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# Sustainable Land Management for the Oxisols of the Latin American Savannas

## Dynamics of Soil Organic Matter and Indicators of Soil Quality

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**Cover photograph:**

A medium-scale farmer shows off a paddock, planted with a *Brachiaria* grass, on his farm in the Brazilian *Cerrados*, Municipality of Prata, State of Uberlândia.

Photo by Eduardo Figueroa, CIAT.

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# Contents

# Preface

The Oxisols (Latosols or Ferralsols) cover around 46% of the tropics and are characterized by good physical structure but low fertility and high acidity. They are more susceptible to degradation than most soils, often degrading within 5 years of being opened for agricultural production. In Latin America, most of these soils are found in the Brazilian savannas or *Cerrados*. Brazil has opened up vast areas of this region, where around 46% of the area, or 98 million hectares, are Oxisols. As much as 40 million hectares of these areas are already suffering land degradation caused by the loss of soil organic matter, soil compaction and erosion, weed invasion, pests and diseases, contamination of rivers, destruction of native vegetation, and loss of biodiversity. To halt or reverse these trends, we need to know more about the dynamics of soil organic matter in Oxisols. This was the main objective of the project reported here.

To halt or reverse land degradation, farmers, extension workers, and policymakers need early warning signals of degradation as, by the time degradation is visible, the costs of remedial treatment are often too high to be implemented. In terms of soil indicators, measurements of bulk soil are often not sensitive enough to detect the initiation of the processes of degradation. This study investigated changes in the bulk soil and its fractions under different land uses to identify more sensitive parameters that could be used as early warning signals of land degradation.

The project has produced several potential indicators of soil quality for the major Oxisol types in the *Cerrados* (latossols vermelho-amarelo and vermehlo-escuro, according to the Brazilian system, and Anionic Acrustox and Typic Haplustox, after the USA system). These represent 18% of the *Cerrados* region. However, Oxisol taxonomy is incomplete and the findings need to be tested on a larger number of Oxisols and other soil types. We hope that this publication will stimulate further development and testing of soil quality indicators in the Latin American savannas to ensure that exploitation of these soils avoids the environmental damage experienced in other areas of the world where frontier expansion has proven to be unsustainable.

We thank Professor Wolfgang Zech and his students from the Institute of Soil Science and Soil Geography at Bayreuth University, Germany, for conducting most of the research in this project with great dedication and enthusiasm; the staff of EMBRAPA-CPAC and the Department of

Geography, Universidade Federal de Uberlândia, for technical and logistic support; and the farmers at Fazenda Santa Terezinha, Fazenda Bom Jardin, Fazenda Cossisa, Fazenda Cruzeiro, and Fazenda Pinusplan near Uberlândia, Minas Gerais, without whom this study would not have been possible.

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## CHAPTER 1

# Introduction: Sustainable Land Management for the Oxisols of the Brazilian *Cerrados*

*Henry Neufeldt**, *Wolfgang Zech**, and *Richard Thomas***

## Introduction

This publication is a unique collection of state-of-the-art scientific findings on the dynamics of soil organic matter (SOM) in the *Cerrados* of central Brazil. These extensive savannas comprise the second largest biome of South America and one of the world's most rapidly expanding agricultural frontiers. Land degradation has already occurred, making urgent a better understanding of the dynamics of land management, particularly of SOM, to ensure that the *Cerrados* are exploited sustainably, and that current trends toward further land degradation are reversed.

Such understanding will also be of value to other areas having similar soils and climate, for example, in Colombia, Venezuela, Bolivia (Vera et al. 1992), and even the Miombo woodlands of Africa, which cover about 100 million hectares in Angola, Zaire, Zambia, Malawi, Mozambique, and Tanzania (Sánchez 1997).

The research presented here is a result of collaboration among the Centro Internacional de Agricultura Tropical (CIAT), the Centro de Pesquisa Agropecuária dos Cerrados (CPAC) of EMBRAPA[1], the Department of Geography at the Universidade Federal de Uberlândia (UFU, Brazil), and the Institute of Soil Science and Soil Geography of Bayreuth University (BU, Germany). Financial support was provided by the German Agency for Technical Cooperation (GTZ) and the Soil, Water, and Nutrient Management Program of the CGIAR. CIAT's expertise on tropical land-use systems, CPAC and UFU's expertise and knowledge of the *Cerrados*, and that of BU in SOM studies were brought together under one project.

Each contribution to this publication can be read separately, as it covers important aspects of sustainable land use. The articles are linked, however, by the fact that all studies were carried out on two sites only: one at the CPAC experiment station near Brasília and the other on a farm, near the city of Uberlândia and where the same conventional and improved land-use systems were used. Results can therefore be compared directly. The articles are also brought together in that they form the basis on which conclusions are drawn up and future research needs are identified.

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[1] For an explanation of this and other acronyms, see "Acronyms and Abbreviations Used in the Text", pages 228-231.

*Keywords:* Brazilian savannas, *Cerrados*, Oxisols, soil organic matter

## Background and Research Problem

Only 3 decades ago, the *Cerrados* were regarded as unsuitable for agriculture because of their harsh climate and poor soils. Since then much has changed and today the *Cerrados* are among the world's most highly productive agricultural frontiers. One quarter of Brazil's grain and 40% of its beef are produced there (Alho et al. 1995; Garda 1996). The cultivated area tripled from 10 million hectares in 1970 to 30 million hectares in 1985, and this figure will be doubled again by the end of the millennium (Alho et al. 1995; Goedert 1983). This enormous expansion was accomplished with the introduction of improved agricultural methods, government subsidies, and heavy investments in fertilizers and machinery. Much of the advance in knowledge was accompanied by pioneering research from CPAC.

Although decreasing, population growth rates are still elevated, and rapid urbanization has changed the formerly rural country into a nation of city dwellers with more than 75% of its population living in the cities. High agricultural growth rates and competitiveness are therefore needed to keep up with increasing food demands and to reduce Brazil's external debts through exports of agricultural products.

The necessary growth rates can only be achieved by either cultivating less accessible *Cerrados* soils and expanding the agricultural frontier into the Amazonian rain forest or by intensifying land use on soils already under cultivation (Villachica et al. 1990). Furthermore, the technologies in use have proven to be unsustainable. Soil organic matter contents have gradually decreased, reducing soil fertility (Silva et al. 1994), and excessive seedbed preparation has led to the destruction of the favorable physical soil structure, accompanied by subsoil compaction and soil sealing that eventually promoted severe erosion, even on gentle slopes (Klink et al. 1993). Soil preparation and cultivation techniques therefore need to be adapted to the *Cerrados* soils to reverse degradation while maintaining high yields.

## Sustainable Land Use

The term "sustainability" appears in most research proposals and projects but the debate on its definition continues. At the 1996 ISCO conference, entitled "Towards Sustainable Land Use", a definition of sustainability could not be agreed upon (Fleischhauer and Eger 1998). Instead, the great diversity of approaches indicated that sustainability cannot be understood via technical definitions alone.

Sustainability varies according to perspective and to the scale at which processes are observed. For example, no-tillage systems are considered highly sustainable at site level because, in contrast to mechanized seedbed preparation, they do not degrade soil structure. But they require much higher biocide applications than conventionally managed soils and thus may not be sustainable at the watershed level because they may significantly increase the levels of biocides and metabolites in ground water. This suggests that sustainability must be viewed holistically. When social and economic aspects are considered, the definition of sustainability becomes more complex. In Brazil, land use is unsustainable because smallholders have no access to bank credit to buy fertilizers and thus augment their yields, feed their families, and educate their children. Yet their form of land use is more sustainable in ecological terms because they have no heavy equipment to seal the topsoil and thus lead to widespread erosion.

One research project certainly cannot cope with all aspects of sustainability. The project reported here is necessarily restricted to the technical side of managing soils. Consequently, smallholder land-use systems are not the center of interest. Instead, intensively managed cash crops like maize and soybean, but also pastures for beef and milk production and tree plantations for cellulose production are studied. One could argue that if no effects are apparent in intensively managed systems, then similar problems are unlikely to occur in smallholder land use. Management effects that become visible after intensive cultivation could be of significance for smallholders.

To study the effects of different land-use systems, it is important to identify sensitive and significant indicators that will allow estimates of the sustainability of the land-use systems under study. These estimates would naturally be relative because a reference (or "control") must exist with which to compare systems. For soils in the *Cerrados*, this control is likely to be the natural vegetation, because it is adapted to the prevalent climatic and edaphic conditions. Therefore, sensitive and significant indicators in this context are those that identify, at an early stage, management-induced changes leading to soil degradation in relation to the native savanna.

## Aspects of Sustainability of Land-Use Systems Found in the *Cerrados*

Soil organic matter is considered key to sustainable management of the highly weathered soils that typify the *Cerrados* because it stands at the center of both chemical and physical soil properties. Thus, 17 of the book's 19 chapters discuss processes that are directly or indirectly linked to SOM. The exceptions are the article on soil genesis and landscape evolution of the study area near Uberlândia (Chapter 2) and the article on biocides (Chapter 18).

### *Improved land-use systems*

In the humid and subhumid tropics, where high temperatures and precipitation have led to variable-charge dominated soils with low exchange capacities, SOM is even more important than in most soils of temperate regions because it serves both as the most important nutrient sink and nutrient source (Coleman et al. 1989). Agricultural activities should therefore strive to maintain SOM contents through adequate crop/pasture rotations, tillage, or agroforestry systems. CIAT has developed promising techniques for the recuperation of degraded soils by introducing legume-based pastures and crop/pasture rotations on acid savanna soils (CIAT 1992; Vera et al. 1992). These systems are based on the beneficial synergistic effect on both productivity and soil when annual and perennial species are combined (Lal 1991; Spain et al. 1996; Thomas et al. 1994). In Chapter 3, the effects of these introduced land-use systems on productivity in Oxisols of the *Cerrados* are described.

## *Aggregation in Oxisols of the* Cerrados

The close relationship between soil aggregation and SOM has been reported repeatedly (Degens 1997; Tisdall and Oades 1982). Mechanized seedbed preparation leads to a disruption of macroaggregates and, subsequently, to a loss of SOM through increased mineralization (e.g., Beare and Bruce 1993). No-tillage systems and pastures are therefore more sustainable in terms of aggregate stability than conventional tillage systems (Gijsman 1996). Liming has been shown to affect clay dispersion and thus aggregation of Oxisols as well (Castro Filho and Logan 1991; Roth and Pavan 1991). This can be explained by an elevated surface charge and concomitant reduction of the electrostatic intra-aggregate bondings between SOM and Fe and Al oxyhydroxides (Bartoli et al. 1992; Gillman 1974; Tama and El Swaify 1978). The influence of selected typical and improved savanna land-use systems on aggregation are described in Chapters 4, 5, 6, and 7.

Chapter 4 gives an overview of the main physical and chemical properties of selected Oxisols, and emphasizes the effect of land use on the interactions of flocculation and water retention characteristics. In Chapter 5, land-use effects on water-stable aggregates are studied and related to the main aggregating agents of these soils. In addition, the chemical composition between aggregates of different sizes was analyzed to test the hypotheses of Oades and Waters (1991) on aggregate hierarchy in Oxisols. In Chapter 6, the interactions between plowing, liming, and loss of SOM were studied, using laser grain-size analysis to establish a hierarchy of aggregating effects and determine the size ranges of aggregates in Oxisols of the *Cerrados*. Chapter 7 addresses the short-term variation of aggregation. Special emphasis is given to differently accessible pools of particulate organic matter as binding agents of macroaggregates, which might be used to characterize land-use systems.

## *The significance of soil organic matter*

Despite the high significance of SOM for soil fertility and aggregate stability, SOM contents in whole soil samples are frequently not sufficiently sensitive to characterize SOM dynamics in soils because SOM ranges from undecomposed plant fragments to highly humified organic substances that differ greatly in turnover and characteristics. Differently available fractions of SOM may explain conflicting results concerning the depletion of SOM in cropped savanna soils (Mendonça and Rowell 1994; Nascimento et al. 1991; Resck et al. 1991; Silva et al. 1994).

It is therefore important to group SOM with similar characteristics and turnover rates in pools of different activities.

This pool concept has already been taken into account with good results in all models that attempted to simulate SOM dynamics in temperate soils (Parton et al. 1987; Paul 1984; Smith 1979). However, the well-known CENTURY model has not adequately simulated SOM dynamics in highly weathered soils (Gijsman et al. 1996). Turnover rates different to those used for temperate soils and, possibly, SOM compounds in other proportions have to be considered.

Because few studies have taken the heterogeneity of SOM into account for savanna soils, little information exists on these aspects of SOM dynamics. In Chapters 8, 9, and 10, the dynamics of soil organic matter in typical and improved land-use systems of the

*Cerrados* are therefore discussed in terms of differently active SOM pools and of SOM quality. Two basic approaches were chosen to deal with the heterogeneity of SOM: (1) the separation into primary organo-mineral complexes by particle-size fractionation (Christensen 1992), and (2) a chemical separation by oxidation with $KMnO_4$ (Blair et al. 1995). Both approaches separate labile from stable SOM fractions and allow the quantification of SOM compounds as they are affected by land use.

