0.013	0.167	0.216	0.016	0.200	-0.003	-0.033	-0.036
Eg1	0.11	1.58	0.17	1.24	0.012	0.158	0.211	0.015	0.196	-0.003	-0.038	-0.041
Eg2	0.21	1.54	0.32	1.22	0.034	0.286	0.390	0.041	0.349	-0.007	-0.063	-0.070
Eg/Btg	0.26	1.61	0.42	1.20	0.072	0.348	0.504	0.086	0.418	-0.014	-0.070	-0.084
Btng/Eg	0.32	1.78	0.57	1.15	0.140	0.430	0.655	0.161	0.494	-0.021	-0.064	-0.085
Btkng1	0.25	1.85	0.46	1.15	0.119	0.341	0.529	0.137	0.392	-0.018	-0.049	-0.067
Btkng2	0.42	1.87	0.79	1.08	0.204	0.586	0.853	0.220	0.633	-0.016	-0.047	-0.063
C'	0.45	1.45	0.65	1.00	0.078	0.572	0.650	0.078	0.572	0.000	0.000	0.000
TOTALS			3.56		0.671	2.888	4.008	0.754	3.254	-0.082	-0.364	-0.446

(*) BD = oven dry bulk density
(**) IM = mineral index (gkg^{-1}/gkg^{-1})

retransported in a fluviatile-deltaic environment and not a true loess.

The results of the balance indicate a net translocation in all horizons and no accumulation because the C' horizon is an artifact in this balance. If the C' horizon is not used in the balance technique, accumulation of soil materials occur in the Btng1 and Btng2 (Table 5.1). There is an increase in clay content of 8 % with respect to the Btkng horizons. The accumulation of clay in this first discontinuity is due to the changes in the hydraulic properties of the material at a wavy diffuse interface between the lighter Btng1 horizon and the Btng2 finer-textured horizon. The balance also reveals that clay has been loss from the B horizons (Eg/Btg, Btng/Eg, Btkng1, Btkng2). This is well correlated with the increase of ESP with depth. The balance shows that the non-clay fraction has been translocated in larger amounts than the clay. However, the finer non-clay fractions were in part weathered and transported in solution. The major non-clay losses are in the Eg2, Eg/Btg and Btng/Eg horizons. This corresponds to the glossic features in the profile.

The CEC of the clay was estimated from the graphic analysis (Fig. 5.3) for all horizons. They are plotted with respect to depth as well as the clay content in Fig. 5.4. The increase of clay with depth is not followed by an steady increase in the clay CEC. Clay CEC has an irregular profile and it indicates that ferrolysis is not an important process
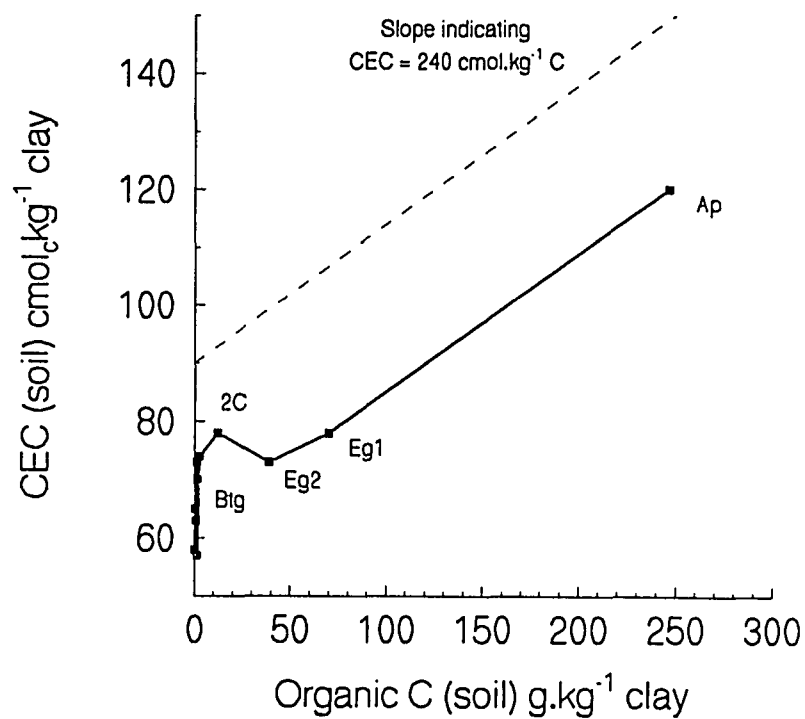
Fig. 5.3. CEC (soil) in relation to organic C recalculated per kg clay fraction for Verdun soil.
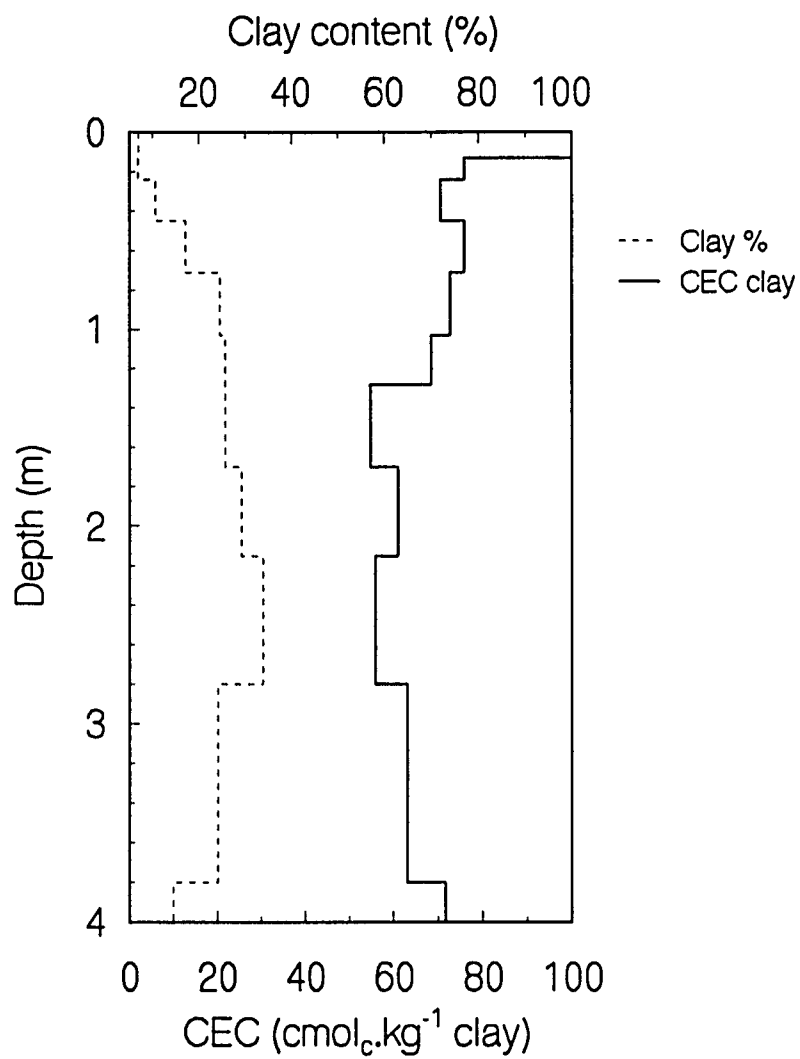
Fig. 5.4. Depth function of clay content and estimated CEC clay for Verdun soil.

in the formation of the B horizons in this soil. This is also evident from the low amount of free iron oxides in the profile (Table 5.1). This observation is supported by Brinkman (1978). He points out that the quantity of iron reduced in the wet season and/or the soil CEC determine the rate of ferrolysis. We conclude that the mechanism of clay degradation is not ferrolysis, but hydrolysis. However, ferrolysis may still occur at soil microsites.

Translocation of Soil Colloids

Translocation and degradation processes in the Verdun soil are a consequence of the interaction of the Na chemistry, parent material and the soil aquic conditions. The continuous leaching of the upper part of a sodic soil occurs as a consequence of dispersion of soil colloids. The soil colloids include the clay and fine-silt fractions (0.01 to 10 μm) according to Sposito (1989). The conditions that favor dispersion of soil colloids are a high state of hydration and an electrolyte concentration in the soil solution that is smaller than that required to flocculate clay particles. Dispersion of smectites particles occur at an ESP > 15 or SAR > 13 (Sposito, 1989). Dispersed clay particles will produce a reduction in pore diameters because of clogging and swelling phenomena as documented by Yaron and Thomas (1968) and Frenkel et al. (1978). The low electrolyte concentrations in sodic soils that are the consequence of dispersion of clays is

produced by rainfall under natural conditions as demonstrated by Shainberg et al. (1981a). The evidence of dispersion, translocation and development of B horizons with reduction of pore size diameter by clogging and expansion of the smectitic clays are presented in Table 5.1. There is an steady increase in clay content, bulk density and COLE to the depth of the first lithological discontinuity (2.80 m). COLE values > 0.03 indicates that a significant amount of smectites is present in the soil (Borchardt, 1989). The Figs. 5.5, 5.6, and 5.7 show the net effect of the dispersion and translocation processes in the equivalent pore diameter distribution calculated from soil moisture characteristic curves for the Ap, Eg2 and Btkng horizon. The elluvial horizons (Ap and Eg2) have greater porosity than the natric horizon. The porosity of the Ap is greater than that of the Eg2 because of a larger content of organic matter (Table 5.1).

Degradation of Clay Minerals

A process concomitant with clay dispersion is hydrolysis by water containing CO_2 that produces H_2CO_3. The H_2CO_3 dissociates releasing H^+ that attacks the structure of the soil silicates (Buol et al. 1989). The sources of CO_2 are rain water and respiration of roots and soil living organisms. This process leads to the acidification of the upper horizons. However, the soil pH given in Table 5.1 are not those usually found in the field when the soil is wet. The field pH of the
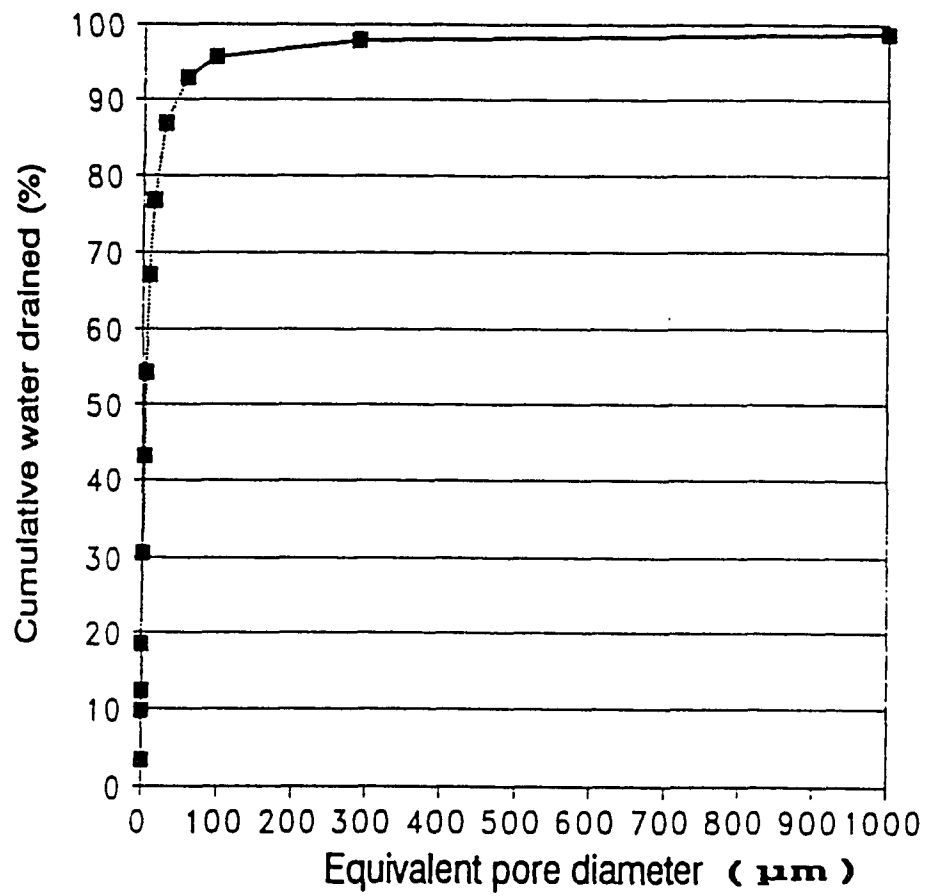
Fig. 5.5. Equivalent pore diameter distribution calculated from the soil moisture characteristic curve for the Ap horizon of Verdun soil.
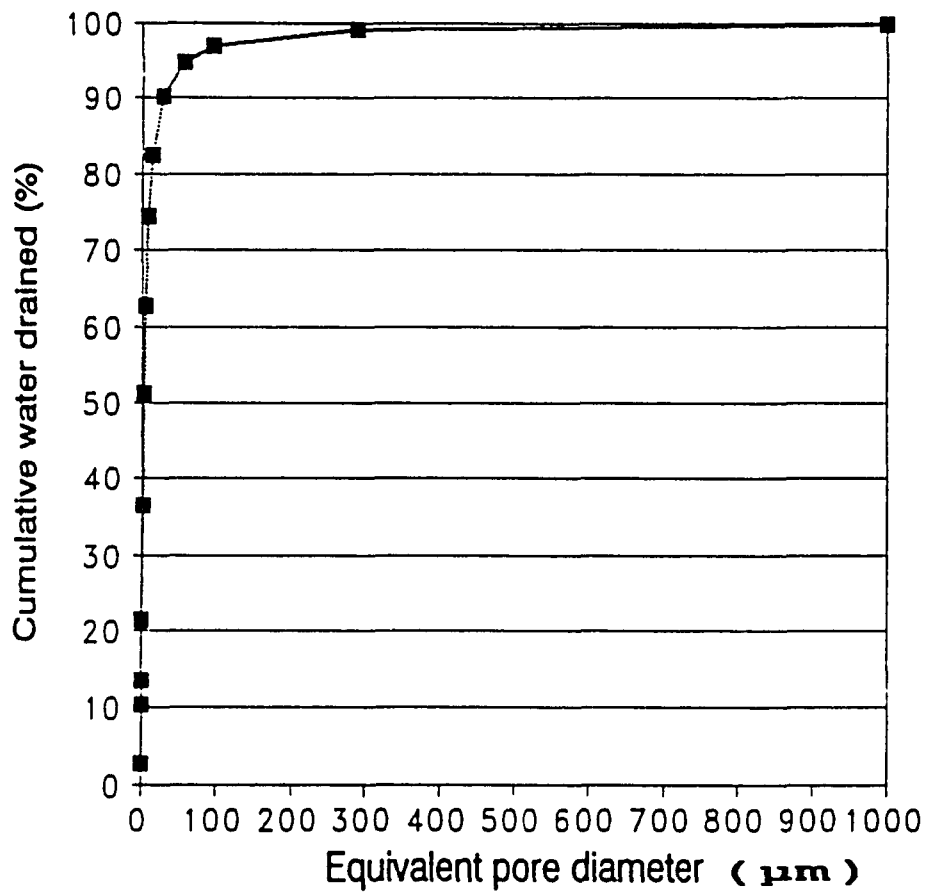
Fig. 5.6. Equivalent pore diameter distribution calculated from soil moisture characteristic curve for the Eg2 horizon of Verdun soil.
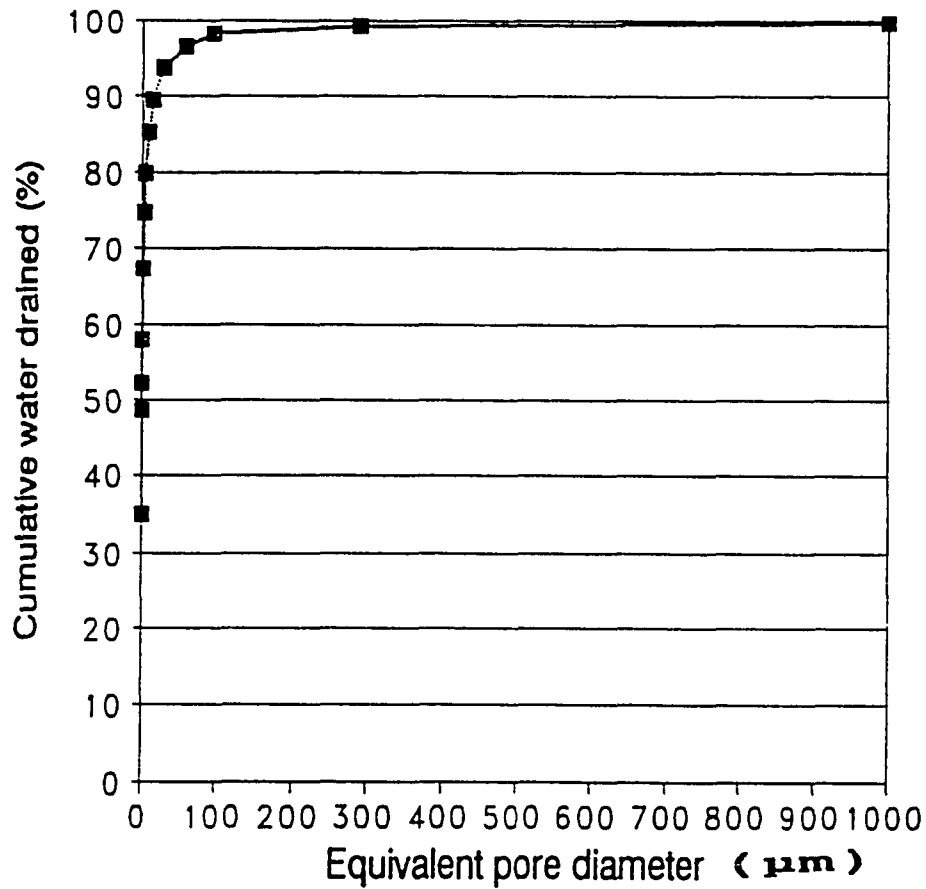
Fig. 5.7. Equivalent pore diameter distribution calculated from soil moisture characteristic curve for the Btkng1 horizon of Verdun soil.