In Chapter 8, land-use effects on soil organic carbon, polysaccharides, and lignin in particle-size separates are described and related to the soils' water retention characteristics and texture. In addition, the transformation of these compounds during SOM degradation are highlighted and discussed with respect to sustainable land use.

Chapter 9 shows the effects of improved land-use systems on amino sugars and correlates them with the amount of potentially mineralizable N (Keeney 1982). Nitrogen is a limiting element and is needed for biomass production, whereas amino acids are a source of easily mineralizable organic N. Moreover, amino acids of different decomposer communities can be used to distinguish between SOM decomposition by bacteria and that by fungi. In Chapter 10, $KMnO_4$ oxidation and water-extractable organic carbon are used to evaluate short-term effects on biological activity and nutrient availability for the selected land-use systems.

## *Nitrogen dynamics in Oxisols of the* Cerrados

In Chapters 11 and 12, oxidation with $KMnO_4$ was also used to assess nitrogen availability in selected soils and characterize the nitrogen fractions oxidized. During plant decomposition, organic N is mineralized and made available again for plant uptake. The amount of mineralizable organic N is strongly management dependent and affects the productivity of the land-use systems. The nitrogen management index, established in analogy to the carbon management index (Blair et al. 1995), closely correlated with mineralizable N and, in the future, might thus be used as a simple but, nevertheless, sensitive indicator of nitrogen availability.

## *Phosphorus dynamics in soils of the* Cerrados

Low phosphorus supply is well known to be a major agronomic constraint in the highly weathered soils of the *Cerrados* (Goedert 1983; Leal and Velloso 1973), caused by the strong phosphate sorption to Fe and Al oxyhydroxides (Fontes and Weed 1996; Mesquita Filho and Torrent 1993). Agricultural practices that allow a reasonable economic return are therefore possible only after heavy applications of P fertilizer (Sousa and Lobato 1988). Yet, little is known about phosphorus cycling in soils of the *Cerrados* because, in the past, only readily available P was determined (Sousa and Lobato 1988). According to Stewart and Tiessen (1987) and Beck and Sánchez (1994), this may not effectively reflect plant-available P because organic fractions are believed to contribute proportionately more with increasing P deficiency. A sequential P fractionation (Hedley et al. 1982) that consecutively extracts more recalcitrant P fractions has therefore been applied to temperate soils with good results, whereas data on tropical soils are still scarce (Cross and Schlesinger 1995). Therefore, in Chapters 13 and 14 soil phosphorus dynamics are studied.

In Chapter 13, P cycling in particle-size separates and whole-soil samples are discussed to estimate the relevance of organic P forms to plant nutrition and follow the dynamics of labile and recalcitrant inorganic phosphorus. In this context, the ratio of bioavailable inorganic P to organic P is introduced as a sensitive indicator of the status of P in soils. Chapter 14 deals with P transformations in different aggregate fractions and analyzes the structural differences of organic P with $^{31}$P NMR.

### *Microbial parameters in Oxisols of the* **Cerrados**

According to Carter (1986), microbial parameters indicate land-use changes very quickly. This is probably because microbial activity is strongly related to water-extractable organic matter, a very labile C pool of soils (McGill et al. 1986; Zsolnay 1996). In particular, the ratio of microbial C to total organic C is believed to be a sensitive indicator of future soil degradation or amelioration (Anderson and Domsch 1989) but, for the *Cerrados*, no information on microbial parameters are available. In Chapters 15 and 16, the relationship of SOM to microbial biomass and microbial activity is established for conventional and improved land-use systems in the *Cerrados*, giving priority to the question of whether these parameters would serve as indicators of sustainable land use.

### *The significance of termites for the* **Cerrados**

Another important question is posed by the occurrence of termites in the *Cerrados* ecosystem. Numerous studies have been done on their ecology and biology (Coles de Negret and Redford 1982; Godinho et al. 1989; Gontijo and Domingos 1991; Raw 1996). But little is known about the role of termite mounds as potential sinks and/or sources of carbon and nutrients, or their role in the dynamics of SOM (Anderson and Flanagan 1989). These questions are important for evaluating the relevance of termites for *Cerrados* soils. So far, termites are treated as pests only, feeding on crops and forage grass, and their mounds are considered as obstacles to machinery. Hence, they are controlled with pesticides and their mounds destroyed. Any potentially beneficial influence has not yet been foreseen and little interest has been shown in understanding their significance for the ecosystem (MLRCL Assad 1997, personal communication). But, because termites are ubiquitously found throughout the *cerrados* biome, an article on the relationship between termites and SOM is included in Chapter 17.

### *Biocides in soils of the* **Cerrados**

Other aspects of sustainable land use in the *Cerrados* have only recently received more attention. For example, the question of whether the increasing use of biocides in the *Cerrados* has implications for contaminating the water table or soils has been little studied (Schneider 1996). The growing relevance of no-tillage systems in the *Cerrados* has also made higher application rates of herbicides necessary. However, no methods for quantifying biocides in tropical soils in the field exist (V Laabs 1997, personal communication). Sensitive methods are therefore needed to quantify biocides and their derivatives in soil and water samples and to monitor their distribution. The biocide concentrations on-site and in the aquifers could then be quantified and eventually biocide dynamics in the soils evaluated to foresee possible dangers for the environment and human health (Chapter 18).

Finally, a concluding chapter synthesizes the results obtained in this project and additional information from

CIAT's studies in the Colombian savannas is considered in terms of identifying potential soil quality indicators.

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# CHAPTER 2

# Oxisol Development along a Compound Catena of the Araguari River, Central Brazil

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## Abstract

Several Oxisols, containing different parental materials, were studied along a compound catena of the Araguari River, central Brazil. Their development, age, and genetic features were analyzed by morphological, chemical, and mineralogical methods. Results indicated continuously decreasing weathering from tableland (also known as *chapada*) to valley floor. Soils on the *chapada* probably developed during middle and upper Tertiary, and are considered relict. Their different types of quartz sand clearly show that they derive from pre-weathered sediments of distinct locations, suggesting a polygenetic origin that may reach as far back as the Cretaceous. Soils on the pediment, inserted into the slope toward the Araguari River, developed in situ and may have been formed at the beginning of Pleistocene but still indicate ongoing ferralitization. A ferralitized paleosol that developed in situ near the river's present base level is apparently from late Pleistocene. Recent pedological processes are characterized by strong leaching and hillwash.

*Keywords:* Central Brazil, landform evolution, Oxisol development, paleosols

## Introduction

Oxisols are strongly weathered soils. The dominant chemical process in their formation is desilication (or ferralitization), leading to the nearly complete dissolution of weatherable minerals and the relative accumulation of stable secondary minerals in the clay fraction, particularly kaolinite, gibbsite, goethite, and hematite. This very slow process requires high temperatures and leaching rates, so that Oxisols are highly restricted to humid and subhumid climates of the tropics and subtropics (Buol et al. 1997).

Aubert (1960, cited in Buol et al. 1997) reported a formation rate of 75 millions of years (Ma) for an Oxisol 1 m deep in Africa. Leneuf (1959, cited in Maignien 1966) believed that 20 to 192 Ma would be sufficient for Oxisol formation, depending on parent rock and climate. But most Oxisols are probably much older, especially those that occur on old planation surfaces that reach as far back as the Mesozoic (Alexandre and Alexandre-Pyre 1987; Bourman et al. 1987; O'Connor et al. 1987). However, age determination

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of Oxisols is frequently difficult because datable material is scarce or absent.

Moreover, many Oxisols have a polygenetic origin (Bremer 1967), that is, the soil developed from the transported pre-weathered sediments of an earlier soil formation. And because almost all weatherable minerals have long since been desilicated, they do not evolve any more, regardless of current climatic conditions. Hence, many Oxisols must be regarded as relict end products of weathering. This explains why many Oxisols are found under climatic conditions that do not support their formation (Buol et al. 1997). Assuming several erosion cycles during geological times, Stoops (1989) also believes that the origin of most Oxisols is polygenetic. Nonetheless, many Oxisols have shown to be currently developing in situ (see review by Maignien 1966).

Little is known about the genesis of Oxisols in central Brazil, or of their age and possible polygenetic origin. However, based on profile discontinuities, some authors have suggested a climatically induced, polycyclic soil development on planation surfaces (Emmerich 1988; Lichte 1990; Semmel and Rohdenburg 1979).

In this paper, we discuss the results of morphological, chemical, and mineralogical analyses conducted to determine the genetic properties of Oxisols found along a compound catena of the Araguari River in central Brazil. The studied area contained a wide variety of geological formations on a small scale, thus providing a source of potentially valuable information about the weathering, age, and origin of Oxisols derived from different parental materials.

# Materials and Methods

## *Study area*

The study area is located close to Uberlândia, Minas Gerais State, and belongs to the southern part of central Brazil (Figure 1). The average annual temperature is 22 °C, with a maximum in October and a minimum in July. Mean annual precipitation is 1650 mm, 90% of which falls in the rainy season from October to April. Natural zonal vegetation is *cerrado*, typical of the Brazilian savannas (Eiten 1972). Gallery forests and palm groves occur along watercourses. Extensive pastoralism, highly mechanized agriculture, and reforestation are the dominant land-use systems (Neufeldt 1998).

## *Geological and paleoecological setting*

The study area is situated at the northeastern border of the Paraná sedimentation basin, which formed when the Arcane Goiânia base and Proterozoic sediments of the Araxá Group were lowered during Devon (Schobbenhaus et al. 1984). At the end of the Jurassic and lasting throughout the Cretaceous, the basin was filled with vast basalt layers of the Serra Geral Formation. Beginning in the Neocretaceous, the sandy sediments of the Bauru Group (to which the Adamantina and the Marília Formations belong) were deposited under semiarid to arid conditions in function of the Alto Paranaíba uplift (Sad et al. 1971). After the tectonic processes had calmed down, the sediments were leveled to the South American surface, which is characteristic of large areas of central Brazil (King 1956). During mid-Tertiary, fine sediments were deposited on top of the leveled Marília sandstones under humid tropical conditions (Nishiyama 1989), followed

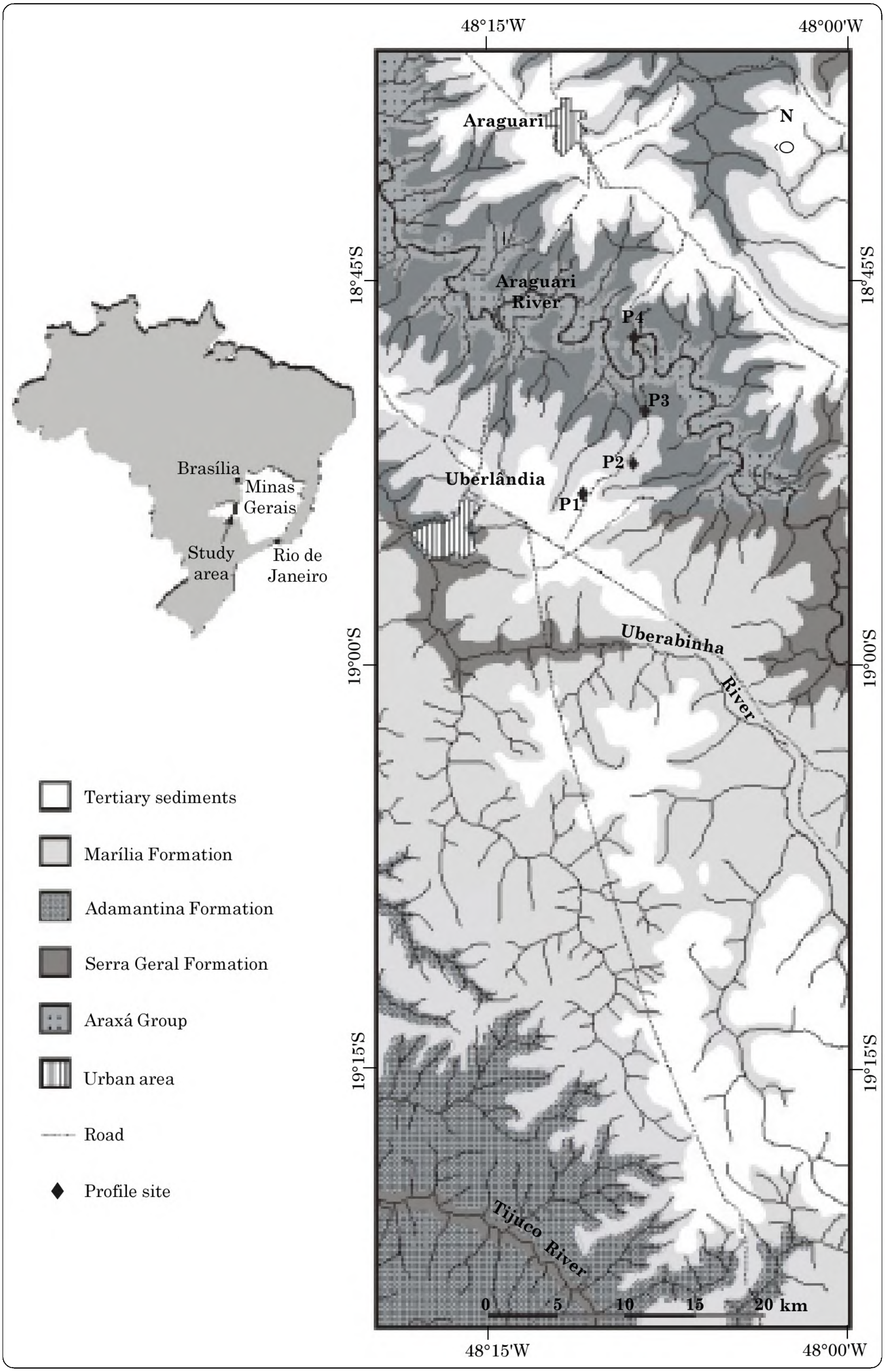

Figure 1. Geology of the study area in southern central Brazil.

by a drier climate and the installation of the *cerrado* biome (Wolfe 1971). After tectonic reactivation and further climatic changes between the Oligocene and the Miocene, the planation surface was dissected and ultimately lowered during the so-called Velhas cycle (King 1956). In the study area, the Velhas surface only forms a pediment inserted into the Araguari River valley and sustained by the Serra Geral basalts (Baccaro 1994). Finally, Quaternary changes between semiarid and humid phases, in synchrony with ectropical cooling and warming cycles, formed several pediments and terraces at different base levels (Bigarella and Mousinho 1966), eventually dissecting the existing planation surfaces strongly and leaving only minor remnants of a formerly homogenous landscape.

Outcrops of the Arcane base and the Araxá Group, mainly granites, gneisses, and schists, appear only close to the current base level of the Araguari River, whereas the Serra Geral basalts above are also uncovered by the river's larger tributaries (Figure 1). The Marília sandstones are exposed along all minor watercourses and therefore represent the most common parent material in the study region. Because the Tertiary sediments do not exceed 20 m in thickness, they are restricted to the top of the tablelands, or *chapadas*.

### *Location of soil profiles and sampling procedures*

The soils were selected along a catena from tableland to valley floor of the Araguari River, and cover the main geological units (Figure 1). Profile P1 was located on clay-rich Tertiary sediments and P2 was on the sandy Marília Formation. Profiles P3 and P4 were located on Serra Geral basalt and Araxá mica-schist, respectively. For greater comparability, only soils with pasture vegetation were selected. Samples were taken from all horizons, air dried, and sieved through a <2-mm mesh to obtain the fine-earth fraction.

### *Analytical methods*

Analyses were carried out on air-dried samples of the fine-earth fraction. Bulk density was determined gravimetrically from soil cores dried at 105 °C. Grain-size analysis was done with the sieve-pipette method after dispersion in 0.1 *N* NaOH. Then $C_{org}$ and N were measured with a CN-analyzer (Elementar Vario EL). Soil pH was determined in $H_2O$ and 1 *M* KCl at a soil-to-solution ratio of 1:10. The effective cation-exchange capacity ($CEC_e$) was determined according to EMBRAPA (1979). Total Fe, pedogenic Fe, and X-ray amorphous Fe were extracted, following Lim and Jackson (1982), Mehra and Jackson (1960), and Blume and Schwertman (1969), respectively, and detected by atomic absorption spectrometry (Shimadazu AA-660). A D5000 X-ray diffractometer (Siemens) was used for X-ray diffraction (XRD) of $MgCl_2$-treated clay. Identification of the reflections followed Brown and Brindley (1980). Polarization microscopy was applied to thin sections of the fine- and coarse-sand fractions.

## Results and Discussion

### *Morphological and chemical characterization*

Profiles P1, P2, and P3 were classified as Oxisols according to *Soil Taxonomy* (Soil Survey Staff 1994), and showed the typical morphological characteristics, that is, an "earthy" feeling, created by a strong microstructure despite high clay contents, and a very low bulk density, which leads to excellent drainage (Table 1). Profile P4 was a Mollisol but a ferralitized horizon (2C/Bw) below a stone line, containing about 70%

ssification, coordinates, and main analytical data of the soils from the Araguari River catena, central Brazil.

| *oil subgroup*<br>position | Horizon | Depth (cm) | Color[a] (moist soil) | pH |  | $C_{org}$ (g/kg) | C/N ratio | Specific $CEC_e$ ($cmol_c$/kg) | Bulk density (g/cm$^3$) | Grain-size distribu |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | $H_2O$ | KCl |  |  |  |  | >2/<2 | Sand | S |
| *Acrustox* | Ap | 0-20 | 7.5 YR 3/4 | 5.3 | 4.7 | 24.8 | 18 | 2.48 | 0.87 | -/100 | 19 | 1 |
| , 18°54'36"S | A2 | 20-40 | 7.5 YR 3/6 | 5.5 | 4.5 | 16.8 | 18 | 1.10 | 0.91 | -/100 | 15 | 1 |
| ° | BoA | 40-63 | 6.3 YR 3/6 | 5.2 | 4.6 | 13.3 | 18 | 0.35 | 0.89 | -/100 | 15 | 1 |
|  | Bo | 63-150+ | 5.0 YR 3/6 | 5.1 | 5.2 | 10.1 | 18 | 0.17 | 0.85 | -/100 | 16 |  |
| *plustox* | Ap | 0-18 | 10.0 YR 3/4 | 5.4 | 4.5 | 7.7 | 17 | 1.30 | 1.23 | -/100 | 81 |  |
| 18°52'12"S | A2 | 18-30 | 10.0 YR 3/5 | 5.4 | 4.4 | 6.3 | 17 | 0.65 | 1.24 | -/100 | 81 |  |
| E 2° | BoA | 30-55 | 10.0 YR 3/6 | 5.3 | 4.3 | 5.4 | 18 | 0.44 | 1.28 | -/100 | 80 |  |
|  | Bo | 55-155+ | 7.5 YR 3/6 | 5.3 | 4.6 | 4.0 | 18 | 0.11 | 1.16 | -/100 | 77 |  |
| *aplustox* | Ap | 0-20 | 10.0 R 3/2 | 5.2 | 4.2 | 18.7 | 14 | 3.96 | 0.99 | 5/95 | 12 | 2 |
| 18°49'48"S | Bo | 20-90 | 10.0 R 3/2 | 5.3 | 4.4 | 5.3 | 15 | 1.79 | 0.88 | -/100 | 7 | 2 |
| E 4°-5° | Bo/C | 90-185+ | 10.0 R 3/2 | 5.3 | 4.0 | 2.4 | 13 | 7.18 | 0.80 | 25/75 | 9 | 3 |
| *plustoll* | Ap | 0-20 | 10.0 YR 2/2 | 5.8 | 4.6 | 24.5 | 13 | 6.93 | 1.33 | 5/95 | 59 | 1 |
| 18°47'24"S | Bw | 20-45 | 10.0 YR 3/3 | 6.2 | 5.0 | 13.9 | 14 | 6.25 | 1.47 | 10/90 | 60 | 1 |
| ° | 2C/Bw | 45-60 | 7.5 YR 3/4 | 6.4 | 5.1 | 11.1 | 14 | 5.69 | n.d.[b] | 70/30 | 60 | 1 |
|  | 3Bo | 60-105 | 5.0 YR 3/6 | 6.7 | 5.5 | 4.9 | 15 | 4.76 | 1.61 | -/100 | 49 | 1 |
|  | 3Bw | 105-145 | 10.0 YR 4/4 | 6.7 | 5.1 | 2.4 | 15 | 6.79 | 1.53 | -/100 | 72 | 2 |
|  | 3CB | 145-245+ | 10.0 YR 4/4 | 6.9 | 4.8 | 0.2 | _ | 6.24 | 1.31 | -/100 | 86 | 1 |

r color according to Munsell Color Company (1975).
etermined.

quartz gravel, indicated advanced soil weathering at a former time. According to a soil survey in the study area, hillwash and hillslide are common along the slopes (EMBRAPA 1982). Soil weathering was usually indicated by the soils having redder hues, higher color saturation, and increasing clay contents toward the horizons with maximum weathering (Bo horizons). However, profile P3 showed no change in color whatsoever, probably because of the dark bedrock.

Considering only Bo horizons, the degree of soil weathering was greatest in P1 and decreased toward the valley floor. This was indicated by an increasing specific $CEC_e$ ($CEC_e$ per kg clay) and a rising $\Delta pH$ ($pH_{KCl}$ - $pH_{H_2O}$) in the respective Bo horizons. A low specific $CEC_e$ is characteristic of variable charge clays while a high $\Delta pH$ reflects the presence of secondary Fe and Al oxyhydroxides, which may result in a net positive charge of the exchange complex. Near the weathering front of P3 and P4, the specific $CEC_e$ rose again (Table 1) considerably, reflecting the reduced soil development. For P3, this was also indicated by the presence of strongly decomposed basalt cherts (25% of contents) in horizon Bo/C.

Total Fe ($Fe_t$) was closely related to the parent substrate, whereas pedogenic Fe depended on both substrate and weathering degree (Table 2). Dithionite-extractable Fe ($Fe_d$) was more than 50% of $Fe_t$, except near the weathering front of P4, suggesting an overall advanced stage of soil development (Arduino et al. 1984). Oxalate-extractable Fe ($Fe_o$) was partly dependent on substrate, but normally decreased with depth because the higher organic matter contents in the surface horizons reduced crystallization by complexation (Schwertmann and Taylor 1989). $Fe_o$ increased again near the weathering front of P3 and P4 due to freshly liberated primary Fe. The $Fe_o/Fe_d$ ratio (Alexander 1974; Aniku and Singer 1990) was therefore always lowest in

Table 2. Iron contents (in g/kg) and weathering indices ($Fe_d/Fe_t$, $Fe_o/Fe_d$)[a] from the Araguari River catena, central Brazil.

| Profile no., Soil subgroup | Horizon | $Fe_t$ | $Fe_d$ | $Fe_o$ | $Fe_d/Fe_t$ ($\times 10^2$) | $Fe_o/Fe_d$ ($\times 10^3$) |
|---|---|---|---|---|---|---|
| P1, Anionic Acrustox | Ap | 82 | 54 | 1.8 | 66 | 33 |
| | Bo | 87 | 58 | 0.6 | 67 | 10 |
| P2, Typic Haplustox | Ap | 28 | 16 | 0.8 | 57 | 50 |
| | Bo | 33 | 19 | 0.3 | 58 | 16 |
| P3, Rhodic Haplustox | Ap | 246 | 151 | 3.3 | 61 | 22 |
| | Bo | 262 | 159 | 3.6 | 61 | 19 |
| | Bo/C | 264 | 144 | 4.1 | 55 | 28 |
| P4, Typic Haplustoll | Ap | 36 | 17 | 3.3 | 47 | 194 |
| | Bw | 39 | 16 | 2.7 | 41 | 169 |
| | 2C/Bw | 54 | 21 | 1.7 | 39 | 81 |
| | 3Bo | 60 | 33 | 1.4 | 55 | 42 |
| | 3Bw | 70 | 18 | 1.1 | 26 | 61 |
| | 3CB | 93 | 19 | 1.4 | 20 | 74 |

a. Mur ratio $Fe_d$ = dithionite-extractable iron; $Fe_t$ = total iron; $Fe_o$ = oxalate-extractable iron.

the horizon of maximum soil development and increased where crystallization was either inhibited or where the weathering activity was high. Hence, the $Fe_o/Fe_d$ ratio of the Bo horizons can be used to compare the weathering degree of the soils under study. According to the results, weathering degree continuously decreased from the tableland to the valley floor, apparently corresponding to soil formation along with valley incision.

### *X-ray diffraction analysis*

The results of the XRD analysis showed a complete absence of weatherable primary and secondary minerals and a predominance of kaolinite and gibbsite, thus indicating an extreme degree of weathering in P1 and P2 (Table 3). Profiles P1 and P2 should therefore be considered stable end products of weathering because the soils will not develop any further, regardless of prevailing climatic conditions.

In P3, weathering was slightly less advanced, as reflected by the presence of illites, while the high contents of hematite can be attributed to the soil's parental material. The mineralogy of P3 therefore seems to support the hypothesis of ongoing Oxisol formation in the subsoil because the illites and basalt cherts permit continued desilication under the current subhumid tropical climate.

Although the strong reflections of illite and biotite indicate a much lower weathering degree than in the other profiles, chemical weathering in P4 must be considered as advanced, because of the high contents of kaolinite and gibbsite. Their presence suggests high leaching rates under the present climate and, according to Bowden (1987), strongly pre-weathered bedrock. The presence of biotite in all horizons of P4 also shows that the whole solum derived from the Araxá schist, despite the profile's discontinuities.

### *Polarization microscopy*

Polarization microscopy of thin sections from the sand fractions revealed that quartz dominated in P1 and P2 (Table 3). In P3, basalt-derived hematite concretions were enriched, pointing to a monogenetic origin of P3. P4 showed decreasing quartz and increasing mica contents with profile depth, suggesting stronger degrees of weathering in the surface horizons. Albites were present in low amounts, too (data not shown). Nonetheless, even in horizon 3CB, feldspars and micas were all strongly decomposed, indicating deep chemical (pre-) weathering of the bedrock.