Verdun profile is close to neutral (6.5 to 7.2). At this pH and in wet conditions, the dominant carbonate species is HCO_3^- with concentrations between 10^{-3} to 10^{-2} M. These values agree with the values given by Van Beek and Van Breemen (1973).

The products of hydrolysis are SiO_2, sesquioxides and bases. In poorly drained soils, the SiO_2 accumulates in the form of quartz and amorphous SiO_2 forming the characteristic bleached E horizons. A portion of the dissolved SiO_2 moves to lower horizon as H_2SO_4 in solution (Szabolcs et al., 1980).

The average concentration of dissolved SiO_2 in the form of H_2SO_4 in the ground water of the Verdun soil is 1.5 x 10^{-3} M (Mean = 12.5 mgl^{-1} Si, S.D. = 5.3, n=41). This concentration is higher than the solubility of quartz at 25° C (10^{-4} M). It is in the range between the solubility of soil-SiO_2 (7.9 x 10^{-4} M) and amorphous-SiO_2 (1.8 x 10^{-3} M) given by Lindsay (1979). The accumulation of SiO_2 in the upper horizons is shown in Table 5.3. The SiO_2 accounts for more than 90% of the total chemical composition of the Ap, Eg1 and Eg2 horizons. The BCg horizon also has more than 90 % SiO_2, but it is the result of the discontinuity and mixing with the underlaying sandy loam sediment.

The Al^{3+} and Fe^{2+} released from the clay lattice by hydrolysis are leached to lower horizons where they become trapped in interlayers or are incorporated into the structure of smectitic clays. Only minute amounts of exchangeable Al^{3+} and Fe^{2+} are present in the illuvial horizon because of neutral

pH that favors the formation of Al polymers, and of drying cycles during which Fe^{2+} is oxidized to form goethite. Table 5.3 shows clearly this trend: i) an increase of Al_2O_3 down to the BCg horizon; ii) an increase of Fe_2O_3 with depth with a maximum in the Btng/Eg and Btkng1 horizon; iii) a small decrease in the Btkng2 horizon; and iv) a slight increase in the two following horizons. The reported total Fe_2O_3 % does not imply that Fe is in the ferric form in the structure of silicates. Total Fe_2O_3 is affected by the free Fe oxihydroxides % (Table 5.3) and by the occurrence of some structural Fe in smectitic clays in the ferrous form (Weaver and Pollard, 1973).

Two molar SiO_2/sesquioxide ratios are presented in Fig. 8. Both follow the same trend. They indicate with a constant high value the accumulation of SiO_2 in the Ap, Eg1 and Eg2 horizons (0-0.45 m). The decrease of these ratios with respect to the upper horizons in the Eg/Btg horizon (0.45-0.71 m) and Btng/Eg horizon (0.71-1.03 m) correlate with the presence of glossic features and the relative degree of degradation of the prismatic structure of the natric horizon. The smallest ratios occur in the Btkng horizons (1.03-1.70 m) probably due to the accumulation of Al-Fe interlayered smectites. Below 1.70 m depth, the ratio increases due to the increase in kaolinite. It was probably deposited with the parent material or formed via weathering of aluminosilicates

during a period of better drainage in earlier stages of soil formation.

The Btkng1 and Btkng2 horizon with hig ESP (Table 5.1) have a small SiO_2/sesquioxide ratio (Fig. 5.8) and low clay CEC (Fig. 5.4). This means that the dispersive effect of ESP is counteracted by an increase of structural stability that leads to a decrease the clay CEC and swelling. The increase of Al and Fe in the interlayer and in the lattice structure of smectites is analogous to a buffer effect against dispersion. The stabilizing effects of Al-Fe polymers in the soil structure of sodic smectitic soils are documented by Frenkel and Shainberg (1980) as well as the effect of mineral weathering on clay dispersion of sodic soils by Shainberg et al. (1981b).

The reducing conditions and the neutralization of HCO_3^- by dissolution of aluminosilicates buffer the soil system. The presence of calcic horizons (Btkng) in the profile are a consequence of the increase of alkalinity and the formation of pedogenic powdery $CaCO_3$ at the expense of the migration of $CaHCO_3^+$. It is most likely a by-product of hydrolysis in the elluvial horizons and maintained at that depth by the fluctuation of the water table as demonstrated by Qualls (1984). Data in Table 5.3 show that the total amount of Ca in the form of CaO is low such that the formation of $CaCO_3$ in subhorizons is a process of relative importance in this soil.

Table 5.3. Total chemical composition of the Verdun Soil.

	CaO	MgO	K$_2$O	Na$_2$O	Al$_2$O$_3$	Fe$_2$O$_3$	MnO$_2$	SiO$_2$	TiO$_2$	ZrO$_2$
					%					
Ap	0.203	0.113	0.542	0.612	3.613	0.698	0.012	93.19	0.956	0.057
	0.183	0.099	0.527	0.651	3.954	0.828	0.012	92.63	1.051	0.063
Eg1	0.225	0.151	0.532	0.650	3.821	0.812	0.011	92.79	0.946	0.063
	0.230	0.164	0.540	0.520	3.720	0.851	0.011	92.97	0.933	0.062
Eg2	0.267	0.216	0.544	0.581	4.794	1.228	0.011	91.34	0.961	0.065
	0.275	0.247	0.591	0.572	4.724	1.246	0.011	91.30	0.967	0.060
Eg/Btng	0.384	0.371	0.679	0.604	6.668	2.390	0.013	87.91	0.922	0.062
	0.368	0.352	0.679	0.623	6.272	2.226	0.012	88.45	0.919	0.064
Btng/Eg	0.551	0.580	0.867	0.776	8.434	3.429	0.130	84.22	0.957	0.063
	0.550	0.604	0.940	0.737	8.590	3.363	0.122	84.70	0.969	0.062
Btkng1	0.550	0.558	0.781	0.656	8.504	3.105	0.096	84.71	0.988	0.066
	0.567	0.598	0.824	0.651	8.727	3.117	0.111	84.33	1.016	0.060
Btkng2	0.386	0.337	0.437	0.509	7.286	2.460	0.032	87.43	1.070	0.055
	0.356	0.297	0.383	0.401	6.920	2.478	0.038	88.01	1.067	0.059
Btng1	0.433	0.406	0.450	0.488	7.350	2.785	0.045	86.98	1.013	0.051
	0.458	0.461	0.495	0.464	7.848	3.158	0.044	85.96	1.059	0.055
Btng2	0.462	0.611	0.697	0.403	9.455	3.347	0.024	84.21	0.748	0.048
	0.443	0.597	0.695	0.416	9.434	3.237	0.032	84.37	0.740	0.048
BCg	0.269	0.332	0.377	0.271	5.830	1.695	0.005	90.88	0.319	0.022
	0.238	0.237	0.365	0.184	5.133	1.495	0.005	92.02	0.304	0.023

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Molar SiO_2 / sesquioxide ratios
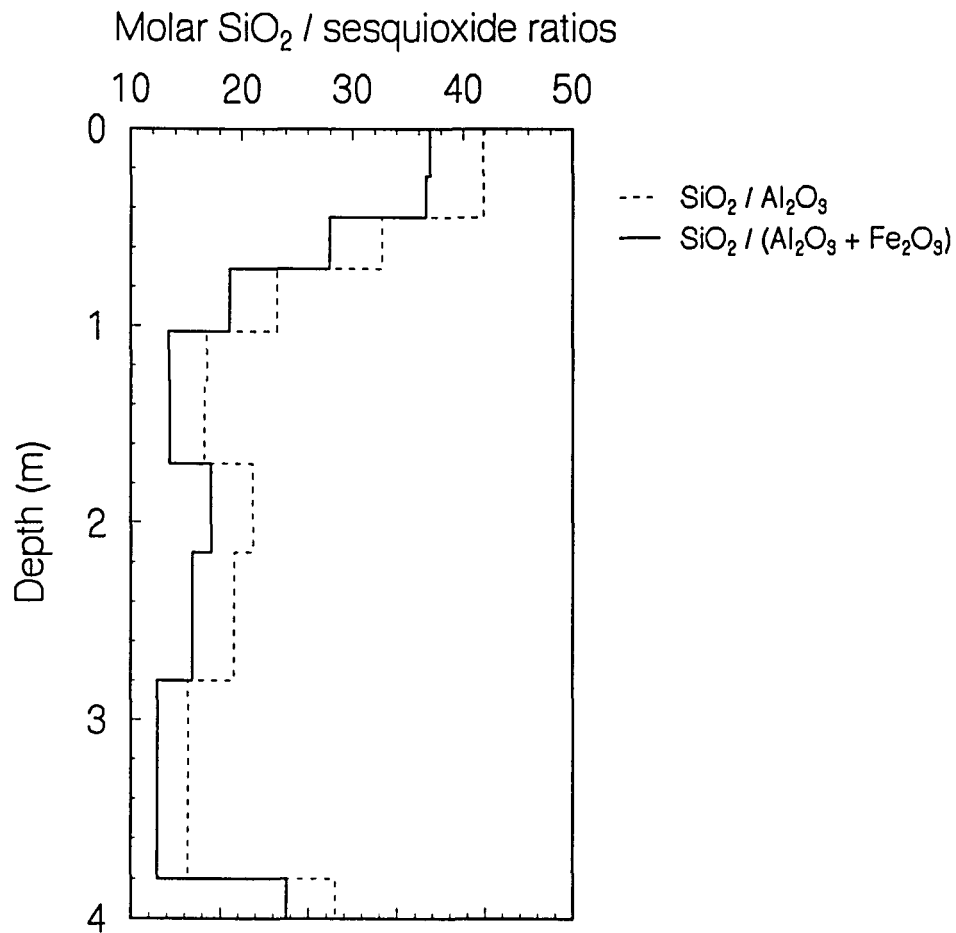
Fig. 5.8. Molar SiO_2/sesquioxide ratios in function of depth for Verdun soil

We can conclude that the degradation of clay minerals in this solodic soil is due to the process of hydrolysis. When rainwater leaches through the soil it lowers the Na activity. The Na^+ is removed from the clay exchange complex when Na activity reaches values comparable to the H activity. The displacement of Na^+ by H^+ produces an unstable smectite. A certain maximum level of exchangeable H^+ is reached while the remainder of the CEC is saturated by Al, Fe or Mg ions diffusing from the structural lattice to the exchange sites (Eeckman and Laudelot, 1961; Bar-On and Shainberg, 1970; Shainberg, 1973). The Na supplied by capillary rise of salts during a dry season or by rising of the salt water table (secondary salinization) during the wet season may replace Mg on the exchange sites by the passing salt solution. At the same time, the pH rises and exchangeable Al may be neutralized and polymerized occupying non-exchangeable sites in the interlayers of clay minerals and blocking part of the CEC. The Fe^{2+} during the dry season is oxidized to form oxides. During the wet season, with the rise of salt water and anaerobic conditions Fe^{2+} is exchanged by Na^+ and moves to lower horizon where either forms oxides or contributes to the formation of Al-Fe interlayered smectites.