The quartz grains were apparently inherited from distinct locations because of their differing roundness and light-breaking characteristics. Many of the larger, angular quartz grains showed undulose extinction, indicating metamorphic stress (Harwood 1989), whereas the rounded grains showed straight extinction and reflected long-distance transport. The third group consisted of rounded quartz grains, stained with hematite and frequently broken into numerous subcrystals. According to Stoops (1989), hematite infillings indicate materials derived from disintegrating laterite.

In P1, rounded quartz of the hematite-stained type may indicate that the Oxisol derived from sediments of a denuded planation surface. Nonetheless, the substrate's overall fine texture suggests that at least part of the parental material was derived from Proterozoic rock from the Canastra and Araxá Groups at the northern and eastern borders of the Paraná Basin (Schobbenhaus et al. 1984). The rounded quartz grains of ay diffraction analysis of oriented clay and polarization microscopy of the sand fractions from the Araguari River catena, central Brazil.[a]

| oil subgroup | Clay type[b] | | | | | a:r:s[c] | Polarized sections (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | kao | ill/bio | gib | goe | hem | (%) | Quartz | Opaque | Mica |
| crustox | | | | | | | | | |
| | + + | – | + + + | + + | + | 30:20:50 | >80 | 10 | – |
| plustox | | | | | | | | | |
| | + + | – | + + + + | + + | – | 30:50:20 | >90 | <5 | – |
| aplustox | | | | | | | | | |
| | + + | + | + + + | + | + + | 45:45:10 | <50 | >50 | tr. |
| | + + + | + | + + | + | + + | 60:30:10 | <30 | >70 | tr. |
| plustoll | | | | | | | | | |
| | + + + | + + + | + | + | – | 90:10:0 | >80 | tr. | <10 |
| | + + + | + + + | + | + | – | n.d. | n.d. | n.d. | n.d. |
| | + + + | + + + | + + | + | – | 100:0:0 | >60 | <10 | >20 |
| | + + + | + + + | + | + | – | 100:0:0 | <50 | – | >50 |
| | + + + | + + + | – | tr. | – | 100:0:0 | <30 | – | >70 |

tected; tr. = traces or 0%-1%; + = 2%-10%; ++ = 11%-30%; +++ = 31%-70%; ++++ = >70%; n.d. = not determined.

nite; ill/bio = illite and/or biotite; gib = gibbsite; goe = goethite; hem = hematite.

o of angular to rounded to hematite-stained quartz grains.

P2 were probably inherited from the Marília sandstones. According to Bigarella and Ab'Sáber (1964), the Bauru sediments derived from the Puruná surface, which was lowered during Eocretaceous. Its remnants constitute the Ponta Grossa Plateau in Paraná State. Thus, both P1 and P2 probably have polygenetic origins. The quartz grains of P3 clearly showed some contamination from the Marília sandstones but the angular grains were probably inherited from the basalt as their proportion increases with depth. In P4, only metamorphically stressed angular quartz was present, which derived from the Araxá schist. This points to a basically monogenetic origin of the soil, despite the intense hillwash, thus reinforcing the XRD results.

### *Chronology of soil development in southern central Brazil*

We can now see the chronology of Oxisol development at the northeastern border of the Paraná Basin. In P1, soil development may have begun after sedimentation on top of the South American surface finished and, according to King (1956), would therefore be of late Oligocene to early Miocene. Because the material seems to be partially pre-weathered, an earlier denudation cycle is manifested, which must be pre-Tertiary (King 1976).

Profile P2 on the Marília sandstones could only have formed after the Araguari River cut into the South American surface during the Velhas cycle and, hence, must be of Miocene or younger. Because this sediment may have derived from the Ponta Grossa Plateau (Bigarella and Ab'Sáber 1964), a Cretaceous soil evolution seems probable.

Soil development of P3 on the Velhas pediment, which, in the study area, is sustained by basalts of the Serra Geral Formation, could only have begun after the pediment was sufficiently well modeled, that is, at the end of the Pliocene (King 1956). However, considering the easily weatherable parent rock, soil development could have begun considerably later.

After the base level of the Araguari River had been lowered to a recent position by the end of Pleistocene, the paleosol sequence of profile P4 developed from (pre-weathered) Araxá mica-schist and eventually reached an advanced stage of desilication before the soil was truncated. Erosion of the surface soil very likely occurred during a semiarid phase with sparse vegetation and heavy rainfalls, and probably during a glaciation period in the higher latitudes (Bigarella and Ab'Sáber 1964); Emmerich 1988; Semmel and Rohdenburg 1979). Recent palynological analyses provided evidence of changing climatic conditions in central Brazil during late Quaternary, confirming the hypothesis of a cool and dry phase during the Wisconsin Glaciation, which was preceded and followed by warmer and moister epochs (Behling 1998; Ferraz-Vicentini and Salgado-Labouriau 1996; Salgado-Labouriau et al. 1997).

The stone line (2C/Bw) above horizon 3Bo either remained as a residue of this erosion process or it was deposited later, together with hillwash. The formation of the stone line could have coincided with the Wisconsin Glaciation because benchmark stone lines have been found all over Brazil, and are thought to reflect the semiarid to arid climate at the end of Pleistocene (Bigarella and Ab'Sáber 1964). The development of the paleosol would then probably have begun during the Wisconsin-Illinoian Interglacial and may therefore be older than 34 Ma (Salgado-Labouriau et al. 1997). This age corresponds to the pollen rain of a tropical humid to subhumid climate before the latest cool and dry phase. However, evidence could come only from radiocarbon dating of P4's 3Bo horizon. Holocene hillwash finally covered the paleosol, filling the voids between the gravel, and, hence, led to the soil's final stratigraphy.

## Conclusions

The chemical and XRD analyses and the weathering index ($Fe_o/Fe_d$) show a continuously decreasing degree of weathering from the tableland to the valley floor, reflecting the soils' decreasing age. The soils on the tableland probably developed during middle and upper Tertiary. However, their different types of quartz sand clearly show that they derived from pre-weathered sediments of distinct locations, suggesting a polygenetic origin that may reach as far back as the Mesozoic.

Soils on the pediment might have formed at the beginning of Pleistocene, and soils near the present base level are apparently from late Pleistocene. The types of quartz sand suggest a monogenetic origin for soils that derived either from basalt or schist. Recent pedological processes are characterized by strong leaching and hillwash.

A more detailed chronology of Oxisol development and formation rates in central Brazil could be achieved with radiocarbon dating of appropriate paleosols. Correlation with results from palynological analyses could further elucidate the paleoecological conditions.

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## CHAPTER 3

# Agropastoral Systems Based on Legumes: An Alternative for Sustainable Agriculture in the Brazilian *Cerrados*

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## Abstract

Grain, meat, and milk production systems in the Brazilian savannas, also known as the *Cerrados*, are currently experiencing increasing economic and environmental problems. These problems could have detrimental effects on the natural resource base and on the sustainability of agriculture in the region over the long term if alternative systems are not developed. One option that would intensify agricultural production while minimizing negative impacts on soil and water involves the integration of cropping and livestock systems in time and space (agropastoralism). Since 1992, CIAT and EMBRAPA-CPAC have worked together with other institutions to develop agropastoral systems that are based on forage legumes adapted to low and high inputs, and to quantify their impact on productivity and on soil. Most of these activities were carried out on farms in the Uberlândia region of the State of Minas Gerais in central Brazil. Experiments with the legumes *Stylosanthes guianensis* cv. Mineirão and *Arachis pintoi* BRA-031143 in crop/pasture systems showed that while the first legume was effective in low-input systems, the latter was better adapted to high-input systems, crop rotation (ley farming), or as a permanent ground cover in direct sowing. However, chemical or mechanical methods were needed to control *A. pintoi*'s competitiveness with crops. The results of a crop/livestock case study confirmed the synergistic effect on production and soil quality. Soil fertility increased during the cropping cycle, whereas soil aggregation and soil organic matter increased under the pasture phase. Organic matter also underwent a process of physical protection under pastures, especially in sandy soils. Subsequent surveys showed that crop/livestock integration is gaining acceptance amongst grain producers.

*Keywords:* *Arachis*, Brazilian savannas, *Cerrados*, crop/pasture systems, crop rotations, ley farming, *Stylosanthes*

## Introduction

In less than 30 years, the Brazilian savannas, also known as the *Cerrados*, were converted into Brazil's most important agricultural frontier. Of the 204 million hectares that make up this ecosystem, 47 million are under

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agriculture and a further 89 million are estimated to have similar potential (Macedo 1995).

This rapid transformation is a result of technological advances made in soil management, selection of cultivars adapted to the soil conditions and climate of the *Cerrados*, and to investment in infrastructure and development programs made by the State of Minas Gerais.

Growth in agriculture in the region has had positive impact on wealth and employment, but with some negative environmental impact. Soil erosion and compaction increased under annual crops (Ayarza et al. 1993). Agrochemical use, to control weeds, pests, and diseases, rose sharply. Pastures degraded to the extent that more than 50% of the pastures sown in the *Cerrados* show problems of loss of vigor, weed invasion, and disease (Macedo 1995).

Alternative systems are being developed to reduce this negative impact. Traditional soil preparation practices are being changed to minimum-tillage practices where crops are sown into crop residues or into ground covers controlled with herbicides. At the same time, soybean monocropping is being replaced by crop rotation. This reduces the incidence of weeds, pests, and diseases. In grazing systems, grasses resistant to spittlebug (*Deois flavopicta*) and crops are being used to recuperate degraded pastures (Klutchcouski et al. 1991).

A highly successful strategy for intensifying agricultural production sustainably and reversing problems of degradation involves the integration of crop/livestock systems in time and space (agropastoralism). The strategy is based on the assumption that a beneficial synergistic effect on productivity and on soil occurs when annual and perennial species are combined (Lal 1991; Spain 1990). Available nutrients are used more efficiently and the chemical, physical, and biological properties of the soil are improved. In addition, economic risk is decreased, compared with either crops or livestock enterprises alone.

For 4 years, CIAT and EMBRAPA-CPAC[1] have worked together with other institutions to develop agropastoral systems for the Brazilian *Cerrados*. Specific objectives of the project were (1) to develop agropastoral systems based on multiple-purpose legumes, (2) evaluate the productivity of the systems on-farm, (3) quantify the impact of integrated crop/livestock systems on production and on soil quality, and (4) characterize the dynamics of the production systems and their adoption.

In this chapter, we describe the main results and discuss the potential use of agropastoral systems in the context of current production systems.

## Materials and Methods

Most of the work was done on-farm in the Uberlândia region, State of Minas Gerais (19°6'S, 48°6'W). Most of the agroecological classes of the *Cerrados* are found in this region (Jones et al. 1992), which has been undergoing a rapid process of intensification of land use in recent years (Schneider 1996). The soils are deep, well structured, but with low fertility and high phosphorus-fixation capacity. They are classified according to the Brazilian system as "latossolos vermelho-amarelo" and "vermelho-escuro" (Anionic Acrustox and Typic Haplustox, according to the USA system). Mean annual rainfall is about 1600 mm, concentrated between

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[1] For an explanation of this and other acronyms, see "Acronyms and Abbreviations Used in the Text", pages 228-231.

November and March. There is a severe dry season between June and September, when relative humidity falls to 15% during the day.

The project focused on developing agropastoral systems based on legumes with potential to adapt to both grazing systems of low inputs and to cropping systems of high inputs, and as components of rotations and permanent ground covers. Studies from other tropical regions indicate that legumes are a key component for increased sustainability of production systems (Boddey et al. 1996; McCown et al. 1993; Thomas et al. 1995).

*Stylosanthes guianensis* cv. Mineirão and *Arachis pintoi* BRA-031143 were evaluated as potential legume components. They are adapted to the climatic and soil conditions of the *Cerrados*, and have a large production potential (CPAC 1993; Pizarro and Rincón 1994).

A schematic representation of the process involved is shown in Figure 1. Compatibility studies of *Stylosanthes guianensis* cv. Mineirão and *Arachis pintoi* BRA-031143 were done in small plots under cutting with forage grasses. In other studies, legume establishment was examined with crops and grasses on sandy soils with two levels of fertility. The potential use of *Stylosanthes* and *Arachis* as ground covers was evaluated in pure stands.

The impact of the legumes on production was evaluated in four 4-ha prototypes of improved agropastoral systems on-farm either in pastures with low inputs, or in annual cropping systems with high inputs on clay and sandy soils. Table 1 shows the soil characteristics of each system used. The experimental design included a comparison between a crop + grass-only pasture system and a crop + grass pasture + legume cocktail, each with two replicates.