Clay Mineralogy

The processes described above are supported by the mineralogical composition of the total clay fraction of the

different soil horizons. The X-ray diffractograms for four different horizons are presented in Figs. 5.9 to 5.12. According to the relative peak sizes, smectites (2θ = 5.2 Mg-Gly.) and kaolinite (2θ = 12.3 Mg-Gly, K-Sat 300° C) are the dominant clay minerals. The kaolinite content increases in the lower Btkng1 and Btng1 horizons. This is concluded from its peak size shown in Figs. 5.11 and 5.12. These data support our idea of an early transport of kaolinite from the top soil to the lower horizon and/or the weathering of smectites to kaolinite in a previous better drained environment. The shoulder of smectite peaks in Fig. 5.9 for the Eg2 horizon and Fig 5.10 for the Btng/Eg indicate the presence of illitic clay (2θ = 8.8 Mg-gly, K-Sat 300 and 500 °C) interstratification with the smectite. These peaks indicate the presence of illite in the Btkng1 horizon (Fig. 5.11).

Analysis from the TEM showed that the smectites in the Ap horizon (Fig 5.13) have a Mg:Al:Si$\approx$1:2:1 ratio that was estimated from the EDAX spectra in Fig. 5.14. These data explain the higher CEC estimated for the Ap horizon (Fig 5.4) probably because the smectites do not have Fe-Al interlayers. Spectral analysis of the Btkng1 horizon reveal the presence of a Mg-smectite associated with Al-Fe interlayered clay (Fig 5.15). These clays are indicators of the clay degradation process by entering of Fe and Al in the interlayer spaces. The interstratified mineral detected in the X-ray diffractograms is a highly weathered illite (Fig. 5.16).

File: 90110544A.SM
Additional files: 90110544B.SM   90110544C.SM   90110544D.SM   18-AUG-92 11:44

SM Smectite
IL Illite
KK Kaolinite
QZ Quartz

x10³

1.90
1.71
1.52
1.33
1.14
0.95
0.76
0.57
0.38
0.19

0.0   5.0   10.0   15.0   20.0   25.0   30.0   35.0

SM
KK
IL
QZ
Mg-RT
Mg-GLY
K-300
K-500
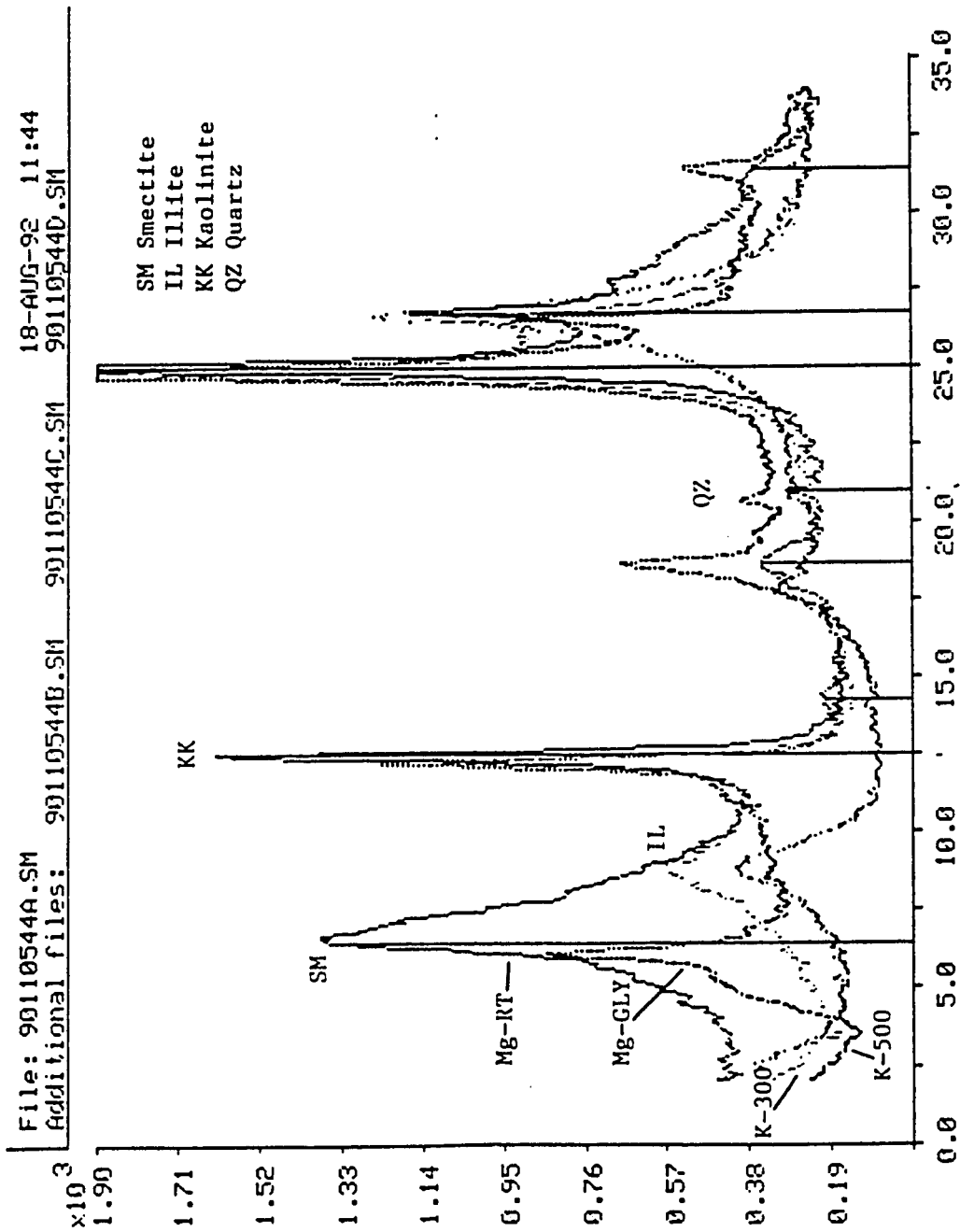
Fig. 5.9. X-ray diffractograms of Verdun Eg2 horizon (0.24-0.45 m).

File: 90110546A.SM   18-AUG-92 11:57
Additional files: 90110546B.SM   90110546C.SM   90110546D.SM

SM Smectite
IL Illite
KK Kaolinite
QZ Quartz

KK

SM

Mg-GLY   Mg-RT

IL

QZ

K-300

K-500
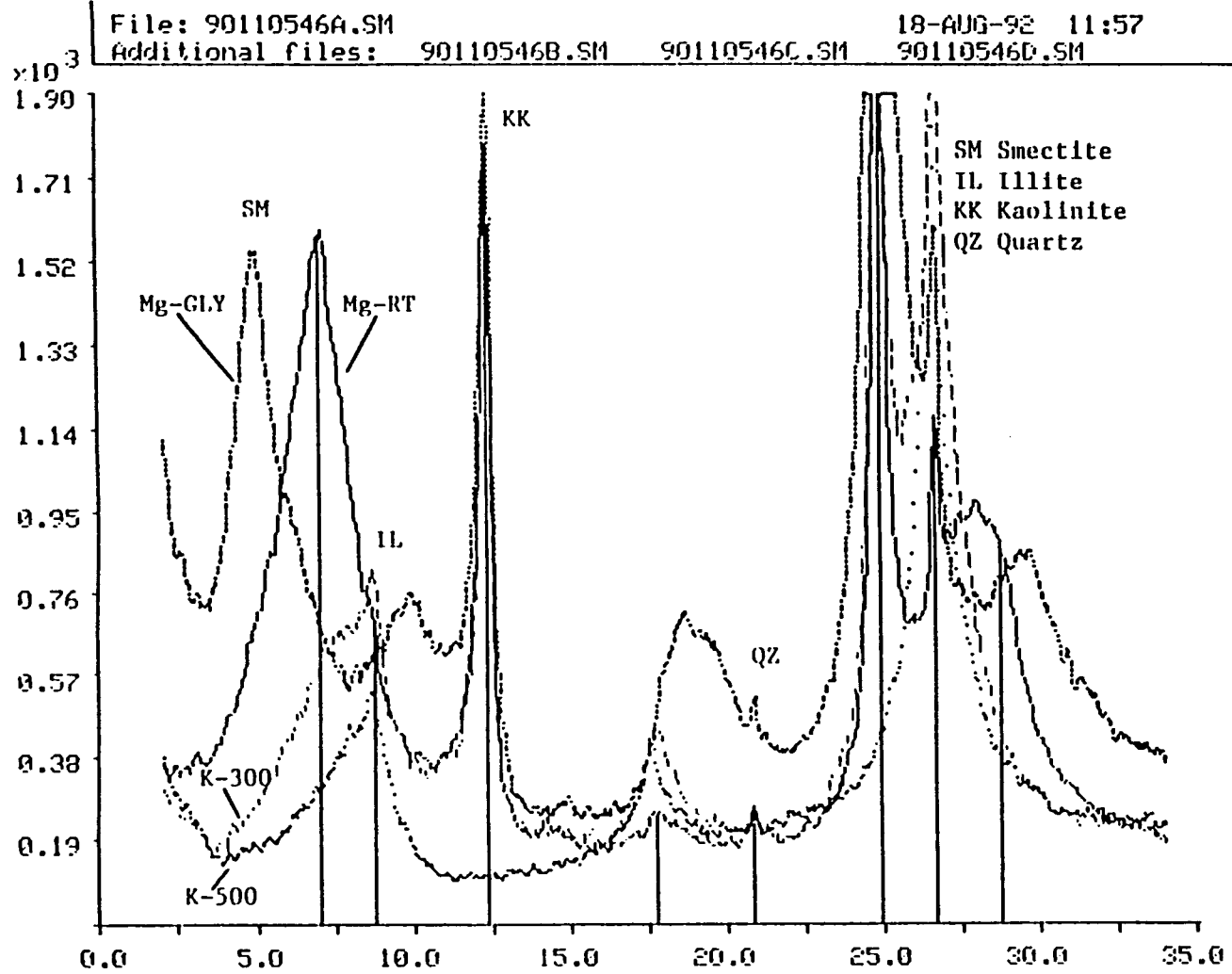
Fig. 5.10. X-ray diffractograms of Verdun Btng/Eg horizon (0.71-1.03 m).
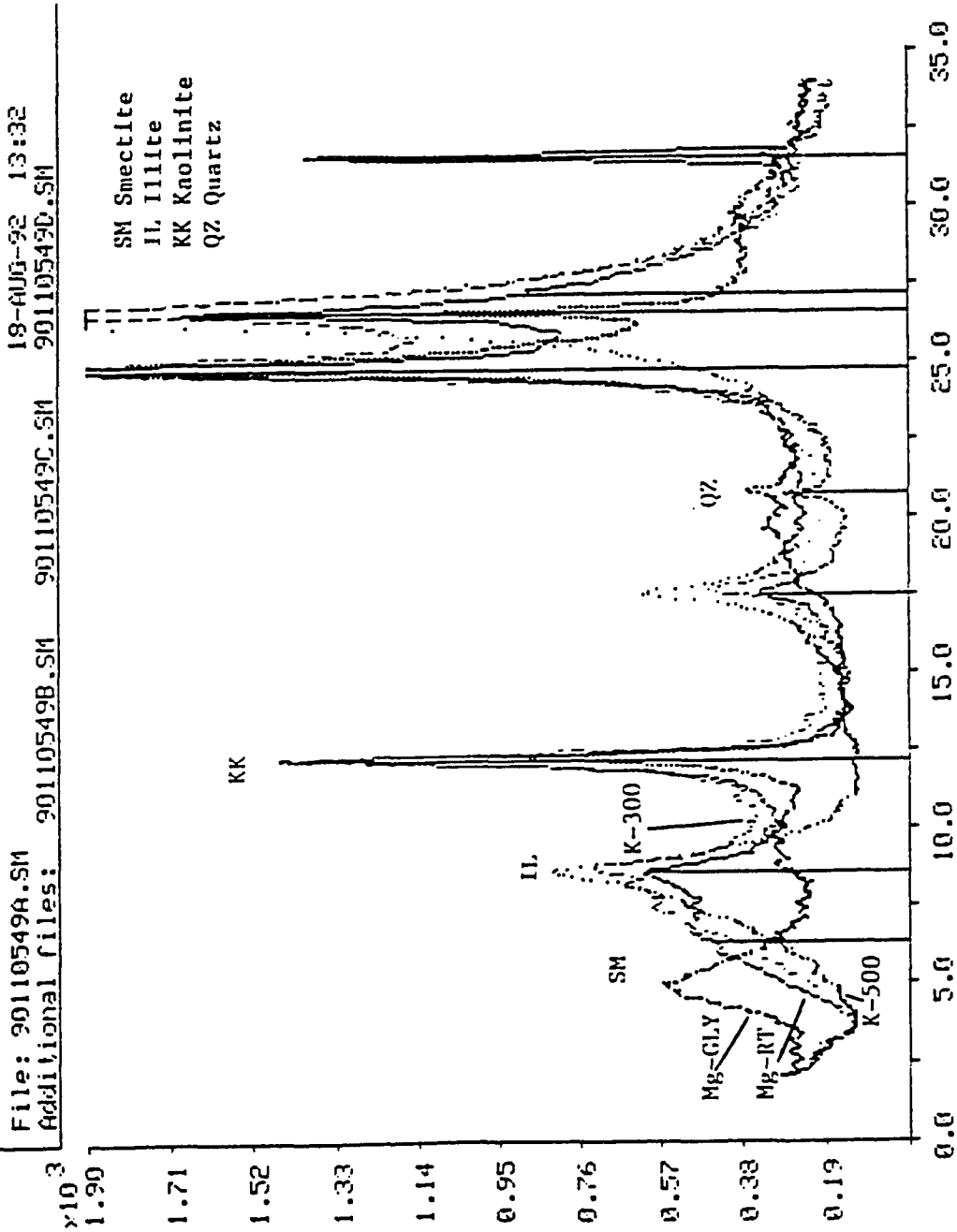
Fig. 5.11. X-ray diffractograms of Verdun Btkng1 horizon (1.03-1.28 m).
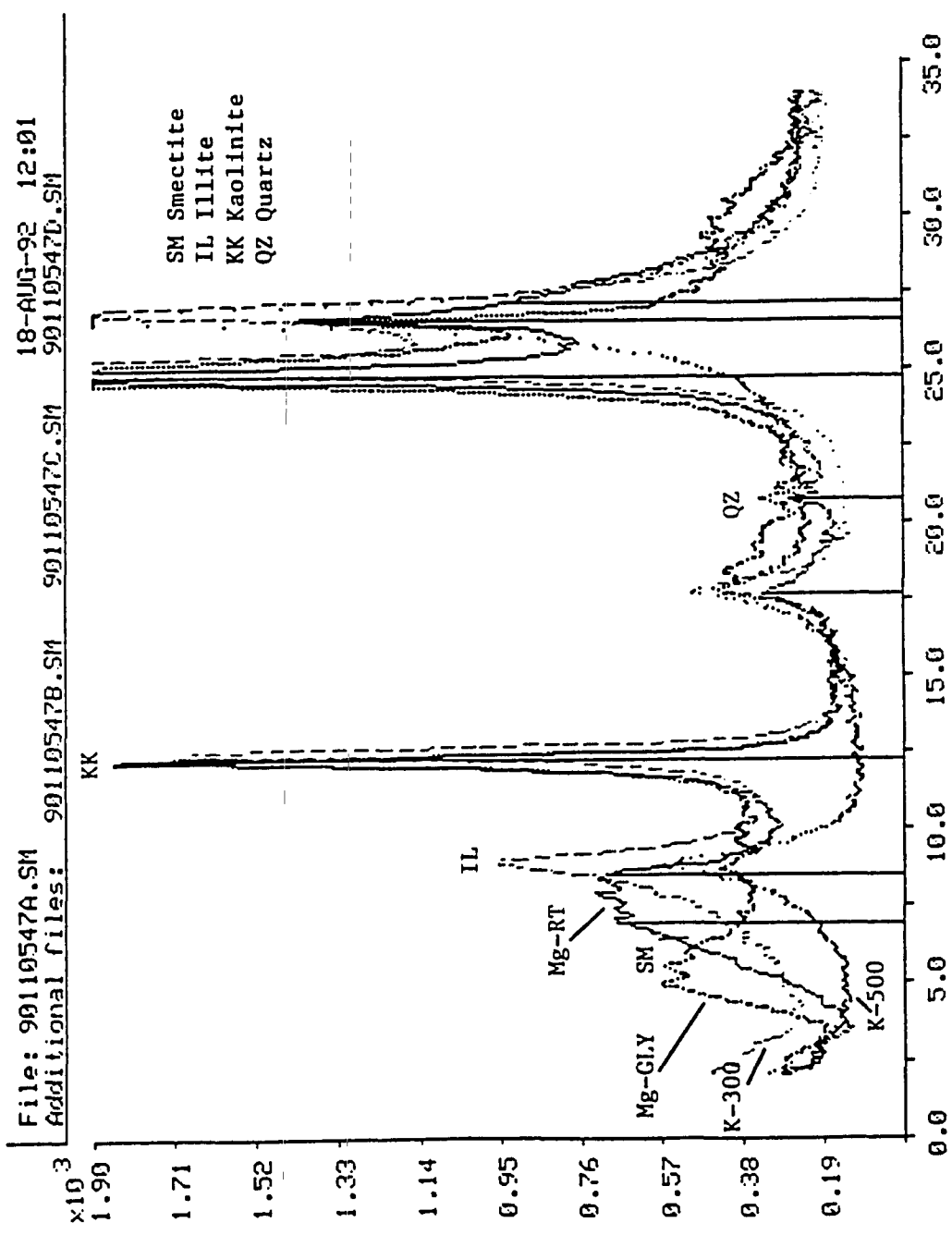
Fig. 5.12. X-ray diffractograms of Verdun Btng1 horizon (1.70-2.15 m).

Clay mineral →

0.2μm
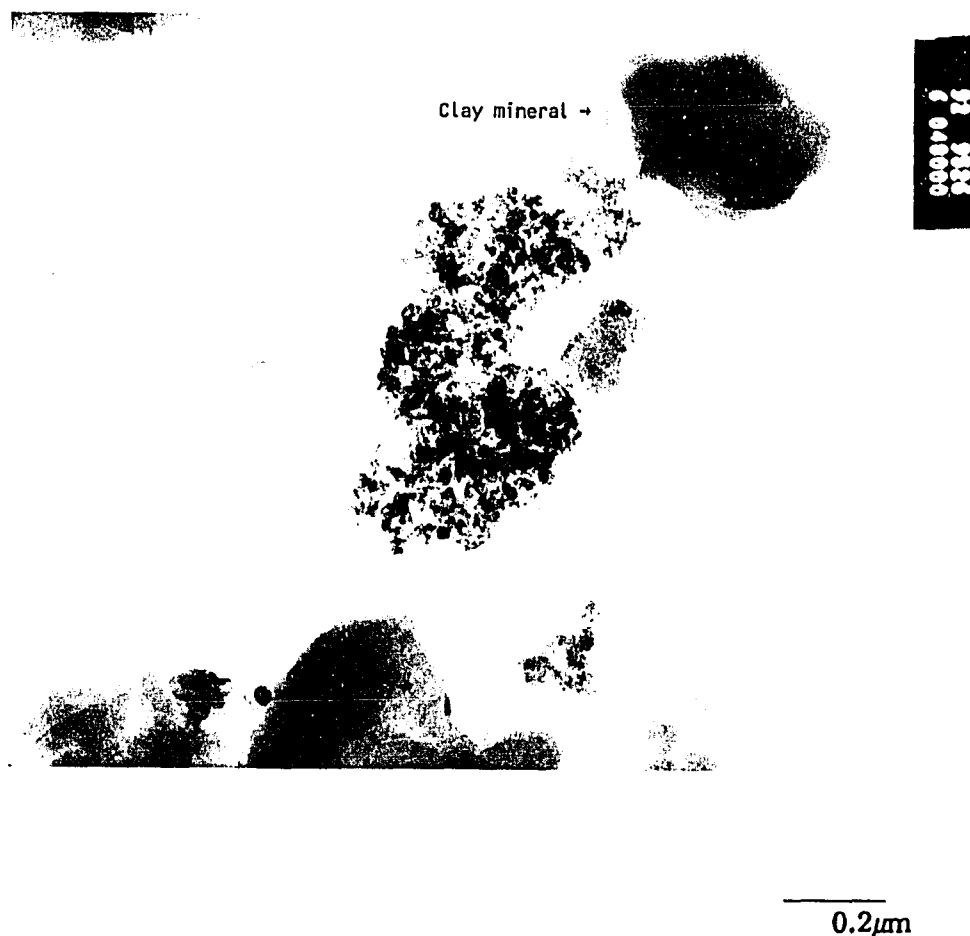
Fig. 5.13. Electron micrograph of the clay fraction from
Verdun Ap horizon. The clay mineral is partly coated
with Fe oxide/oxyhydroxides.

Verdun Ap. 9256.
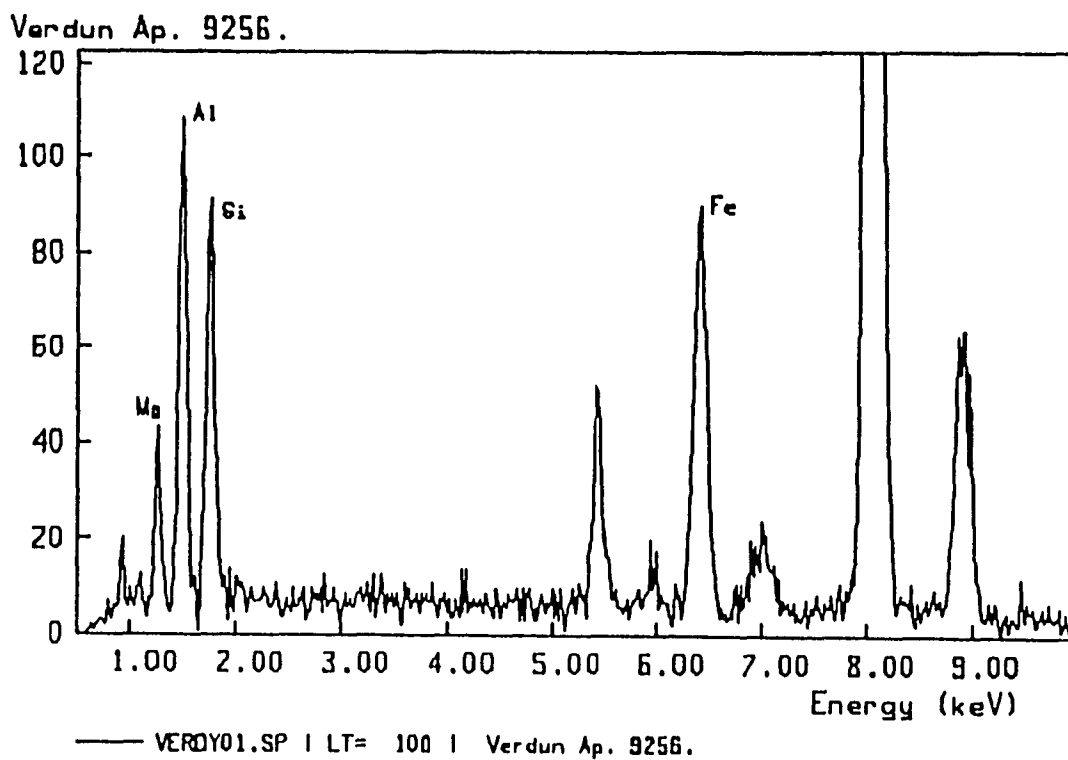
Fig. 5.14.   EDAX spectogram of the smectite shown in Fig.
5.13.   The relative peak sizes indicate a Mg:Al:Si ratio
close to 1:2:1.

0.5μm
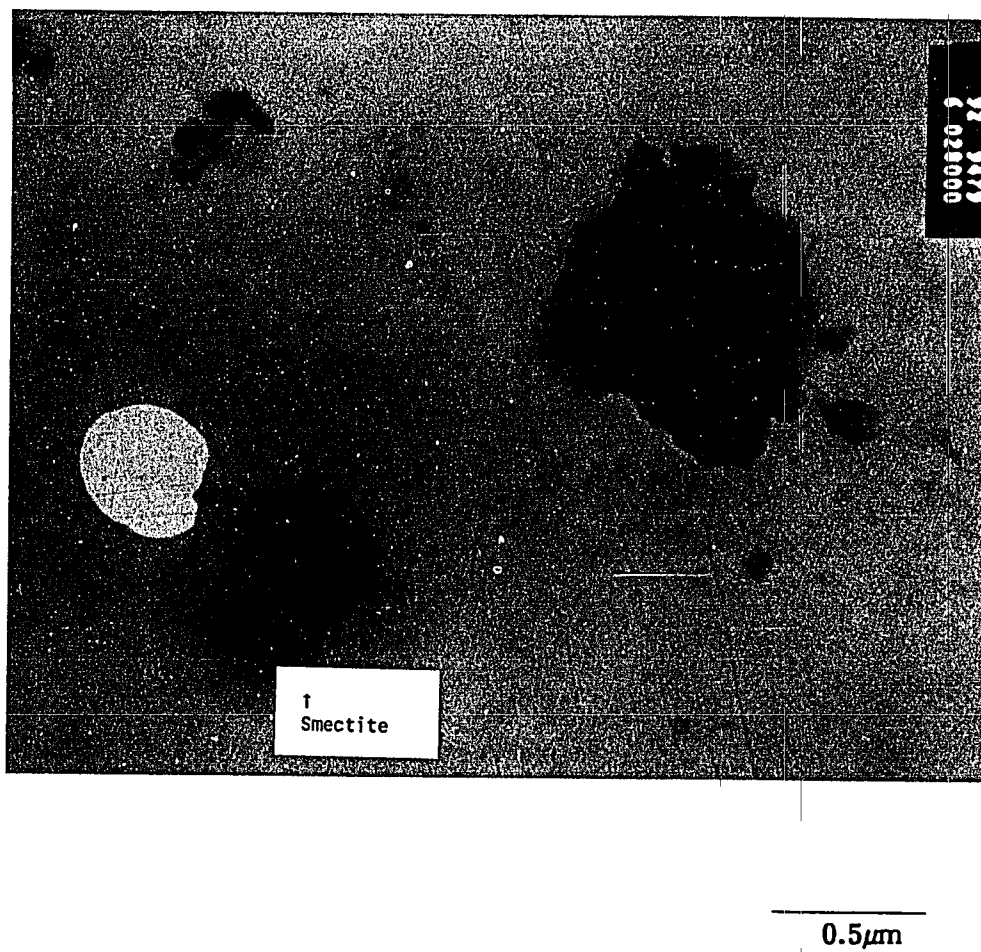
Fig. 5.15.   Electron micrograph of the clay fraction from
       Verdun Btkng1 horizon.   Part of the labeled Mg-smectite
       has a Al-Fe interlayer.
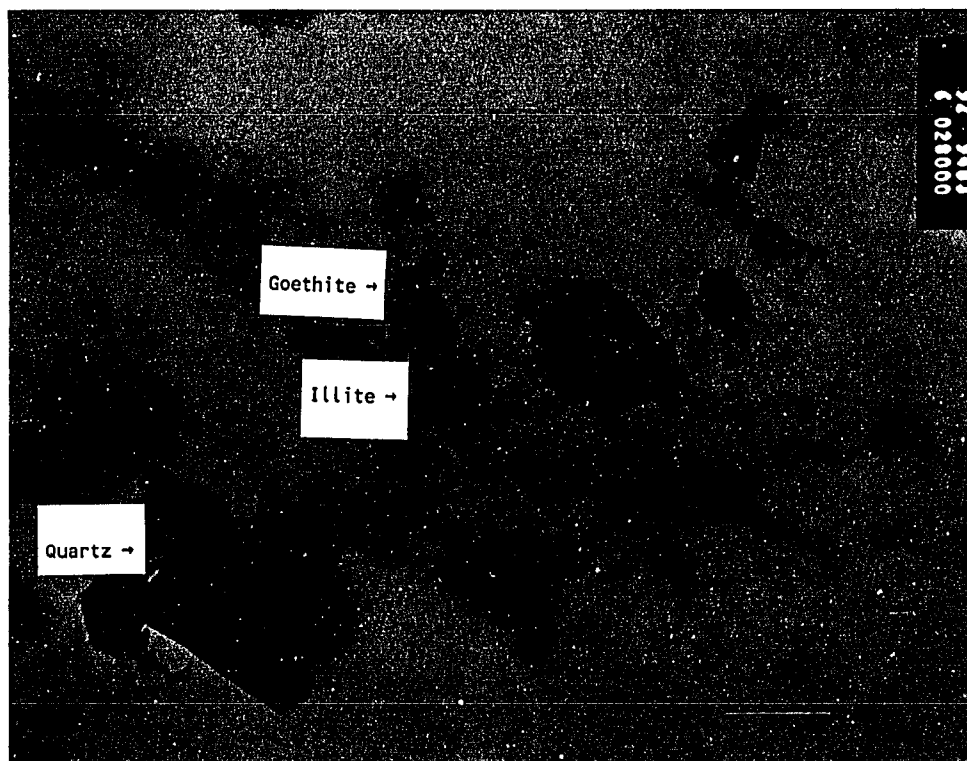
0.2μm