The crops and forage grasses used varied with the production system and fertility level applied. Pastures with low inputs were sown with upland rice and *Brachiaria decumbens* and *B. ruziziensis*. The high-input systems were sown with maize and *Panicum maximum* cv. Vencedor. All prototypes sown with legumes used a cocktail that included *S. guianensis* cv. Mineirão, *Neonotonia wightii* cv. Tinaroo, and

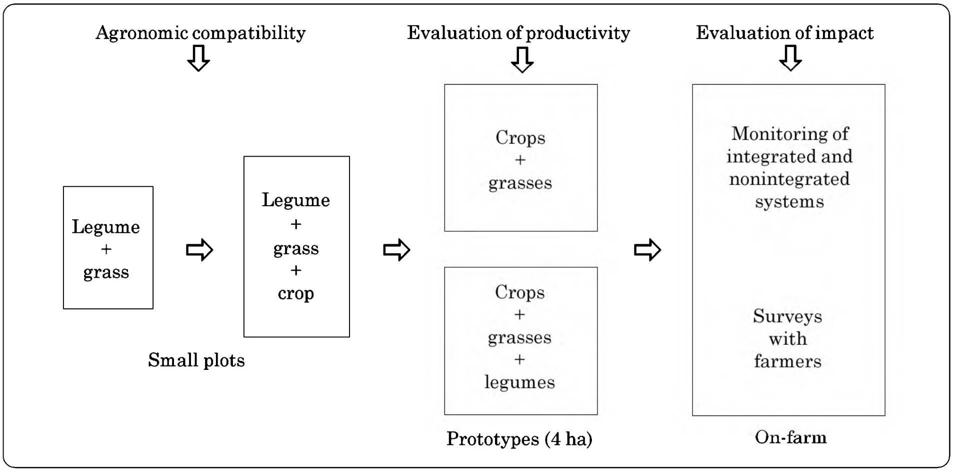

Figure 1. Sequence of activities in the development of improved agropastoral systems for the Brazilian savannas.

Table 1. Chemical and physical characteristics of the top 20 cm of soil from selected areas used for four 4-ha prototypes of improved agropastoral systems in Uberlândia, central Brazil. Mean of 20 samples per hectare.

| Agropastoral system | OM (%) | pH | P (ppm) | Ca + Mg | K | Al | Aggregates (% >2 mm) |
|---|---|---|---|---|---|---|---|
| | | | | (meq/100 g) | | | |
| Pastures, few inputs[a] | | | | | | | |
| Clayey soil (57% clay) | 3.7 | 5.1 | 0.9 | 0.5 | 0.07 | 0.5 | 77 |
| Sandy soil (17% clay) | 0.7 | 5.3 | 1.1 | 0.4 | 0.13 | 0.6 | 73 |
| Crops, many inputs[b] | | | | | | | |
| Clayey soil (57% clay) | 3.4 | 6.2 | 34 | 4.9 | 0.12 | 0 | 50 |
| Sandy soil (13% clay) | 0.7 | 6.3 | 26 | 2.4 | 0.25 | 0 | 46 |

a. Low fertilization + upland rice + two *Brachiaria* spp. + four legumes.
b. High fertilization + maize + *Panicum maximum* cv. Vencedor + three legumes.

*Calopogonium muconoides*. The last two legumes are used commercially and were included as controls. *Arachis pintoi* BRA-031143 was not sown in the high-input systems for lack of seed. The fertilization applied in the high-input systems included 1 t/ha of lime, 70 kg/ha $P_2O_5$, 35 kg/ha $K_2O$, and 12 kg/ha N applied at sowing. After 60 days, N at 20 kg/ha and $K_2O$ at 60 kg/ha were also applied. For the low-input systems, P was applied at 20 kg/ha $P_2O_5$, together with the legume seed. Maize was fertilized according to local recommendations given to farmers.

The evaluation of the prototype systems included grain and animal production. Biomass production and botanical composition of the pastures were measured three times per year. Soil samples were taken at various depths to evaluate changes in aggregate stability, soil organic matter (SOM), and N availability. A degraded pasture *B. decumbens* was included as control for low-input systems.

Seed multiplication plots of *S. guianensis* and *A. pintoi* BRA-031143 were set up in farmers' fields and visits to the prototype system sites were used to promote the legumes while evaluating their effectiveness in the systems.

The impact of integrated crop/livestock systems on productivity and on soil was quantified in a case study on the Santa Terezinha Farm in Uberlândia. This farm has sandy soils and a 10-year history of crop/pasture integration. Information on the use of soils, and crop and animal productivity was available. In addition, changes in chemical and physical properties of the soil in areas used for crops and pastures were monitored. This work was complemented by a detailed study on SOM and soil aggregation (see Chapters 4 to 8).

To study the dynamics of grain production systems and technological changes occurring over time, surveys were carried out on farm, complemented with remote-sensing studies. The studies focused on three watersheds situated in three municipalities: Rio Uberabinha (Uberlândia), Ribeirão Santa Juliana (Sta. Juliana), and Rio Bagagem (Iraí de Minas).

# Results

### *Agronomic compatibility of* S. guianensis *cv. Mineirão and* A. pintoi *BR-031143 with grasses and annual crops*

The aggressiveness of forage grasses and associated crops influence legume establishment in systems where they are simultaneously sown. In an experiment with 19 forage grass ecotypes, *S. guianensis* cv. Mineirão grew better with ecotypes of *Paspalum* spp. and *B. brizantha* than with *P. maximum* and *B. decumbens*. However, differences occurred among ecotypes of the same genus. For example, differences in compatibility of *S. guianensis* with ecotypes of *B. brizantha* were inversely correlated with the dry matter production of the grasses ($r^2 = -0.83$). With ecotypes of *P. maximum* and *B. decumbens*, the negative effect of the grasses was related to other characteristics such as shading, root production, and nutrient uptake. *Stylosanthes* is a genus that is highly sensitive to shading and to competition from the grasses for N, Ca, and P (Rao et al. 1995).

In other experiments, the compatibility of various ecotypes of *A. pintoi*, *Centrosema macrocarpum*, *C. brasilianum*, and *Calopogonium mucunoides* was compared when sown in association with *B. decumbens* CIAT 16488. Most legumes disappeared (but not *Arachis*), mainly as a result of poor adaptation and diseases. All *Arachis* ecotypes grew well with the grass and retained their leaves during part of the dry season (Pizarro et al. 1996). Large differences in dry matter production between the *Arachis* commercial cultivar Amarillo and the accession BRA-031143, which is considered promising for the *Cerrados* (Figure 2).

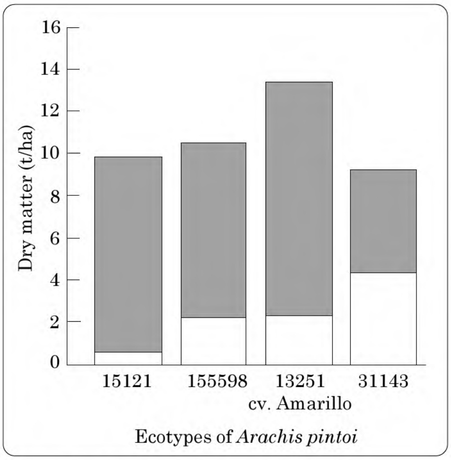

Figure 2. Accumulative production of four ecotypes of *Arachis pintoi* (□), sown with *Brachiaria decumbens* CIAT 16488 (■), in a clay loam soil in Uberlândia, central Brazil.

Sowing *P. maximum* cv. Vencedor and *B. brizantha* simultaneously with rice and *S. guianensis* cv. Mineirão significantly reduced rice production and the establishment of the legumes, compared with *P. atratum* BRA-009610 (Table 2). Competition was greater with the higher level of fertilization. *Stylosanthes* practically disappeared when sown with *P. maximum* cv. Vencedor and maize in a high-input system (Table 3). Maize yields were little affected by the grasses (14% reduction in yield). Competition from the grasses was significantly reduced if they were sown 30 days after the crops and forage legumes (Tables 2 and 3). Dry matter production of *A. pintoi* BRA-031143 was very low in both high- and low-input systems but the legume established better with high inputs after the maize was harvested.

Table 2. Yields of rice and of dry matter in *Stylosanthes guianensis* cv. Mineirão and *Arachis pintoi* BRA-031143, according to planting times of three grasses. Crops grown on sandy soils in Uberlândia, central Brazil. Mean of three replicates.

| Species[a] | Grass planted simultaneously with crop and legume (kg/ha) | | | Grass planted 30 days after crop and legume (kg/ha) | | |
|---|---|---|---|---|---|---|
| | Grass | Rice | 'Mineirão' | Grass | Rice | 'Mineirão' |
| Dry season | | | | | | |
| *P. atratum* | 4808 | 1106 a | 1375 a | 628 | 2189 a | 1829 a |
| *B. brizantha* | 7299 | 1208 a | 558 b | 714 | 2556 a | 957 a |
| *P. maximum* | 7458 | 194 b | 274 c | 1417 | 2156 a | 1389 a |
| Wet season | | | | | | |
| *P. atratum* | 5677 | 1014 a | 169 a | 1988 | 2445 a | 21 a |
| *B. brizantha* | 6187 | 1023 a | 137 a | 1612 | 2570 a | 43 a |
| *P. maximum* | 7166 | 314 b | 74 a | 2733 | 2203 | 60 a |
| Rice monocrop (control) | | 2662 | | | 2437 | |

a. *P. atratum* = *Paspalum atratum* BR-009610;
*B. brizantha* = *Brachiaria brizantha* cv. Marandu;
*P. maximum* = *Panicum maximum* cv. Vencedor.

Table 3. Grain and forage dry matter production (kg/ha) in a maize/pasture system with two sowing dates for the grass on a sandy soil in Uberlândia, central Brazil. Mean of three replicates.[a]

| Sowing system | Grass | 'Mineirão' | Arachis | Maize |
|---|---|---|---|---|
| Monocropped maize | – | – | – | 6364 a |
| Maize + legumes | – | 1814 a | 569 a | 6400 a |
| Grass sown simultaneously with crop and legume | | | | |
| Maize + legumes + *P. atratum* | 4700 | 144 b | 221 b | 6500 a |
| Maize + legumes + *P. maximum* | 6200 | 11 c | 96 c | 5586 b |
| Grass sown 30 days after crop and legume | | | | |
| Maize + legumes + *P. atratum* | 1200 | 1078 b | 618 a | 6484 a |
| Maize + legumes + *P. maximum* | 1500 | 723 c | 545 b | 6594 a |

a. Grass = *P. atratum* = *Paspalum atratum* BR-009610;
*P. maximum* = *Panicum maximum* cv. Vencedor;
'Mineirão' = *Stylosanthes guianensis* cv. Mineirão;
Arachis = *Arachis pintoi* BRA-031143.

Values followed by the same letter in each column are not significantly different (Tukey's test = $P < 0.05$).

## *Potential of* Stylosanthes *and* Arachis *as permanent ground covers in annual cropping systems*

Ground covers of *S. guianensis* cv. Mineirão and *A. pintoi* BRA-031143 had different effects on the growth and production of maize. In a preliminary experiment on a sandy soil, *Stylosanthes* had little effect on grain production but *A. pintoi* severely inhibited the growth of maize, which showed nutrient deficiency symptoms.

This was associated with the large root biomass production by *A. pintoi* in the top 10 cm of soil and a vigorous regrowth of the legume at the start of the rains. Later experiments showed that competition from *A. pintoi* BRA-031143 could be reduced temporarily by applying 3.5 L/ha of Roundup® (glyphosate) + 1% urea or by passing the subsoiler before sowing the maize (Figure 3). Other more intensive mechanical methods, such as a harrow or plow also reduced competition from the legume but stimulated weed infestation (Table 4). Exploratory work with a range of herbicides showed that various alternatives for controlling *Arachis* exist. In all studies, *Arachis* eventually and completely covered the ground. In contrast, *Stylosanthes* disappeared after the maize harvest.

Table 4. Effect of tillage intensity and herbicide use on dry matter production (kg/ha) of *Arachis pintoi* BRA-031143 and weeds.[a]

| Tillage intensity | No herbicide | | With herbicide | |
|---|---|---|---|---|
| | *Arachis* | Weeds | *Arachis* | Weeds |
| No tillage | 10895 a | 427 a | 602 b | 463 a |
| Subsoiler | 4050 b | 745 a | 86 a | 2168 b |
| Harrow | 2280 c | 3366 b | 2773 c | 7775 c |
| Plow + harrow | 2008 c | 3373 b | 1581 c | 8219 c |

a. Values followed by the same letter in each column are not significantly different (Tukey's test = $P < 0.05$).