Fig. 5.16.   Electron micrograph of the clay fraction from
     Verdun Btkng1 horizon.   The illite is in a highly
     weathered state.

5.4. CONCLUSIONS

The processes leading to the differentiation of elluvial and illuvial horizons in Verdun soils are the translocation and the degradation of clay minerals. Both processes may occur simultaneously. Both are related to the dispersion and the weathering of clay minerals in the elluvial horizons by the effect of exchangeable Na and hydrolisis. SiO_2 is released as a result of weathering of aluminosilicates producing the relative increase of quartz and amorphous SiO_2 in the bleached elluvial horizons. The other weathering products (Al and Fe) contribute to decrease the CEC of the translocated clay minerals by forming Al-Fe hydroxide interlayers that stabilizes the clays in the illuvial horizons against an increase of ESP.

CHAPTER 6.

SUMMARY AND CONCLUSIONS

Soil characterization data, field records of soil saturation and reduction, morphological descriptions, water chemistry and mineralogical analysis were used to investigate the aquic conditions and its relationship with the morphology, and soil environmental processes in two Natraqualfs in the Coastal Plain of Louisiana.

The results and conclusions obtained from this study are the following:

1. Verdun and Brimstone soils support aquic conditions. These to soils belong to an aquic suborder: saturation and reduction occur within the 50 cm depth at least 30 days a year.

2. Redoximorphic features found on both soil profiles follow the different theoretical models found in the literature. However, they do not define uniquely episaturation or endosaturation of the soil.

3. Episaturation as a result of perched water tables has an ephemeral character. A minimum of one week monitoring period is needed in order for it to be detected precisely. In winter, when precipitation exceeds largely evapotranspiration rates, the episaturation is expressed as stagnation that may last two to three months.

5. The estimation of the oxidative capacity (OXC) is an useful method to predict the redox status in soils. The prediction of anaerobiosis by the OXC depends very much on the dominant

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redox species and its inherent ease of reduction as demonstrated by the OXC of the Verdun soil dominated by SO_4^{2-} and the OXC of the Brimstone soil dominated by NO_3^- except in the Ap horizon. This different dominance of redox species influences the field Eh measurements because nitrates are reduced first and at higher potentials than sulfates.

6. An alternative, simpler method to predict soil anaerobiosis was derived from the OXC. The aerobic capacity (AC) is used only to predict oxic and anoxic conditions by computing the difference between the oxidant equivalents accepted by oxygen and the reductant equivalents donated by organic carbon. If the difference is positive or zero, the environment is predicted oxic. This estimation must be confirmed by DO measurements in the field to test the prediction of soil anaerobiosis ($[O_2] < 1$ μmol kg^{-1}).

7. The Verdun soil has a well developed natric profile. Its morphology would indicate that leaching of Na was sometime a predominant process in the soil. However, presently the soil is undergoing secondary salinization. The discharging ground water is brackish, of probable marine origin as indicated by the strong relationship Cl - Na and Cl - Na+Mg.

8. The origin of the ground water in Brimstone soil is not saline ground water but infiltrating rain water as demonstrated by the weak relationship between Cl and Na. It receives water from the adjacent landscape with addition of NO_3, as well as it yields water to the ground water system.

Na and Cl are leached out by this means and accumulated at short distances in microdepressions.

9. The processes leading to the differentiation of E and B horizons in Verdun soils are the translocation and the degradation of clay minerals. Both processes may occur simultaneously. Both are related to the dispersion and the weathering of clay minerals in the elluvial horizons by the effect of exchangeable Na and hydrolisis. SiO_2 is released as a result of weathering of aluminosilicates producing the relative increase of quartz and amorphous SiO_2 in the bleached elluvial horizons. The other weathering products (Al and Fe) contribute to decrease the CEC of the translocated clay minerals by forming Al-Fe hydroxide interlayers that stabilizes the clays in the illuvial horizons against an increase of ESP.

The results of this study reaffirmed the applicability of the aquic conditions concepts to classify soils in aquic suborders according its three diagnostic properties: saturation, reduction and presence of redoximorphic features. The interaction of aquic conditions with the sodium chemistry of these soils result in complicated processes of clay translocation and degradation that are useful to know in order to manage and restore them.

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APPENDIX A

Field description: Verdun soil

Ap--0 to 13; grayish brown (10YR 5/2) silt loam; weak fine granular structure; friable; common medium and coarse roots throughout; many fine tubular pores; moderately acid (pH 5.5); clear wavy boundary.

Eg1--13 to 24 cm; light gray (10YR 7/2) silt loam; weak fine subangular blocky structure; firm; many fine roots throughout and common medium roots throughout; many fine tubular pores; strongly acid (pH 5.0); gradual wavy boundary.

Eg2--24 to 45 cm; 80% light gray (10YR 7/2) silt loam; common coarse distinct yellowish brown (10 YR 5/8), and strong brown (7.5 YR 5/8) mottles; weak fine subangular blocky structure; friable; many fine roots throughout; common fine tubular pores; moderately acid (pH 5.5); clear wavy boundary.

Eg/Btg--45 to 71 cm; 60% light gray (10YR 7/2), and 40 % yellowish brown (10 YR 5/6) silt loam; weak medium subangular blocky structure; friable; common fine roots; common fine pores; very few patchy clay films; moderately acid (pH 5.5); clear wavy boundary.

Btng/Eg--71 to 103 cm; 50 % yellowish brown (10YR 5/6), and 40% yellowish brown (2.5YR 6/2) silty clay loam; weak coarse prismatic fine roots and few medium roots; many fine pores; (2.5Y 6/2) in tongues 2-3 cm wide; 10% MnO_2 stains and soft bodies; few prominent black (10YR 2/1) manganese or iron-manganese stains, and discontinuous clay films; moderately alkaline (pH 8.0); gradual wavy boundary.

Btkng1--103 to 128 cm; 65% light yellowish brown (10YR 6/4), and 30 % light brownish gray (2.5Y 6/2) silty clay loam; common medium distinct yellowish brown (10YR 5/8) mottles; moderate coarse prismatic structure parting to moderate medium subangular blocky; firm; few very fine roots; many fine pores; 5% MnO_2 stains and soft bodies; few prominent black (10YR 2/1) manganese or iron-manganese stains, and discontinuous clay films; moderately alkaline (pH 8.0); gradual wavy boundary.

Btkng2--128 to 170 cm; light yellowish brown (2.5Y 6/4) silty clay loam; many coarse distinct light brownish gray (2.5Y 6/2), and common medium yellowish brown (10YR 5/6) mottles; moderate medium prismatic structure parting to moderate medium subangular blocky; firm; many very fine pores; few prominent black (10YR 2/1) manganese or iron-manganese stains, and discontinuous clay films; common medium and coarse irregular lime concretions; moderately alkaline (pH 8.0); gradual wavy boundary.

Btng1--170 to 215 cm; light brownish gray (2.5Y 6/2) silty clay loam; common coarse distinct yellowish brown (10YR 5/8) mottles; firm; many very fine pores; few prominent black (10YR 2/1) manganese or iron-manganese stains on vertical faces of peds, and discontinuous clay films; few medium and coarse irregular lime concretions; moderately alkaline (pH 8.0).

Btng2--215 to 280 cm; light brownish gray (2.5Y 6/2) clay; common distinct olive yellow (2.5Y 6/6) mottles; friable; very few prominent manganese or iron-manganese stains on vertical and horizontal faces of peds; moderately alkaline (pH 8.0).

BCg--280 to 380 cm; light gray (10YR 7/2) sandy loam; common medium distinct yellowish brown (10YR 5/8) mottles; friable; stratified; moderately alkaline (pH 8.0).

2C--380 to 400 cm; light gray (10YR 7/2) sandy loam; few medium distinct strong brown (7.5YR 5/6) mottles; single grain; moderately alkaline (pH 8.0).

S88LA-063-002

*** PRIMARY CHARACTERIZATION DATA ***

PRINT DATE 08/24/92

SAMPLED AS : VERDUN
REVISED TO :

; FINE-SILTY, MIXED, THERMIC GLOSSIC NATRAQUALF
(LIVINGSTON PARISH, LOUISIANA)

SSL - PROJECT 89P 8, (CP89LA011) ICOHAQ-LA-1988
- PEDON 89P 49, SAMPLES 89P 542- 552
- GENERAL METHODS 1B1A, 2A1, 2B

U. S. DEPARTMENT OF AGRICULTURE
SOIL CONSERVATION SERVICE
SOIL SURVEY LABORATORY
NATIONAL SOIL SURVEY CENTER
LINCOLN, NEBRASKA 68508-3866

SAMPLE NO.	HORIZON	DEPTH (CM)	TOTAL CLAY LT .002	TOTAL SILT .002-.05	TOTAL SAND .05-2	CLAY FINE LT .0002	SILT CO3 LT .002	SILT FINE .002-.02	SILT COARSE .02-.05	SAND VF .05-.10	SAND F .10-.25	SAND M .25-.50	SAND C .5-1	SAND VC 1-2
89P 5425	AP	0- 13	7.0	76.3	16.7	4.1		38.9	37.4	5.3	4.6	6.8	0.7	0.1
89P 5435	EG1	13- 24	6.9	77.0	16.1	3.7		42.2	34.8	5.3	4.5	5.8	0.5	
89P 5445	EG2	24- 45	10.6	74.3	15.1	6.5		43.5	30.8	5.3	4.1	5.2	0.4	0.1
89P 5455	EG/BTG	45- 71	17.2	70.7	12.1	12.3		40.4	30.4	4.2	3.2	3.4	0.4	0.2
89P 5465	BTNG/EG	71-103	24.6	64.8	10.6	16.0		39.0	25.8	3.5	3.0	4.0	0.6	0.2
89P 5475	BTKNG1	103-128	25.8	62.5	11.7	16.0		40.2	22.3	4.6	3.4	4.4	0.4	
89P 5485	BTKNG2	128-170	29.2	60.0	14.2	14.3		41.8	18.2	4.8	4.6	4.8	0.8	
89P 5495	BTNG1	170-215	34.8	57.6	13.2	16.9		39.1	18.5	11.0	4.3	4.4	0.6	
89P 5505	BTNG2	215-280	34.0	42.0	24.0	20.3		21.2	20.8	5.8	6.9	8.1	2.6	0.1
89P 5515	BCG	280-380	24.2	19.3	56.5	15.6		9.8	9.5	1.2	7.2	39.2	6.6	5.8
89P 5525	2C	380-400	14.6	8.7	76.7	7.7		5.3	3.4	1.2	7.2	60.9	7.2	0.2

SAMPLE NO.	ORGN TOTAL C 6A1c PCT	TOTAL N 6B3a <2MM	EXTR P 6S3 PPM	— DITH-CIT — FE 6C2b	AL 6G7a	MN 6D2a <2MM -->	RATIO/CLAY CEC 8D1	RATIO/CLAY 15 BAR 8D1	ATTERBERG LL 4F1	ATTERBERG PI 4F PCT <0.4MM	BULK DENSITY FIELD MOIST 1/3 BAR 4A3a G/CC	BULK DENSITY FIELD MOIST 4A3a	BULK DENSITY OVEN DRY 4A1h	COLE WHOLE SOIL 4A1d	WATER CONTENT FIELD 1/10 BAR 4B4	1/3 BAR 4B1c	15 BAR 4B2a	WRD WHOLE SOIL 4C1 CM/CM
89P 5425	1.73	0.092		0.2	0.1			0.94	0.69		1.33		1.36	0.007	24.2	24.2	4.8	0.26
89P 5435	0.48	0.019		0.1	TR			0.59	0.49		1.55		1.58	0.006	20.8	20.8	3.4	0.27
89P 5445	0.41	0.015		0.2	0.1			0.64	0.64		1.50		1.54	0.009	21.1	21.1	4.9	0.24
89P 5455	0.21	0.033		0.5	0.1			0.62	0.54		1.56		1.61	0.011	19.6	19.6	9.3	0.16
89P 5465	0.07			0.9	0.1			0.66	0.50		1.63		1.78	0.030	19.8	19.8	12.2	0.12
89P 5475	0.04			1.0	0.1		0.1	0.49	0.49		1.70		1.85	0.029	18.5	18.5	12.6	0.10
89P 5485	0.03			0.6	TR		0.1	0.55	0.46		1.72		1.87	0.028	18.0	18.0	11.8	0.11
89P 5495	0.02			0.6	TR		TR	0.59	0.46		1.67		1.84	0.033	21.0	21.0	13.3	0.13
89P 5505				0.4	0.1		TR	0.59	0.48								16.2	
89P 5515	0.01			0.2	TR			0.63	0.46								11.2	
89P 5525	0.02			0.1	TR			0.66	0.45								6.6	

AVERAGES, DEPTH 71-121: PCT CLAY 25 PCT .1-75MM 8

AVERAGES, DEPTH 71-121: PCT CLAY 25 PCT .1-75MM 8

*** P R I M A R Y   C H A R A C T E R I Z A T I O N   D A T A ***

S88LA-063-002
SAMPLED AS   : VERDUN   ; FINE-SILTY, MIXED, THERMIC GLOSSIC NATRAQUALF   PRINT DATE 08/24/92
USDA-SCS-NSSC-SOIL SURVEY LABORATORY ; PEDON 89P 49, SAMPLE 89P 542- 552

	-1--	-2--	-3--	-4--	-5--	-6--	-7--	-8--	-9--	-10-	-11-	-12-	-13-	-14-	-15-	-16-	-17-	-18-	-19-	-20-
	(- NH4OAC EXTRACTABLE BASES -)					ACID-	EXTR	(- -CEC- -)		EXCH	SAR	BASE		CO3 AS	RES.	CASO4 AS		(- - - -PH - - -)		
	CA	MG	NA	K	SUM	ITY	AL	SUM	NH4-	NA		SATURATION		CACO3	OHMS	GYPSUM		SAT	CACL2	H2O
DEPTH	5B5a	5B5a	5B5a	5B5a	BASES			CATS	OAC			SUM	NH4OAC	<2MM	/CM	<2MM	<20MM	PASTE	.01M	
(CM)	6N2e	602d	6P2b	6Q2b		6H5a	6G9b	5A3a	5A8b	5B5b	5E	5C3	5C1	6E1g	8E1	6F1a	6F4	8C1b	8C1f	8C1f
	<- - - - - - - - - -MEQ / 100 G - - - - - - - - - ->									PCT		<- -PCT- >		PCT		<- -PCT ->			1:2	1:1
0- 13	1.3	0.4	0.3	TR	2.0	6.4	1.5	8.4	6.6	2	3	24	30					4.3	3.8	4.2
13- 24	1.5	0.5	0.5	--	2.5	2.9	0.6	5.4	4.1	6	6	46	61					4.4	4.1	4.6
24- 45	2.2	0.8	1.1	--	4.1	3.6	0.9	7.7	6.8	8	7	53	60					4.3	4.0	4.4
45- 71	5.2	2.7	2.1	0.1	10.1	3.4	0.4	13.5	10.6	12	11	75	95					4.6	4.2	4.7
71-103	8.3	4.5	3.6	0.1	16.5	1.7		18.2	16.3	14	14	91	100			--		6.1	6.2	6.5
103-128	8.4	4.6	3.8	0.1	16.9	1.2		18.1	15.3	19	13	93	100		1000			7.0	6.9	7.6
128-170	7.1	3.8	3.0	0.1	14.0	0.8		14.8	14.3	15	15	95	98	TR				7.4	6.9	7.5
170-215	8.7	5.0	3.5	0.1	17.3	1.0		18.3	17.1	16	14	95	100	TR				7.4	6.9	7.5
215-280		6.4	3.5	0.2		1.1			19.9	15	13		100	1				7.3	7.0	7.3
280-380	7.6	4.8	2.4	0.1	14.9	0.9		15.8	15.2	13	11	94	98	TR				7.3	6.9	7.9
380-400	5.6	2.9	1.5	0.1	10.1	0.6		10.7	9.6	12	12	94	100	TR				7.3	6.8	7.6

	(- - - - - - - -WATER EXTRACTED FROM SATURATED PASTE- - - - - - - - - -)											
	CA	MG	NA	K	CO3	HCO3	CL	SO4	NO3	H2O	TOTAL SALTS EST.	ELEC. COND.
DEPTH												8A3a
(CM)	6N1b	601b	6P1b	6Q1b	611b	6J1b	6K1c	6L1c	6M1c	8A	8D5	MMHOS
	<- - - - - - - - - -MEQ / LITER - - - - - - - - ->									<- -PCT ->		/CM
0- 13	2.0	0.8	4.1	0.1	--	--	4.5	1.6	TR	39.2	TR	0.87
13- 24	2.3	0.9	7.1	TR	--	--	7.7	2.2	--	35.8	TR	1.22
24- 45	4.1	1.8	12.8	0.1	--	--	14.0	4.5	0.2	41.6	0.1	2.13
45- 71	2.4	1.5	15.3	TR	--	--	14.7	4.6	0.1	55.9	0.1	2.20
71-103	2.1	1.5	18.2	--	--	TR	17.5	2.6	--	69.3	0.1	2.59
103-128	1.3	0.8	13.0	TR	--	0.1	12.2	3.5	--	71.5	0.1	1.81
128-170	0.9	0.7	13.4	--	--	0.4	11.3	3.3	--	67.0	0.1	1.67
170-215	0.8	0.5	11.1	TR	--	0.6	10.4	2.0	--	67.9	0.1	1.46
215-280	0.4	0.2	7.2	TR	--	0.6	5.8	1.7	--	82.0	TR	0.92
280-380	0.6	0.4	7.7	0.1	--	0.5	8.6	1.6	--	55.8	TR	1.04
380-400	0.7	0.5	9.0	0.1	--	0.3	8.7	1.6	--	40.1	TR	1.19

ANALYSES: S= ALL ON SIEVED <2mm BASIS

*** P R I M A R Y   C H A R A C T E R I Z A T I O N   D A T A ***

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S88LA-063-002                                                                              PRINT DATE 08/24/92
SAMPLED AS    : VERDUM          ; FINE-SILTY, MIXED, THERMIC GLOSSIC NATRAQUALF
USDA-SCS-NSSC-SOIL SURVEY LABORATORY ; PEDON 89P  49, SAMPLE 89P  542- 552
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           -1--  -2--  -3--  -4--  -5--  -6--  -7--  -8--  -9--  -10-  -11-  -12-  -13-  -14-  -15-  -16-  -17-  -18-  -19-  -20-
---------  ---------------------------------------------- CLAY MINERALOGY (<.002mm) ----------------------------------------------
           < - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - - >
           FRACT < - - - - - X-RAY - - - - - ->< - - - THERMAL - - - ->< - - - - - - ELEMENTAL - - - - - - - ->< - -> EGME  INTER
SAMPLE     ION <                            >< - DTA - ->< - TGA - -> SIO2 AL2O3 Fe2O3  MgO   CaO   K2O   Na2O <     > RETN  PRETA
           < - - - - 7A2I - - - - - - ->< - 7A6  - >< - 7A4b - >< - - - - - - - - - 7C3 - - - - - - - - - -><     > 7D2   TION
NUMBER     <- - >< - - - - peak size - - - - ->< - - - Percent - - - ->< - - - - - - - - - - Percent - - - - - - - - ->< - -><mg/g>< - ->

89P 544    TCLY  MT 4  KK 4  MM 1                                      20.0  6.3               0.4
89P 546    TCLY  MT 4  KK 4  MI 2  MM 1  QZ 1                          21.0  7.7               0.6
89P 547    TCLY  KK 4  MT 3  MM 2  MI 1  QZ 1                          21.0  7.4               0.6
89P 549    TCLY  KK 3  MT 3  MI 1  MM 1  CL 1                          21.0  7.0               0.5
89P 549    TCLY  QZ 1

---------  ---------------------------------- SAND - SILT MINERALOGY (2.0-0.002mm) -----------------------------------------------
           < - - - - - - - - - - - - - - - ->< - - - - SAND - SILT MINERALOGY (2.0-0.002mm) - - - - - - - - - - - - - - - - - - >
           FRACT < - - - - - X-RAY - - ->< - - - THERMAL - - - ->< - - - - - - - OPTICAL - - - - - - - - -><           > INTER
SAMPLE     ION <                        >< - DTA - ->< - TGA - ->TOT RE< - - - - - GRAIN COUNT - - - - - -><           > PRETA
           < - - - - 7A2I - - - - ->< - 7A3b - >< - 7A4b - >< - - - - - - - - - 7B1a - - - - - - - - - -><           > TION
NUMBER     < - ->< - - - Peak Size - - ->< - - - Percent - - - ->< - - - - - - - - - Percent - - - - - - - - ->< - - - - - - - ->< - ->

89P 544    CSI                                              90  QZ87  FK 7  OT 2  OP 2  PO 1  TM
89P 544    CSI                                                  MS    HNtr  ZRtr  RUtr
89P 546    CSI                                              82  QZ80  FK12  OT 3  OP 2  MS 1  HN 1
89P 546    CSI                                                  TM    GE    BT    ZR    PR    FPtr
89P 546    CSI                                                  POtr
89P 551    CSI                                              85  QZ83  FK 8  OT 4  OP 2  MS 2  RU
89P 551    CSI                                                  PO    ZRtr  TMtr  HNtr  SStr

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FRACTION INTERPRETATION:

TCLY Total Clay, <0.002mm   CSI   Coarse Silt, 0.02-0.05mm

MINERAL INTERPRETATION:

20	15	4	1	MT montmoril	KK kaolinite
MM mont-mica	QZ quartz	FK potas-feld	OT other	OP opaques	PO plant opal
TM tourmaline	MS muscovite	HN hornblende	ZR zircon	RU rutile	MI mica
GE goethite	BT biotite	PR pyroxene	FP plag-feld	CL chlorite	SS smectite

RELATIVE PEAK SIZE: 5 Very Large   4 Large   3 Medium   2 Small   1 Very Small   6 No Peaks

INTERPRETATION (BY HORIZON):

PEDON MINERALOGY
  BASED ON SAND/SILT:
  BASED ON CLAY:
  FAMILY MINERALOGY:
  COMMENTS:

173

SOIL WATER RETENTION DEPTH CURVE

Field description: Brimstone soil.

Ap--0 to 15 cm; brown (10YR 5/3) silt loam; weak medium subangular blocky structure parting to moderate fine granular; friable; many fine and medium roots throughout; Lepidocrocite in root channels; few fine (10YR 7/2) silt pockets; very few distinct brownish yellow (10YR 6/8) iron stains in root channels and/or pores; slightly acid (pH 6.0); abrupt smooth boundary.

Eg--15 to 33 cm; light brownish gray (10YR 6/2) silt loam; moderate coarse prismatic structure parting to moderate medium subangular blocky; friable; common fine roots throughout; common fine vesicular pores; Lepidocrocite; common fine (10YR 7/2) silt pockets; very few distinct dark yellowish brown (10YR 4/6) iron stains in root channels and/or pores; mildly alkaline (pH 7.5); gradual wavy boundary.

E/Btng--33 to 60 cm; light brownish gray (10YR 6/2) silt loam; moderate medium subangular blocky structure; firm; few fine roots throughout; many fine vesicular pores; Lepidocrocite; many fine (10YR 7/1) silt pockets; many horizontal bands in crayfish krotovina of silt (10YR 7/2), sand (10YR 6/2), and clay (10YR 4/2); krotovina lined with (10YR 2/2) clay; very few distinct dark yellowish brown (10YR 4/6) clay films in root channels and/or pores, and patchy manganese or iron manganese stains on vertical faces of peds; moderately alkaline (pH 7.8); gradual wavy boundary.

Btng/E--60 to 81 cm; light brownish gray (10YR 6/2) silty clay loam; strong very coarse prismatic structure parting to moderate medium subangular blocky; firm; few fine roots throughout; few fine and medium vesicular pores; Lepidocrocite; many fine (10YR 7/1) silt pockets; many horizontal bands in crayfish krotovina of silt (10YR 6/2) and clay (10YR 4/2); krotovina lined with (10YR 4/2) clay; very few distinct dark greyish brown (10YR 4/2) continuous clay films on faces of peds, and patchy manganese or iron-manganese stains on vertical faces of peds; moderately alkaline (pH 8.0); gradual wavy boundary.

Btng1--81 to 147 cm; light brownish gray (10YR 6/2) silty clay loam; many coarse faint light brownish gray (2.5Y 6/2), and few medium distinct light olive brown (2.5Y 5/6) mottles; moderate coarse prismatic structure parting to moderate coarse subangular blocky; firm; common fine and medium continuous tubular pores; few large pockets of 10YR silts; common thin and patchy silt coats. Split at 115 cm for sampling; dark grayish brown (10YR 4/2) continuous clay films on face of peds; few rounded soft masses of iron-manganese; moderately alkaline (pH 7.8); gradual wavy boundary.

Btng2--147 to 190 cm; light brownish gray (10YR 6/2) silty clay loam; many coarse faint light brownish gray (2.5Y 6/2), and fine distinct yellowish brown (10YR 5/8) mottles; moderate coarse prismatic structure parting to moderate medium subangular blocky; firm; few fine continuous tubular pores; many fine medium (10YR 7/2) silt pockets; dark greyish brown (10YR 4/2) continuous clay films on faces of peds; moderately alkaline (pH 7.8); gradual wavy boundary.

BCg--190 to 264 cm; light brownish gray (10YR 6/2) silty clay loam; common fine faint light brownish gray(2.5Y 6/2), and distinct light olive brown (2.5Y 5/6) mottles; moderate coarse subangular blocky structure; firm; few pressure faces and slickensides; few fine pockets of silt; moderately alkaline (pH 7.8).