## *Productivity of agropastoral systems*

As observed in the plot experiments, *S. guianensis* cv. Mineirão adapted well to low-input systems on sandy and clayey soils. At rice harvest, there were 3-4 plants/m$^2$ of *Stylosanthes*. Other legumes were also observed but at low densities. Rice yields in these systems were very low because of drought and competition from the grasses. In the high-input systems, the legumes disappeared as a result of competition for light from *P. maximum* cv. Vencedor and maize. Both maize

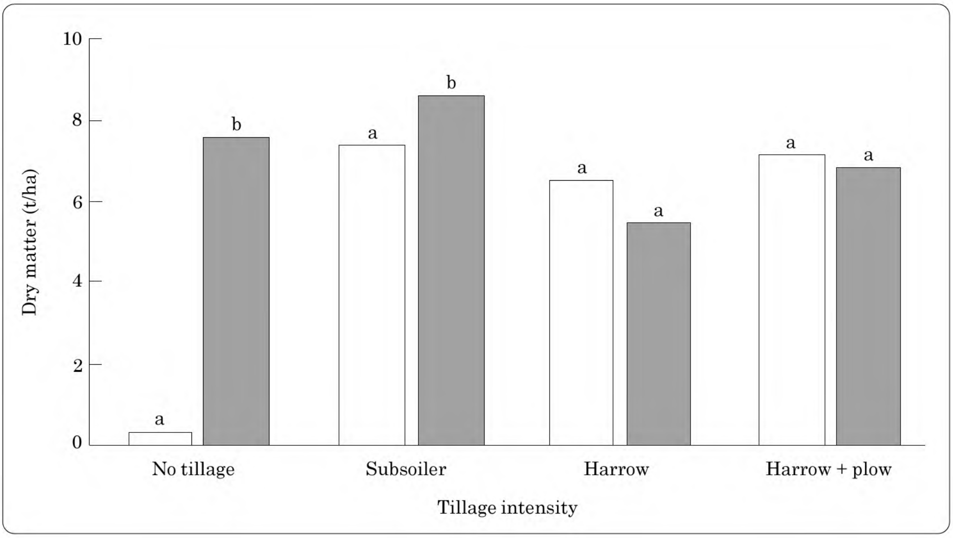

Figure 3. Maize production in a ground cover of *Arachis pintoi* controlled by various mechanical and chemical methods in a sandy loam soil in Uberlândia, central Brazil. Values followed by the same letter are not significantly different (Tukey's test = $P < 0.05$). (☐ = no herbicide; ■ = with herbicide.)

production and grass establishment were excellent, however.

After 3 years under pastures, animal production in the low-input prototypes with legumes was 50% greater than that under crop/pastures without legumes (Table 5). This difference increased to 80% after a maintenance application of 20 kg/ha $P_2O_5$ and 40 kg/ha $K_2O$. The better animal production from systems with legumes was associated with higher carrying capacities, greater individual animal liveweight gains, and a better quality diet. The differences were marked during the dry season as a result of the capacity of *S. guianensis* cv. Mineirão to maintain green material on offer. The proportion of the legume in the pasture remained stable during the evaluation, ranging from 30% to 60% of the total biomass, depending on the season. Animal performance on the crop/grass pastures was similar to that of a degraded pasture on a sandy soil that was used as control.

Table 5. Animal liveweight gain from different treatments under two prototypes of improved agropastoral systems sown in two soil types in Uberlândia, central Brazil. Mean of 3 years.

| Prototype system<br>Treatment | Annual animal production (kg/ha) | Increase (%) |
|---|---|---|
| Pastures, with low inputs, sandy soil | | |
| Crop + grass | 160 | – |
| Crop + grass + legume | 254 | 58 |
| Pastures, with low inputs, clayey soils | | |
| Crop + grass | 230 | – |
| Crop + grass + legume | 354 | 54 |
| Crops, high inputs, sandy soils | | |
| Crop + grass | 236 | – |
| Crop + grass + legume | 267 | 10 |
| Crops, high inputs, clayey soils | | |
| Pure grass | 503 | – |

Animal production from the high-input prototype on a clay soil was two times greater than that on a sandy soil. This was partly because more nitrogen was available from the grass on the clay soil (1.29 mg N per gram of soil) than from the grass on the sandy soil (0.61 mg N per gram of soil). The effect of the low availability of N in the sandy soil was confirmed by the linear response of *P. maximum* cv. Centenario to N fertilizer (Figure 4). Nitrogen limitation was revealed over time by an increasing proportion of perennial soybean (*Neonotonia wightii*) in the pasture and the better animal production in the prototype with legumes (Table 5). At the end of the measurement period, this legume comprised 40% of the biomass on offer.

The results obtained from the prototypes including *S. guianensis* cv. Mineirão and *A. pintoi* BRA-031143 have stimulated farmers' interest in

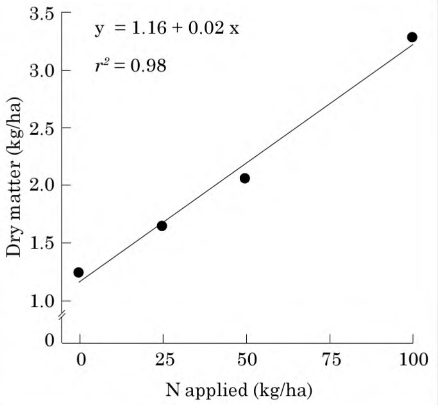

Figure 4. Response of a 4-year-old pasture of *Panicum maximum* cv. Centenario to the application of N fertilizer, Uberlândia region, central Brazil.

seed production of these two legumes. In 2 years, about 8 ha of *Stylosanthes* and 3.5 ha of *Arachis* have been sown, and 122 kg and 235 kg of seed have been obtained, respectively.

### Impact of crop/livestock systems on production and on soil

With the introduction of cropping in 1983, the original grazing enterprise on the Santa Terezinha Farm was transformed into an integrated system where crops and pastures were rotated in time and space. By 1992, all the original pastures of *B. decumbens* cv. Basilisk had been replaced with *P. maximum* sown simultaneously with maize after a cycle of 3-4 years of crops only (Table 6). Since 1992, the percentage of farm area under pasture has been maintained at 40%. Despite the reduced pasture area, animal numbers increased (Table 6). This occurred with an increase in net margins and in the number of calves per hectare when compared with the traditional system (Table 7).

The new integrated system also improved the soil. During crop cycles, soil fertility increased as a result of fertilizer and amendment applications (Table 8). Over 4 years, SOM increased by 30% under pastures, compared with under crops. Soil aggregation also improved (Figure 5). Lilienfein (1996) showed that an enrichment of C, N, and P in macroaggregates occurred in soils under pastures. Further studies are being done to evaluate the effect of the legumes on soil properties. Preliminary results indicate that the mesofaunal populations increased in the litter layer and soil.

### Adoption potential of agropastoral systems

Results of the characterization study of three watersheds show that crops occupy about 72% of the total farm area. The rest is under pastures or under reserve areas where mechanization is not possible (Smith et al. 1997). About half of the farmers surveyed keep livestock for meat and milk production. During the wet season, the animals remain on the pastures and in the dry season they are confined and fed silage and concentrates produced generally from the crops on the farm.

Table 6. Changes in areas under pasture over time on the Santa Terezinha Farm, Uberlândia region, central Brazil, as a consequence of introducing crop/pasture rotations.

| Year | Systems (ha) | | Total area (ha) | Animals (no.) | Carrying capacity (animals/ha) |
|---|---|---|---|---|---|
| | Savanna/pastures | Crop/pastures | | | |
| 1983 | 1014 | 0 | 1014 | 1094 | 1.1 |
| 1984 | 970 | 0 | 970 | 1069 | 1.1 |
| 1985 | 858 | 61 | 919 | 1025 | 1.1 |
| 1986 | 647 | 80 | 727 | 804 | 1.1 |
| 1987 | 521 | 176 | 697 | 862 | 1.2 |
| 1988 | 293 | 296 | 589 | 821 | 1.9 |
| 1989 | 205 | 377 | 582 | 846 | 1.4 |
| 1990 | 115 | 493 | 608 | 892 | 1.4 |
| 1991 | 15 | 632 | 647 | 891 | 1.4 |
| 1992 | 0 | 412 | 412 | 1150 | 1.8 |

SOURCE: Ayarza et al. (1993).

Table 7. Economic efficiency of calf production in three grazing systems with different degrees of intensification in the Uberlândia region, central Brazil.

| Parameter | Grazing system | | |
|---|---|---|---|
| | Traditional | Improved | Crop/pastures |
| Pasture renovated/year (%) | 1 | 10 | 25 |
| Pasture age (years) | 15-20 | 10 | 5 |
| Hectare per cow | 1.85 | 1.3 | 0.96 |
| Calves per hectare | 2.8 | 5.7 | 6.6 |
| Net gain (US$) | 43 | 95 | 110 |
| Area in pastures | 1,728 | 2,110 | 416 |
| Total net gain (US$) | 74,304 | 200,450 | 45,760 |

Table 8. Changes in chemical properties in a sandy Oxisol on the Santa Terezinha Farm, Uberlândia region, central Brazil. Mean of four bulked samples.

| Parameter | Soil depth (cm) | Native savanna | Crops |
|---|---|---|---|
| pH | 0-10 | 5.4 | 6.3 |
| | 10-20 | 5.2 | 5.9 |
| | 20-30 | 5.2 | 5.6 |
| | 30-40 | 5.2 | 5.0 |
| Saturated bases (%) | 0-10 | 19.1 | 82.7 |
| | 10-20 | 22.6 | 84.6 |
| | 20-30 | 21.9 | 69.5 |
| | 30-40 | 17.7 | 52.0 |
| P (ppm) | 0-10 | 1.6 | 24.8 |
| | 10-20 | 0.6 | 2.0 |
| | 20-30 | 0.4 | 1.0 |
| | 30-40 | 0.3 | 0 |

This type of integration has allowed the use of areas unsuitable for agriculture, and has increased income from meat and milk. The farmers perceive that raising livestock complements rather than substitutes their principal activity of grain production. The rotation of crops and pastures is still a relatively unused practice by grain producers. Only about 6% of farmers have sown pastures of high productivity in cropping areas. Most grow pastures in areas unsuitable for mechanization and where crop production is difficult.

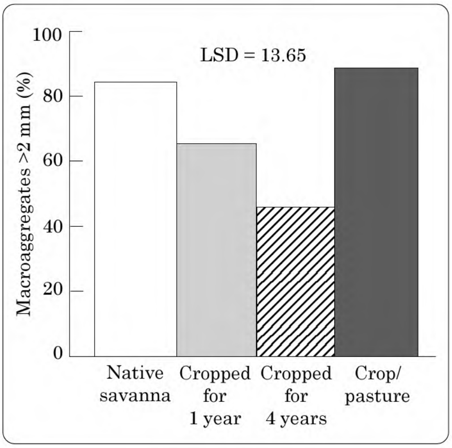

Figure 5. Effect of soil management on the proportion of macroaggregates in a sandy loam in Uberlândia region, central Brazil.

# Discussion

A requirement for a sustainable technology that would be rapidly adopted by farmers is the generation of production benefits and soil improvement over the short and long terms without causing major structural changes in the production systems (Spencer 1991). A possible example is the introduction of *S. guianensis* cv. Mineirão into low-input livestock systems. Seed requirements are relatively small: about 700-1500 g/ha for establishment, no extra labor for soil preparation, and little fertilizer use. *Stylosanthes* legumes are known to be highly efficient in associating with mycorrhizae and thus obtaining a high uptake of P per unit of root, although exactly how is not yet known (Rao et al. 1997). These characteristics, together with the capacity to provide green herbage during the dry season, give this legume clear advantages over other species for the improvement of production during critical periods.

Despite this legume's attributes, the grass and accompanying crop must be carefully selected to avoid problems of competition for light and nutrients. Grasses have a more profuse root system than do legumes, and can therefore better explore the soil for water and nutrient absorption (Rao et al. 1996). Under better soil fertility conditions, *S. guianensis* cv. Mineirão does not survive so well because of the greater capacity of accompanying grasses and crops to respond to increased fertility.

The greater productivity of pastures associated with *S. guianensis* cv. Mineirão is related to the supply of N from the legume to the soil-plant system. Cadisch et al. (1993) and Thomas et al. (1997) have shown that about 80% of the *Stylosanthes* N is derived from biological fixation. Some of this N is consumed by the animals and some is recycled via excreta and plant litter decomposition (Thomas 1992). These processes can increase the levels of mineral N in the soil (Cadisch et al. 1993; Freibauer 1996) and thereby the availability of N for the grasses. This was confirmed by the greater N concentrations in tissues of grasses associated with *S. guianensis* cv. Mineirão, compared with those of pure grass swards (data not presented). The increase in pasture production after P and K fertilization could also be related to a better availability of N. However, the small differences in animal production between pure grass pastures in the crop/pasture systems and the control degraded pasture on sandy soils indicate that the recovery of pastures via crops is of short duration and a source of N must be included to maintain the increased pasture productivity.

The behavior of *A. pintoi* BRA-031143 contrasts with that of *S. guianensis* cv. Mineirão. *Arachis* is a perennial legume with prostrate growth habit and various mechanisms of persistence (Fisher and Cruz 1994). Although growth is initially slow, it produces more roots than other legumes and has a better nutrient absorption efficiency (Rao et al. 1996). It also tolerates temporary shade relatively well. These characteristics, together with an excellent nutritive quality and capacity to cover the soil, suggest that it is a plant better adapted to systems of more intensive management and higher inputs. Once established, *Arachis* can persist in mixtures with grasses as aggressive as *P. maximum* cv. Vencedor and can contribute to the maintenance of animal production in rotation systems with crops in sandy soils. Although this effect could not be demonstrated in this project because of a lack of seed, the legume's persistence was noted in plots under grazing in the prototype experiments.