Cg1--264 to 314 cm; pale yellow (5Y 7/3) silt loam; moderately alkaline (pH 7.8).

Cg2--314 to 325 cm; pale yellow (5Y 7/3) silty clay loam; few fine prominent yellowish brown (10YR 5/8) mottles; moderately alkaline (pH 7.8).

Cg3--325 to 360 cm; light gray (5Y 7/1) very fine sandy loam; moderately alkaline (pH 7.8).

S88LA-019-001

*** P R I M A R Y   C H A R A C T E R I Z A T I O N   D A T A   ***
(CALCASIEU PARISH, LOUISIANA)

PRINT DATE 08/24/92

SAMPLED AS : BRIMSTONE
REVISED TO :

; FINE-SILTY, MIXED, THERMIC TYPIC NATRAQUALF
; FINE-SILTY, SILICEOUS, THERMIC TYPIC OCHRAQUALF

SSL - PROJECT 89P   8, (CP89LA011) ICOMAQ-LA-1988
    - PEDON   89P 41, SAMPLES 89P 459- 469
    - GENERAL METHODS 1B1A, 2A1, 2B

| | | -1- | -2- | -3- | -4- | -5- | -6- | -7- | -8- | -9- | -10- | -11- | -12- | -13- | -14- | -15- | -16- | -17- | -18- | -19- | -20- |

		(- -TOTAL -)(- -CLAY- -)(- -SILT- -)(- -SAND- - - - - - - - -)(-COARSE FRACTIONS(MM)-)(>2MM)
SAMPLE	DEPTH	HORIZON	CLAY SILT SAND FINE LT CO3 FINE COARSE VF F M C VC - - - -)(- WEIGHT -)(- - WT
NO.	(CM)		LT LT .05 .002 .002 .002 .002 .05 .10 .25 .5 1 2 5 20 .1- PCT OF
			.002 -.05 -2 .0002 PCT OF <2MM (3A1) - - - <- PCT OF <2MM(3B1)-> SOIL

SAMPLE NO.	DEPTH (CM)	HORIZON	CLAY	SILT	SAND	FINE		CO3	FINE	COARSE	VF	F	M	C	VC						
89P 459S	0- 15	AP	6.1	81.2	12.7	5.3			48.2	33.0	11.5	1.0	0.2								
89P 460S	15- 33	EG	6.5	84.1	9.4	5.3			57.0	27.1	8.6	0.7	0.1		0.1					TR	TR	
89P 461S	33- 60	E/BTNG	11.4	81.6	7.0	9.4			54.0	27.6	6.2	0.7								T		
89P 462S	60- 81	BTNG/E	15.1	76.9	8.0	11.0			58.6	18.3	7.3	0.7	0.1							T		
89P 463S	81-115	BTNG1	18.8	74.9	6.3	13.9			59.2	15.7	5.5	0.4								T		
89P 464S	115-147	BTNG1	23.8	71.4	4.8	17.6			55.7	15.7	4.2	0.3								TR		
89P 465S	147-190	BTNG2	30.8	64.2	5.0	23.4			45.2	19.0	4.7	0.3				0.2						
89P 466S	190-230	BCG	38.4	50.4	11.2	27.7			31.8	18.6	9.9	1.3								TR		
89P 467S	265-315	CG1	19.6	17.4	63.0	12.3			7.3	10.1	58.6	4.2	0.3							T		
89P 468S	315-325	CG2	39.5	37.1	23.4	20.4			19.6	17.5	20.6	2.7	0.1							T	3	
89P 469S	325-360	CG3	14.2	23.1	62.7	4.5			7.3	15.8	30.4	32.2	0.1								32	

		ORGN TOTAL EXTR TOTAL (- - DITH-CIT - -)(RATIO/CLAY)(ATTERBERG)(- BULK DENSITY -) COLE (- - -WATER CONTENT - -) WRD
		C N P S FE AL MN CEC 15 LL PI 1/3 OVEN WHOLE FIELD 1/10 1/3 15 WHOLE
DEPTH		EXTRACTABLE	BAR BAR 4F1 BAR DRY SOIL MOIST BAR BAR BAR SOIL
(CM)	6A1c 6B3a 6S3 6R3a 6C2b 6G7a 6D2a 8D1 8D1 4A3a 4A1h 4A1d 4A1h 4D1 4B4 4B1c 4B1c 4B2a 4C1
	PCT <2MM PPM <- PERCENT OF <2MM -> <- G/CC -> CM/CM <- PCT OF <2MM -> CM/CM

DEPTH (CM)	ORGN C 6A1c PCT	TOTAL N 6B3a <2MM	EXTR P 6S3 PPM	FE 6C2b	AL 6G7a	MN 6D2a	CEC 8D1	15 BAR 8D1	LL 4F1	PI 4F	1/3 BAR 4A3a	OVEN DRY 4A1h	WHOLE SOIL 4A1d	FIELD MOIST 4A1h	COLE WHOLE SOIL 4D1	1/10 BAR 4B4	1/3 BAR 4B1c	15 BAR 4B1c	WRD WHOLE SOIL 4B2a	4C1
0- 15	0.80	0.071		0.1	0.1	TR	0.82	0.56			1.45	1.54			0.020		25.9	3.4	0.33	
15- 33	0.20	0.017		0.1	0.1	TR	0.95	0.48			1.70	1.76			0.012		18.5	3.1	0.26	
33- 60	0.16	0.024		0.1	0.1	TR	0.82	0.48			1.63	1.73			0.020		21.3	5.5	0.26	
60- 81	0.09	0.011		0.1	0.1	TR	0.75	0.44			1.67	1.74			0.014		20.0	6.7	0.22	
81-115	0.06			0.2	0.2	TR	0.72	0.45			1.66	1.73			0.014		20.0	8.5	0.19	
115-147	0.04			0.3	0.3		0.67	0.43			1.64	1.72			0.016		21.0	10.8	0.17	
147-190	0.02			0.2	0.1		0.62	0.42			1.44	1.78			0.073		29.4	13.2	0.23	
190-230	0.02			0.1	0.2		0.59	0.42			1.41	1.96			0.116		32.0	16.2	0.22	
265-315	0.02			0.1	0.2		0.70	0.46										9.0		
315-325	0.02			0.1	0.3		0.70	0.46										18.2		
325-360	0.01			0.1	0.1		0.76	0.46										6.5		

AVERAGES, DEPTH 60-110: PCT CLAY 17 PCT .1-75MM 1

DEPTH 60-110: PCT CLAY 17 PCT .1-75MM 1

*** P R I M A R Y   C H A R A C T E R I Z A T I O N   D A T A ***

```
S88LA-019-001                                                                    PRINT DATE 08/24/92
SAMPLED AS    : BRIMSTONE            ; FINE-SILTY, MIXED, THERMIC TYPIC NATRAQUALF
USDA-SCS-NSSC-SOIL SURVEY LABORATORY ; PEDON 89P  41, SAMPLE 89P  459-  469
```

	-1--	-2--	-3--	-4--	-5--	-6--	-7--	-8--	-9--	-10-	-11-	-12-	-13-	-14-	-15-	-16-	-17-	-18-	-19-	-20-
	(- NH4OAC EXTRACTABLE BASES -)					ACID-	EXTR	(- -CEC- -)		EXCH	SAR	BASE		CO3 AS	RES.	CASO4 AS		(- - - -PH - - -)		
	CA	MG	NA	K	SUM	ITY	AL	SUM	NH4-	NA		SATURATION		CACO3	OHMS	GYPSUM		SAT	CACL2	H2O
DEPTH	5B5a	5B5a	5B5a	5B5a	BASES			CATS	OAC			SUM NH4OAC		<2MM	/CM	<2MM	<20MM	PASTE	.01M	
(CM)	6N2a	602d	6P2b	6Q2b		6H5a	6G9b	5A3a	5A8b	5B5b	5E	5C3	5C1	6E1g	8E1	6F1a	6F4	8C1b	8C1f	8C1f
	<- - - - - - - - -MEQ / 100 G - - - - - - - - - ->									PCT		<- -PCT- >		PCT		<- -PCT ->			1:2	1:1
0- 15	2.8	0.8	0.4	TR	4.0	3.4	0.1	7.4	5.0	4	4	54	88	TR				5.2	4.3	4.6
15- 33	3.8	1.6	0.6	TR	6.0	0.6		6.6	6.2	6	5	91	97					6.8	6.2	6.6
33- 60	5.4	3.1	1.0	TR	9.5	0.7		10.2	9.3	8	6	93	100					6.8	6.3	6.6
60- 81	5.9	3.9	1.2	0.1	11.1	0.3		11.4	11.3	8	7	97	98					6.7	6.3	6.4
81-115	7.1	5.0	1.3	0.1	13.5	0.3		13.8	13.6	7	6	98	99		1800			6.6	6.3	6.8
115-147	9.2	5.8	1.2	0.2	16.4	0.5		16.9	16.0	8		97	100						6.3	7.0
147-190	10.1	7.2	1.3	0.3	18.9	1.0		19.9	19.1	7		95	99						6.3	6.6
190-230	11.7	8.5	1.4	0.4	22.0	1.2		23.2	22.5	6		95	98						6.3	6.8
265-315	7.1	5.4	0.9	0.2	13.6	0.6		14.2	13.7	7		96	99						6.2	6.7
315-325	14.5	10.7	1.4	0.4	27.0	0.9		27.9	27.5	5		97	98						6.2	6.8
325-360	5.6	4.3	0.6	0.2	10.7	0.1		10.8	10.8	6		99	99						6.2	6.9

	CA	MG	NA	K	CO3	HCO3	CL	SO4	NO3	H2O	TOTAL SALTS EST.	ELEC. COND.
	(- - - - - - -WATER EXTRACTED FROM SATURATED PASTE- - - - - - - - -)											
DEPTH												8A3a
(CM)	6N1b	601b	6P1b	6Q1b	611b	6J1b	6K1c	6L1c	6M1c	8A	8D5	MMHOS
	<- - - - - - - - - -MEQ / LITER - - - - - - - - - ->									<- -PCT ->		/CM
0- 15	1.7	0.8	4.2	0.2	--	0.2	4.1	1.0	1.0	47.3	TR	0.81
15- 33	2.1	1.2	6.8	0.1	--	1.0	7.0	1.5	--	36.1	TR	1.11
33- 60	1.5	1.1	7.3	TR	--	0.7	7.2	1.7	--	43.5	TR	1.16
60- 81	1.0	0.9	6.6	TR	--	0.3	7.0	1.1	--	47.1	TR	1.03
81-115	0.9	0.7	5.5	TR	--	0.2	5.8	0.9	--	53.2	TR	0.86
115-147												0.20
147-190												0.20
190-230												0.18
265-315												0.15
315-325												0.12
325-360												0.06

MMHOS/CM OF 1:2 WATER EXTRACT (81) & EXCH NA AS EXTRACTABLE NA FOR LAYERS 6, 7, 8, 9, 10, 11,

ANALYSES: S= ALL ON SIEVED <2mm BASIS

*** P R I M A R Y   C H A R A C T E R I Z A T I O N   D A T A ***

S88LA-019-001
SAMPLED AS   : BRIMSTONE   ; FINE-SILTY, MIXED, THERMIC TYPIC NATRAQUALF   PRINT DATE 08/24/92
USDA-SCS-NSSC-SOIL SURVEY LABORATORY ; PEDON 89P 41, SAMPLE 89P 459- 469

```
            -1--  -2--  -3--  -4--  -5--  -6--  -7--  -8--  -9--  -10-  -11-  -12-  -13-  -14-  -15-  -16-  -17-  -18-  -19-  -20-
---------  -------------------------------------------------------------------------------------------------------------------------
           <- - - - - - - - - - - - - - - - - CLAY MINERALOGY (<.002mm) - - - - - - - - - - - - - - - - - - - - - - - >
           FRACT < - - - - - X-RAY - - - - - ->< - - - THERMAL - - - ->< - - - - - - - ELEMENTAL - - - - - - ->< - -> EGME  INTER
SAMPLE     ION <                               >< - DTA - ->< - TGA - -> SIO2 AL2O3 Fe2O3  MgO   CaO   K2O   Na2O <    > RETN  PRETA
           < - - - - - 7A2I - - - - - ->< - 7A6  - >< - 7A4b - >< - - - - - - - - - 7C3 - - - - - - - - - -><    > 7D2   TION
NUMBER     <- - >< - - - - peak size - - - - ->< - - - Percent - - - ->< - - - - - - - - - Percent - - - - - - - ->< - -><mg/g>< - ->

89P 462    TCLY  MT 4  KK 3  MI 1  QZ 1                                18.0   6.3                   0.4

---------  -------------------------------------------------------------------------------------------------------------------------
           < - - - - - - - - - - - - - - - - - SAND - SILT MINERALOGY (2.0-0.002mm) - - - - - - - - - - - - - - - - - >
           FRACT < - - - - - X-RAY - - ->< - - - THERMAL - - - ->< - - - - - - - - OPTICAL - - - - - - - - -><                > INTER
SAMPLE     ION <                         >< - DTA - ->< - TGA - ->TOT RE< - - - - - GRAIN COUNT - - - - - -><                > PRETA
           < - - - - 7A2I - - - - ->< - 7A3b - >< - 7A4b - >< - - - - - - - - 7B1a - - - - - - - - -><                > TION
NUMBER     < - -><   - - - Peak Size - - ->< - - - Percent - - - ->< - - - - - - - - Percent - - - - - - ->< - - - - - - -><  - ->

89P 462    VFS                                                 96  QZ95 FK 3  PO 1  OP    ZR    GS
89P 462    VFS                                                     FPtr  BTtr  TMtr  OTtr
```

FRACTION INTERPRETATION:

    TCLY Total Clay, <0.002mm   VFS   Very Fine Sand, 0.05-0.10mm

MINERAL INTERPRETATION:

    19   15   4   3   1   MT montmorill
    KK kaolinite   MI mica   QZ quartz   FK potas-feld   PO plant opal   OP opaques
    ZR zircon   GS glass   FP plag-feld   BT biotite   TM tourmaline   OT other

RELATIVE PEAK SIZE: 5 Very Large   4 Large   3 Medium   2 Small   1 Very Small   6 No Peaks

INTERPRETATION (BY HORIZON):

PEDON MINERALOGY
    BASED ON SAND/SILT:
    BASED ON CLAY:
    FAMILY MINERALOGY:
    COMMENTS:

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SOIL WATER RETENTION DEPTH CURVE
DATE: 11/17/89

CLAY SILT SAND BULK DENSITY
--PERCENT-- (AT 1/3 BAR)
6.1-81.2-12.7   1.45(G/CC)
6.5-84.1- 9.4   1.70(G/CC)
11.4-81.6- 7.0   1.63(G/CC)
15.1-76.9- 8.0   1.67(G/CC)
18.8-74.9- 6.3   1.66(G/CC)
23.8-71.4- 4.8   1.64(G/CC)
30.8-64.2- 5.0   1.64(G/CC)

ID(YR-S0): 890459 MEASURED
ID(YR-S0): 890460 MEASURED
ID(YR-S0): 890461 MEASURED
ID(YR-S0): 890462 MEASURED
ID(YR-S0): 890463 MEASURED
ID(YR-S0): 890464 MEASURED
ID(YR-S0): 890465 MEASURED

STATE: LOUISIANA
SOIL SERIES NAME: BRIMSTONE
HORIZON: AP   0- 15 CM
HORIZON: EG   15- 33 CM
HORIZON: E/BTN 33- 60 CM
HORIZON: BTN/G/ 60- 81 CM
HORIZON: BTNG1 81- 115 CM
HORIZON: BTNG1 115- 147 CM
HORIZON: BTNG2 147- 190 CM

1/10 BAR   1/3 BAR   2 BAR   15 BAR   SAT

VOLUME   PERCENT   WATER

DEPTH IN CENTIMETERS

0 10 20 30 40 50 60 70 80 90 100 110 120

0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360 370

USSL - PEDON NO.
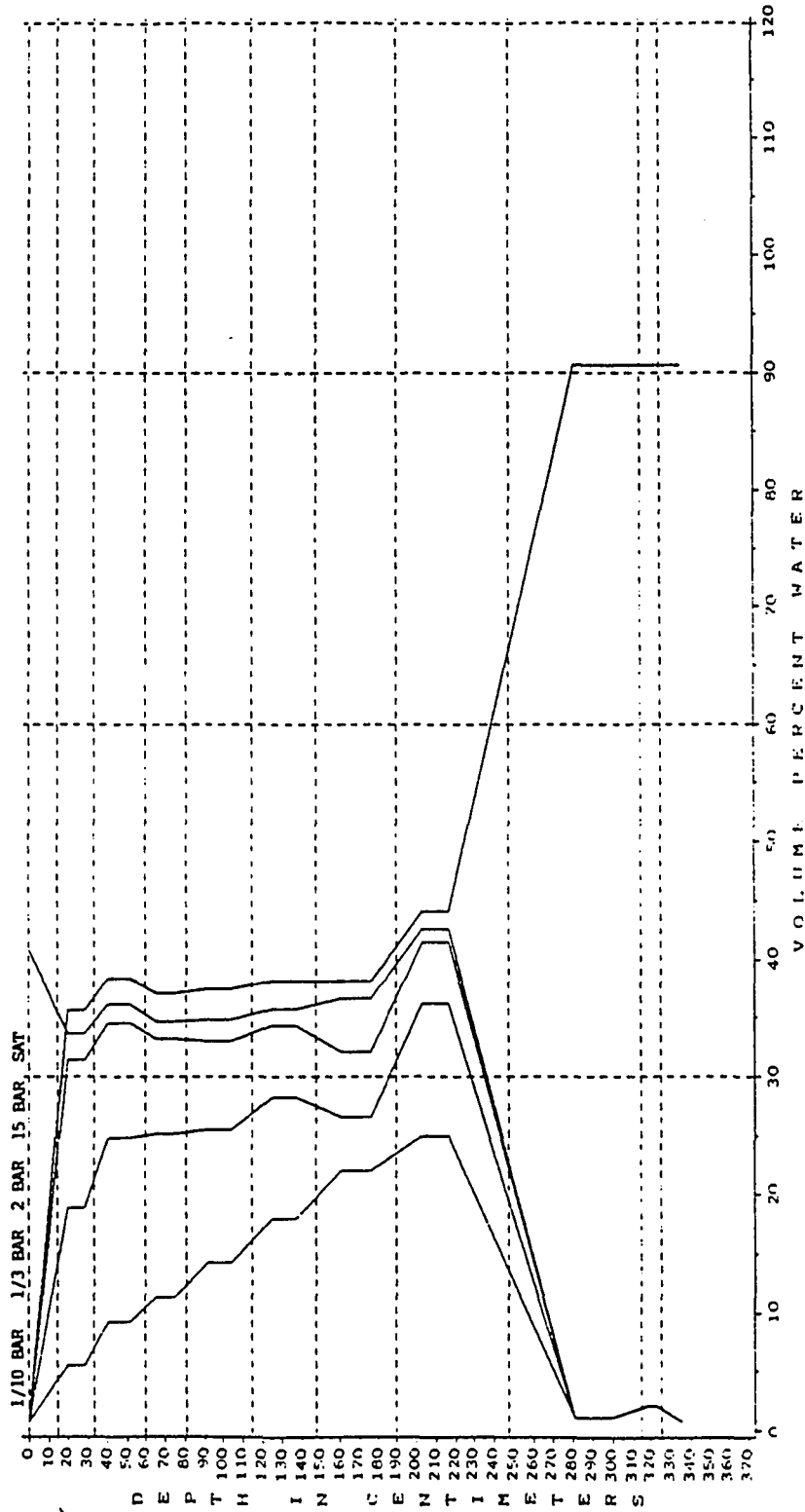
APPENDIX B

DESCRIPTION OF SOIL REDOXIMORPHIC FEATURES.

Redox Concentrations.

Definition: Bodies of apparent accumulation of iron-manganese oxides.

Nodules and concretions

Definition: Firm to extremely firm irregularly shaped bodies. When broken in half, concretions appear to consist of concentric layers organized around a point, whereas nodules have a uniform internal structure.

Quantity:	f	Few	< 2 %
	c	Common	2-20 %
	m	Many	> 20 %

Size:	fi	Fine	< 2	mm
	me	Medium	2-5	mm
	co	Coarse	5-20	mm
	vc	Very coarse	20-76	mm
	ec	Extremely coarse	> 76	mm

Shape:	rn	Rounded
	cl	Cylindrical
	pl	Platelike
	ir	Irregular

Color: Moist

Boundaries:	sh	Sharp	like knife edge
	cl	Clear	color grades over < 2mm
	di	Diffuse	color grades over than 2mm

Composition:	fe/mn	Iron/manganese	material dominated by iron or manganese oxihydroxides and oxides.
	fer	Ferruginous	if the substance impregnates other material to form the mass.
	man	Manganiferous	same as above.

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Masses:

Definition: Soft bodies with variable shape frequently within the matrix.

Quantity:	f	Few	< 2 %
	c	Common	2-20 %
	m	Many	> 20 %

Size:	1	Fine	< 5 mm
	2	Medium	5-15 mm
	3	Coarse	> 15 mm

Contrast: fa Faint same hue as ground color: masses differ < 1 chroma unit or < 2 value unit; different color from ground: masses differ only by 2.5 hue unit.

d Distinct same hue as ground color: masses differ 2 to 4 chroma units or 3 to 4 value units; different color from ground: masses differ by 2.5 hue units and < 1 chroma or < 2 value units.

p Prominent masses contrast strongly with the color to which they arte compared: > 5 hue units; > 4 value units if chroma is the same; > 1 chroma unit or > 2 value units if hue differs by 2.5 units.

Boundaries:	sh	Sharp	like knife edge
	cl	Clear	color grades over < 2mm
	di	Diffuse	color grades over than 2mm

Composition: fe/mn Iron/manganese material dominated by iron or manganese oxihidroxides and oxides.

fer Ferruginous if the substance impregnates other material to form the mass.

man Manganiferous same as above.

Color: Moist.

Shape:	st	Streaks	lines of a different color from the ground.
	bn	Bands	elongated surface or section with roughly paralell sides.
	tn	Tongues	elongated penetrations of materials with different color from the ground.
	sp	Spots	small irregular areas visibly different from the ground.

Pore linings:

Definition: they can be zones of accumulation along pores which may be either coatings on the pore surface or impregnations of the matrix adjacent to the pore.

Since pore linings are associated to pores, the description of pore linings is linked to the description of pores and comes after the description of pores.

Pores:

Quantity: Medium and coarse evaluated/dm^2
              Fine and very fine evaluated/cm^2

	1	Few	< 1 /unit area
	2	Common	1 - 5/unit area
	3	Many	> 5/unit area
Size:	vf	Very fine	< 0.5 mm in diameter
	f	Fine	0.5 - 2 mm in diameter
	m	Medium	2 - 5 mm in diameter
	co	Coarse	> 5 mm in diameter

Continuity:	dis	Discontinuous	pores are interrupted so that continuous passages larger than 0.1 mm at the smallest constriction are few or absent.

	cons	Constricted	pores are medium and coarse, with constrictions at least 2 size classes smaller than the pores; resultant passages larger than 0.1 mm.
	cont	Continuous	pores provide continuous passages, with few constrictions more than 1 class smaller than the pores described.
Orientation for tubular pores	ver	Vertical	most pores oriented within 45° of vertical.
	hor	Horizontal	most pores oriented within 45° of horizontal.
	ran	Random	neither vertical nor horizontal orientation predominates.
	obl	Oblique	pores oriented near a 45° angle to the vertical or horizontal.
Shape:	v	Vesicular	approximately spherical or elliptical; commonly enclosed and discontinuous.
	t	Tubular	approximately cylindrical; elongated in one direction.
	i	Irregular	irregular in shape and bounded by curved or angular surfaces of mineral grains or peds, or both.
Position:	in	Inped	within peds.
	ex	Exped	along interfaces between peds.

Linings:

Color: Moist

Boundary: Same as masses

Kind:	o	Organic
	s	Silt
	sf	Silt flow
	c	Clay
	fe	Iron

mn	Manganese
fer	Ferruginous
man	Manganiferous

Coating type:	ct	Coating	material that lines the surface of the pore.
	hc	Hypocoating	material that occurs immediately adjoining rather than on the surface with which they are associated.
	qc	Quasicoating	material that is related to the pore surface but not immediately adjoining it.

Depletions.

Definition: Bodies of low chroma (< 3) where Fe-Mn oxides alone have been stripped out, or where both iron-manganese oxides and clay have been stripped out.

<u>Redox depletions</u>

Quantity:

1	few	< 20 %
2	common	20 - 50 %
3	many	> 50 %

Size:

1	Fine	< 5 mm
2	Medium	5-15 mm
3	Coarse	> 15 mm

Contrast:	fa	Faint	same hue as ground color: depletions differ < 1 chroma unit or < 2 value unit; different color from ground: masses differ only by 2.5 hue unit.
	d	Distinct	same hue as ground color: depletions differ 2 to 4 chroma units or 3 to 4 value units; different color from ground: masses differ by 2.5 hue units and < 1 chroma or < 2 value units.

p   Prominent depletions contrast strongly with the color to which they arte compared: > 5 hue units; > 4 value units if chroma is the same; > 1 chroma unit or > 2 value units if hue differs by 2.5 units.

Shape: Streaks
Bands
Tongues
Spots
Pockets

Color: Moist.

Boundary: Same as masses.

Origin: fe   Iron depletion bodies which contain low amounts of iron and manganese oxides, but have clay contents similar to that adjacent matrix.

c   Clay depletion bodies which contain low amounts of iron, manganese, and clay along ped surfaces or lining channels.

Kind: in   Depletions within peds occupying a volume of soil.
ex   Depletions along surfaces of peds.

Reduced matrices

Definition: soil matrices that have a low chroma, but whose color increases in hue or chroma when exposed to air.

Original color   Moist color recorded immediately after the sample was taken.

Oxidized color   Moist color after exposition of the sample to the air.

Time for color change   short   within 30 minutes
long   more than 30 minutes.

Other Associated Features.

<u>Burrows:</u>

They are the result of pedoturbation produced by megafauna/flora. They are not different from coarse pores. Some times the macropores are so coarse that their quantity has to be evaluated per square meter.

<u>Krotovinas:</u>

They are irregular tubular streaks within one layer of material transported from another layer. They are caused by the filling of burrows or tunnels made by animals.

Describe quantity, orientation, size and infillings (banding, colors and texture).

<u>Cracks:</u>

They are non permanent voids formed in soils with swelling and shrinking clays. Describe their width, depth, orientation and type of redoximorphic features developed on their walls.

VITA

Ariel Alejandro Szögi was born on July 10, 1957 in Montevideo, Uruguay. He graduated from the Instituto Uruguayo de Estudios Preparatorios (High School) in 1974. He obtained his Ingeniero Agronomo (Agronomist) degree from the Faculty of Agronomy of the University of the Republic, Montevideo in 1983.

He began his professional career working for the Soil Directorate of the Ministry of Agriculture and Fisheries as a soil survey assistant. In 1983, he was promoted to soil scientist.

In 1985, he received an scholarship from the Ministry of Foreign Affairs of The Netherlands to study soil sciences. He obtained his M.S. with honors in Land Evaluation and Agropedology from Wageningen Agricultural University, The Netherlands in 1987.

He immigrated to the U.S. in 1988. He attended Louisiana State University in August, 1989 for advanced studies in soil sciences. He is presently a candidate for the degree of Doctor of Philosophy in Agronomy (Soil Science).

He is married and with his wife Gabriela has a ten year old son, Alejandro and an eight year old daughter Ana Laura.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Ariel A. Szogi

Major Field: Agronomy

Title of Dissertation: A Study on the Aquic Conditions of Two Natraqualfs on the Coastal Plain of Louisiana

Approved:

Wayne H. Hudnall
Major Professor and Chairman

Dan il Pagel
Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

October 29, 1992