The use of *A. pintoi* as permanent ground cover has been reported in plantations of coffee (Staver 1996), banana (Granstedt and Rodrigues 1996; Pérez 1996), and oranges (Pérez-Jiménez et al. 1996) in Central America. These studies illustrate the advantages of *A. pintoi*: weed control, protection of soil against the impact of raindrops, and reduced incidence of nematodes. They also mention the disadvantages: slow establishment, eventual competition with crops, and high costs of establishment. Little information exists on its potential as a permanent ground cover with annual crops.

In this study, the incidence of weeds was greatly reduced once *A. pintoi* was established. However, competition from *A. pintoi* has to be controlled to obtain good yields from crops such as maize. Although the initial competition with the crop needs to be minimized, a complete ground cover must also be established by the end of the crop cycle. The speed of covering the entire ground and weed incidence are influenced by the type of control applied to the ground cover. Methods that destroy the ground cover and disturb the soil stimulate the germination of weed seeds. A subsoiler, by preparing the soil vertically, damages the roots of *A. pintoi* but does not destroy the ground cover. It reduces root competition and improves the soil's physical conditions for the crop.

Various experiments are being done to determine the potential use of this ground cover with other crops, together with a study of the dynamics of the cover, and its effects on N availability and on weeds over time. Data from Australia have shown that clover (*Trifolium subterraneum*) can acidify the soil when used in rotation with crops and pastures (Coventry et al. 1987). This effect needs to be monitored in other systems.

The results from monitoring crop/livestock systems confirmed the beneficial effect of integration on soil quality and system productivity. However, despite its great potential, integrated systems are not widely used, partly because of the changes needed in the infrastructure and administration of the systems to manage both sets of activities. These activities are usually done separately by different farmers (grazers and crop farmers). Thus, both grain farmers and cattlemen have to change their attitudes and perspectives to undertake both activities (Spain et al. 1996). Survey results are showing that this change is occurring. Farmers are seeing the economic benefits of integration but the activities are maintained on separate areas of their farms. The adoption of rotation systems of crops and pastures is likely to take time but appears to be an option for increasing the sustainability of agricultural systems on fragile soils. The inclusion of forage species as ground covers in direct sowing systems has a high potential in that they protect the soil, add value to the cover, and permit its use as part of crop rotation. The identification of other grass and legume species adapted to this region's soil conditions and management systems is needed.

## Conclusions

The project results have demonstrated that agropastoral systems have the potential to increase productivity and improve soil properties while reducing the risks of degradation. The impact of these systems is greatest when *Stylosanthes guianensis* cv. Mineirão and *Arachis pintoi* BRA-031143 are included.

*Stylosanthes guianensis* cv. Mineirão is a legume that is adapted to low fertility soils, and can be easily established in rice/pasture systems to renovate degraded pastures with low-input use. In addition to improving the diet of grazing animals, it can increase the availability of N in the soil-plant system and allow a better pasture establishment.

In contrast, *A. pintoi* BRA-031143 is a legume better adapted to more intensive production systems with higher input. It is relatively tolerant of competition for light and nutrients and has a good ability to cover the ground once established. These attributes are appropriate for rotational use with crops and as a ground cover for direct planting systems.

The integration of crop and livestock activities on-farm is a relatively recent innovation for farmers in the *Cerrados*. Those farmers using the systems see the economic and environmental advantages of this technology, but the widespread adoption of this technology depends on the ability of both grain producers and cattlemen to adapt to the structural changes. Researchers, for their part, need to increase the component options of crops and pastures and identify an adequate management system that maximizes the synergistic effects on production and on soil quality.

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## CHAPTER 4

# Physical and Chemical Properties of Selected Oxisols in the Brazilian *Cerrados*

*Henry Neufeldt**

## Abstract

Profiles of selected very fine, allitic, isohyperthermic, Anionic Acrustox and coarse-loamy, mixed, isohyperthermic, Typic Haplustox under different management systems were analyzed chemically and physically. On each of the two substrates, a conventional crop rotation, a degraded pasture, and a tree plantation were selected. Native savanna was used as control. Exchange capacity, most exchangeable cations, and phosphorus were strongly related to soil organic carbon while pedogenic Fe and Al oxides were less related. Soil organic matter also controlled the formation of stable microaggregates and the degree of clay dispersion, and must therefore be seen as a key component in these soils. Management affected both the physical and chemical properties of the soils. Liming elevated the pH, increased the number of variable exchange sites, and altered clay flocculation. Such changes may have implications for pore-size distribution. Seedbed preparation resulted in soil compaction and reduced total pore volume. The loss was, however, restricted to macropores, whereas mesoporosity even increased. Given the small amount of capillary water available to plants in Oxisols, this change may be seen as positive.

*Keywords:* Aggregation, Brazilian savannas, *Cerrados*, flocculation, Oxisols, point of zero net charge, water retention

## Introduction

Nearly half of the soils in the Brazilian savannas, also known as the *Cerrados*, are Oxisols (EMBRAPA 1981), most of which are naturally Dystrophic (Adámoli et al. 1986). Typically, their clay fraction consists of kaolinite and gibbsite, but may include goethite, and, sometimes, hematite only. High-activity clays are largely absent (Fontes and Weed 1991) as result of advanced ferralitization, a process that leads to the complete dissolution of all weatherable primary minerals and the residual accumulation of secondary Fe and Al oxyhydroxides (Driessen and Dudal 1991).

Because the chemical and physical properties of soil are mainly controlled by mineralogy, cation-exchange capacity is very low, entirely dependent on pH and relying on soil organic matter (SOM) to a great extent (Duxbury et al. 1989). As the pH of Oxisols is generally very low under native savanna (Adámoli et al. 1986),

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Al mainly occupies the exchange sites. Phosphorus is especially limiting as it selectively adsorbs to oxyhydroxides (Leal and Velloso 1973).

However, Oxisols develop a stable microstructure, called pseudosand, as a result of strong binding between positively charged oxyhydroxides and negatively charged kaolinite and organic matter (OM). The high structural stability leads to a unique water retention behavior in Oxisols, which are characterized by extremely high macroporosity and a high number of intra-aggregate pores (Bartoli et al. 1992; Bui et al. 1989). Water quickly drains from these soils at high matric potentials, while at low matric potentials, water contents are relatively high. The strong drainage, in conjunction with the stable structure, explains why Oxisols are much less prone to erosion than many other tropical soils (Driessen and Dudal 1991). The number of ecologically important mesopores is, however, low. Despite high clay contents, plants can therefore suffer quickly from drought during dry spells in the rainy season (Cochrane et al. 1988).

Under these conditions, profitable agronomic activities cannot continue without intensive management, including full fertilization and heavy liming. Yet, cultivation often decreases the amount of OM because of the physical breakdown of aggregates during plowing and the subsequent higher organic carbon mineralization. For the *Cerrados*, these processes have been confirmed by Mendonça et al. (1991) and Resck et al. (1991). The close relationship between the amounts of SOM and exchangeable cations makes the loss of SOM especially critical in Oxisols. Seedbed preparation can also lead to a direct change of pore-size distribution through compaction (Roth et al. 1991, 1992; Santos et al. 1996). Moreover, liming may degrade soil structure by elevating soil pH and exchanging Al for Ca (Castro Filho and Logan 1991; Roth et al. 1992; Westerhof et al. 1999). Hence, necessary management practices may adversely affect exchange capacity, that is, soil fertility, as well as soil structure.

In this chapter, soil morphological, chemical, and physical properties of selected Oxisols are described and discussed in the light of management effects and possible consequences for land use.

## Materials and Methods

### Study area and site history

The study area is situated at 48°6'W and 19°6'S, that is, about 25 km south-southeast of Uberlândia in the State of Minas Gerais, Brazil. Mean annual temperature is 22 °C and average precipitation is 1650 mm, 90% of which falls between October and April. Altitude is between 900 m and 950 m above sea level. We sampled two soils that represented the region's most abundant geological formations (Chapter 2): a coarse-loamy, mixed, isohyperthermic, Typic Haplustox, derived from sandstone of the Eocretaceous Marília Formation; and a very fine, allitic, isohyperthermic, anionic Acrustox, derived from Tertiary unconsolidated sediments. On both soil types, a conventional maize/soybean crop rotation, a degraded *Brachiaria decumbens* pasture, and a reforested site (*Pinus caribaea* on the clayey soil and *Eucalyptus citriodora* on the loamy soil) were selected. The on-farm sites were chosen because of their comparatively long management history and close proximity. For each soil type, a nearby plot native savanna was selected as control. An overview of the management histories is presented in Table 1.

Table 1. Management history of Oxisols in the savannas of the Uberlândia region, central Brazil.

| Oxisol<br>Treatment | Beginning in year: | Fertilization (quantity per hectare)<br>When applied<br>Fertilizer applied | Annual yield or yield potential per hectare |
|---|---|---|---|
| Very fine Anionic Acrustox | | | |
| Conventional crop rotation (maize/soybean) | 1985 | Annual | |
| | | Soybean: 7 N, 70 P, 70 K kg; | 2600 kg |
| | | Maize: 60 N, 80 P, 60 K kg; | 2700 kg as intercrop |
| | | Dolomitic lime | |
| Pasture (*Brachiaria decumbens*) | 1986 | 1986 | |
| | | 300 kg partially acidulated rock phosphate (34 kg P); | 0.5 animals |
| | | 2000 kg dolomitic lime | |
| Reforestation (*Pinus caribaea*) | 1975 | 1975 | |
| | | 20 g monocalcium superphosphate per seedling | 11.7 $m^3$ (pulp production) |
| Coarse-loamy Typic Haplustox | | | |
| Conventional crop rotation (maize/soybean) | 1986 | Annual | |
| | | Soybean: 8 N, 80 P, 80 K kg; | 2400 kg |
| | | Maize: 110 N, 80 P, 80 K kg; | 6300 kg |
| | | Dolomitic lime | |
| Pasture (*Brachiaria decumbens*) | 1987 | 1986 | |
| | | Rice: 8 N, 28 P, 16 K kg; | 0.5 animals |
| | | 1500 kg lime; | |
| | | 700 kg $CaSO_4$ | |
| Reforestation (*Eucalyptus citriodora*) | 1982 | 1982 | |
| | | Ca-apatite | Unknown |

On the clayey crop site, cultivation began in 1985 after clearing native savanna. Until 1989, maize and soybean were alternately grown, following conventional seedbed preparation with disk harrow and chisel. Until 1993, only soybean was planted and after harvest in late February maize was sown as an intercrop. Since 1994, either soybean or maize were planted in a no-tillage system. Average annual N-P-K fertilization was 7-70-70 and 60-80-60 kg/ha for soybean and maize, respectively. In 1992, 2000 kg/ha rock phosphate were additionally given. Dolomitic lime was applied regularly to maintain the pH above 5.5. Average yields until 1995 were 2600 kg soybean per hectare and only 2700 kg maize per hectare because only the intercrop yields were considered. The degraded *Brachiaria decumbens* pasture was planted in 1986 after clearing native savanna and fertilized with 1000 kg Ca-apatite and 2000 kg dolomitic lime. Carrying capacity was only 0.5 cattle per hectare. Because of this low productivity, the pasture was considered degraded. On the reforested site, *Pinus caribaea* ssp. *caribaea* seedlings were planted, 3 x 3 m, after clearing the savanna in 1975. Each seedling was fertilized with 20 g of monocalcium superphosphate. Average annual growth increment was 11.7 $m^3$/ha. The timber is used for cellulose production.

On the loamy soil, cultivation of the crop site began in 1986 with rice after clearing native savanna. During the next 5 years, only soybean was planted, using conventional tillage.

Since then, maize was planted every third year, after 2 years of soybean. On the average, amendments of N-P-K were, for soybean, 8-80-80 and, for maize, 110-80-80 kg/ha per year. Regularly, Ca and Mg were applied as dolomitic lime. Average annual yield per hectare was 2400 kg soybean and 6300 kg maize. The degraded *B. decumbens* pasture was sown in 1987 after growing upland rice for one year when it received 8 kg N, 28 kg P, and 16 kg K per hectare, as well as 1500 kg/ha carbonatic lime and 700 kg/ha $CaSO_4$. Stocking rate was less than 0.5 animals per hectare at sampling time. On the reforested site, *Eucalyptus citriodora* seedlings, fertilized with Ca-apatite, were planted in 1982 after clearing native savanna.

## Soil sampling and pretreatment

On all treatments, a trench was opened in November 1994 and soil collected from each horizon. Additional samples were taken with an Edelman soil auger to as deep as 80 cm from four points at 50-100 m from the trench to verify profile similarity. Using dry soil samples, the soil was carefully broken along fissures and passed through an 8-mm screen. Large roots were discarded. The samples were then dried at 40 °C in a forced-air oven and sieved again through a <2-mm sieve. Visible roots that passed through the sieve were manually picked out. For chemical analyses of whole soil samples, an aliquot of the fine earth was ground with mortar and pestle and then passed through a 0.1-mm sieve.

Four undisturbed samples were taken with 100-$cm^3$ cylinders from the trench at various layers, down to a depth of 1.2 m.

## Analytical methods

Soil organic carbon (SOC) and total N of soil samples were determined by dry combustion (Elementar Vario EL). pH was determined in $H_2O$ and in 1 *N* KCl at a soil-to-water ratio of 1:10. Exchangeable Ca, Mg, Na, and Al were extracted with 1 *N* KCl, according to EMBRAPA (1979). Phosphorus and K were extracted with Mehlich 1 (Nelson et al. 1953). Exchangeable acidity (H + Al) was extracted with 1 *N* Ca-acetate at pH = 7 and titrated against 0.025 *N* NaOH (EMBRAPA 1979). Total pedogenic Fe and Al oxyhydroxides ($Fe_d$, $Al_d$) were extracted with dithionite-citrate-bicarbonate (DCB) solution (Mehra and Jackson 1960). The extraction of X-ray amorphous Fe and Al oxyhydroxides ($Fe_o$, $Al_o$) was carried out with oxalic acid, following Blume and Schwertmann (1969). All cations were determined with a Shimadzu AA-660 AAS. Phosphorus was measured colorimetrically, according to Murphy and Riley (1962). All analyses were duplicated.

The grain-size distribution was determined with the sieve-pipette method after shaking vigorously for 3 h with 0.1 *N* NaOH, according to EMBRAPA (1979). Natural clay was obtained similarly, but deionized water was used for dispersion instead of NaOH. Clay flocculation was calculated as [1 – (natural clay/total clay)]. The pore-size distribution was obtained, according to EMBRAPA (1979). The saturated soil cores were weighed and then centrifuged at subsequently increasing speed until water in the pores at tensions pF 1.8, 2.5, 3.0, and 4.2 had been drawn away. After every centrifugation, the soil cores were weighed. For bulk density and total pore volume (PV), cores were dried at 105 °C for 24 h and subsequently weighed again. Pores were divided into macropores (pF <1.8), mesopores (pF 1.8-4.2), and micropores (pF >4.2). Moist soil color was determined according to Munsell color charts (Munsell Color Company 1975).

The effective cation-exchange capacity ($CEC_e$) was calculated as the sum of exchangeable Ca, Mg, K, and Al, and the potential cation-exchange capacity ($CEC_p$) was calculated as the sum of all exchangeable bases plus (H + Al). The base saturation (BS) was obtained by relating the sum of exchangeable bases to $CEC_e$. Effective and potential CEC as obtained here underestimate the true exchange capacities slightly but correlate well with them (Thomas 1982). Stocks of exchangeable cations and P were calculated on the basis of the bulk density under natural vegetation to correct for soil compaction after land-use change, assuming that bulk density was formerly comparable (Veldkamp 1994).

### *Statistical analysis*

For statistical analyses, Statistica software (Statsoft) was used. Univariate regressions were calculated to correlate profile variables with each other. To compare the effects of soil substrate on pore volume at different tensions, Student's *t*-test was applied.

## Results and Discussion

### *Classifying the soils*

The soils were characterized according to *Keys to Soil Taxonomy* (Soil Survey Staff 1994), with the results as listed in Tables 2 and 3. All soils on the clayey substrate were classified as very fine, allitic[1], isohyperthermic[2], Anionic Acrustox, whereas those on the loamy substrate were classified as coarse-loamy, mixed, isohyperthermic, Typic Haplustox. Following the revised *Soil Map of the World* (FAO and UNESCO 1990), the clayey soils were considered Geric Ferralsols, whereas the loamy soils were characterized as Haplic or Xantic Ferralsols, depending on soil color. According to the Brazilian system, the soils were denominated Cerrado phase, very clayey or medium-textured, albic, dark-red or red-yellow Latosols (EMBRAPA 1982).

### *Morphological features*

The soil color changed from dark brown (7.5 YR) to yellowish red (5 YR) in the clayey soils and from dark yellowish brown (10 YR) to strong brown (7.5 YR) in the loamy soils, reflecting soil development with depth and overall higher Fe contents in the clayey soils (Tables 2 and 3). The yellowish hues (10 YR) under pine could be explained by preferential hematite reduction resulting from the influence of a higher water table as shown for a hydrosequence of Oxisols in the *Cerrados* by Macedo and Bryant (1987, 1989). This may also explain the weak mottling observed.

Under natural conditions, crumbs occurred in the A horizons (Neufeldt 1996) but, under continued cultivation, they were replaced by subangular blocks. This reduction in structural stability was more apparent in the loamy substrate, and could lead to increased surface washing during fallow. Even under natural conditions, with depth, the crumbs are substituted by subangular blocks of gradually weaker development because of decreasing rooting activity and its aggregating influence. Concomitantly, the pseudosand microstructure, which gives clayey soils the typical "earthy" feeling (Driessen and Dudal 1991), diminished with depth, turning the subsoil more plastic. According to Bartoli et al. (1991), microaggregate stability is correlated with OM content

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[1] Gibbsite in the fine-earth fraction was about 35%, using the method of Hashimoto and Jackson (1960).

[2] According to EMBRAPA (1982).

Table 2. Local description and main physical properties of Oxisols in the savannas of the Uberlândia region, central Brazil.

| Oxisol<br>Treatment<br>Location<br>Altitude, exposition | Horizon | | Moist soil color[a] | Texture (%) | | | Flocculation (%) | Bulk density ($g/cm^3$) |
|---|---|---|---|---|---|---|---|---|
| | Layer | Depth (cm) | | Sand | Silt | Clay | | |
| Very fine, allitic, isohyperthermic, Anionic Acrustox | | | | | | | | |
| Native savanna | A1 | 0-10 | 7.5 YR 3/4 | 25 | 7 | 68 | 47 | 0.84 |
| 48°9'W, 19°6'S | A2 | -30 | 7.5 YR 3/5 | 22 | 8 | 70 | 41 | 0.86 |
| 954 m, NW 1-2° | BoA | -48 | 6.3 YR 3.5/6 | 22 | 8 | 72 | 43 | 0.89 |
| | Bo11 | -80 | 5.0 YR 4/6 | 20 | 4 | 76 | 95 | 0.90 |
| | Bo12 | -140+ | 5.0 YR 4/6 | 20 | 5 | 75 | 100 | 0.86 |
| Crop | Ap | 0-30 | 7.5 YR 3/5 | 21 | 13 | 66 | 35 | 0.97 |
| 48°7'12"W, 19°9'S | BoA | -40 | 7.5 YR 3/6 | 18 | 16 | 66 | 33 | 0.99 |
| 950 m, W 1-2° | Bo11 | -80 | 5.0 YR 3/6 | 16 | 10 | 74 | 100 | 0.91 |
| | Bo12 | -140+ | 5.0 YR 5/6 | 17 | 9 | 74 | 39 | 0.91 |
| Pasture | Ap | 0-20 | 7.5 YR 3/4 | 19 | 14 | 67 | 39 | 0.87 |
| 48°7'12"W, 19°9'S | A | -40 | 7.5 YR 3/6 | 15 | 13 | 72 | 35 | 0.91 |
| 950 m, W 1-2° | BoA | -63 | 6.3 YR 3/6 | 15 | 11 | 74 | 39 | 0.89 |
| | Bo11 | -80 | 5.0 YR 3/6 | 15 | 10 | 75 | 89 | 0.86 |
| | Bo12 | -140+ | 5.0 YR 4/6 | 16 | 8 | 76 | 100 | 0.84 |
| Pine | AE | 0-3 | 10.0 YR 3/5 | 22 | 5 | 73 | 58 | 0.92 |
| 48°7'12"W, 19°9'S | A1 | -20 | 10.0 YR 3/4 | 23 | 8 | 69 | 52 | 0.92 |
| 955 m, W 0-1° | A2 | -48 | 10.0 YR 3/5 | 21 | 10 | 69 | 42 | 0.88 |
| | Bo11 | -90 | 8.8 YR 3/6 | 19 | 8 | 73 | 100 | 0.85 |
| | Bo12 | -140+ | 7.5 YR 4/6 | 19 | 6 | 75 | 39 | 0.82 |
| Coarse-loamy, mixed, isohyperthermic, Typic Haplustox | | | | | | | | |
| Native savanna | A1 | 0-10 | 7.5 YR 3/4 | 82 | 0 | 18 | 44 | 1.15 |
| 48°10'12"W, 19°10'12"S | A2 | -36 | 7.5 YR 3.5/4 | 80 | 0 | 20 | 35 | 1.19 |
| 900 m, N 2° | BoA | -65 | 7.5 YR 3.5/6 | 79 | 0 | 21 | 29 | 1.22 |
| | Bo11 | -85 | 7.5 YR 4/6 | 78 | 0 | 22 | 32 | 1.19 |
| | Bo12 | -140+ | 7.5 YR 4/6 | 76 | 0 | 24 | 83 | 1.14 |
| Crop | Ap | 0-24 | 10.0 YR 3/4 | 83 | 0 | 17 | 35 | 1.38 |
| 48°9'W, 19°12'36"S | A | -43 | 10.0 YR 3/5 | 82 | 1 | 17 | 35 | 1.35 |
| 894 m, W 2° | BoA | -65 | 10.0 YR 3/6 | 81 | 1 | 18 | 39 | 1.33 |
| | Bo | -140+ | 8.8 YR 3/6 | 80 | 1 | 19 | 74 | 1.26 |
| Pasture | Ap | 0-18 | 10.0 YR 3/4 | 81 | 0 | 19 | 53 | 1.23 |
| 48°9'W, 19°12'36"S | A | -30 | 10.0 YR 3/5 | 81 | 0 | 19 | 47 | 1.24 |
| 894 m, W 2° | BoA | -55 | 10.0 YR 3/6 | 80 | 0 | 20 | 45 | 1.28 |
| | Bo11 | -80 | 8.8 YR 3/6 | 78 | 1 | 21 | 43 | 1.22 |
| | Bo12 | -135+ | 7.5 YR 3/6 | 77 | 1 | 22 | 68 | 1.16 |
| Eucalyptus | A | 0-35 | 10.0 YR 3/4 | 83 | 0 | 17 | 53 | 1.26 |
| 48°10'48"W, 19°10'12"S | BoA | -53 | 8.8 YR 3/5 | 82 | 0 | 18 | 50 | 1.20 |
| 890 m, NW 2° | Bo11 | -86 | 7.5 YR 3.5/6 | 82 | 0 | 18 | 44 | 1.17 |
| | Bo12 | -140+ | 7.5 YR 4/6 | 80 | 0 | 20 | 100 | 1.15 |

a. YR = Color notation according to Munsell Color Company (1975).

because the amount of dispersible clay in Oxisol A horizons increased significantly after treating the samples with $H_2O_2$. However, Oades and Waters (1991) found no aggregate hierarchy in Oxisols and concluded that microaggregation could be controlled by the electrostatic attraction of low-activity clays and oxyhydroxides rather than by OM.

Table 3. Main chemical properties of Oxisols selected for study in the savannas of the Uberlândia region, central Brazil.[a]

| Oxisol Treatment | Horizon | SOC (g/kg) | C/N ratio | pH | | P (mg/kg) | $CEC_e$ ($cmol_c$/kg) | $CEC_p$ ($cmol_c$/kg) | BS (%) | $Fe_d$ (g/kg) | $Fe_o$ (g/kg) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | ($H_2O$) | (KCl) | | | | | | |
| Very fine, allitic, isohyperthermic, Anionic Acrustox | | | | | | | | | | | |
| Native savanna | A1 | 26.9 | 18 | 4.6 | 4.0 | 1.8 | 1.30 | 7.50 | 22 | 44.2 | 2.1 |
| | A2 | 19.1 | 17 | 4.8 | 4.1 | 0.7 | 0.77 | 5.89 | 18 | 51.7 | 1.8 |
| | BoA | 14.8 | 17 | 5.0 | 4.4 | 0.5 | 0.40 | 3.91 | 20 | 49.0 | 1.1 |
| | Bo11 | 11.5 | 16 | 5.0 | 4.7 | 0.4 | 0.22 | 3.33 | 32 | 49.5 | 0.7 |
| | Bo12 | 8.9 | 17 | 5.2 | 5.2 | 0.4 | 0.08 | 2.16 | 74 | 43.8 | 0.6 |
| Crop | Ap | 20.6 | 17 | 5.6 | 6.0 | 12.0 | 3.81 | 4.73 | 100 | 51.3 | 1.4 |
| | BoA | 17.5 | 17 | 5.3 | 5.8 | 1.7 | 2.70 | 4.23 | 100 | 51.5 | 1.3 |
| | Bo11 | 12.1 | 18 | 5.1 | 5.2 | 0.5 | 0.80 | 2.87 | 97 | 53.5 | 0.8 |
| | Bo12 | 8.5 | 19 | 5.0 | 5.6 | 0.5 | 0.35 | 1.45 | 100 | 49.8 | 0.4 |
| Pasture | Ap | 24.8 | 18 | 5.3 | 4.7 | 0.9 | 2.46 | 5.63 | 96 | 54.4 | 1.8 |
| | A | 16.8 | 18 | 5.5 | 4.5 | 0.6 | 1.09 | 3.71 | 81 | 50.8 | 1.3 |
| | BoA | 13.3 | 19 | 5.2 | 4.6 | 0.5 | 0.35 | 2.67 | 60 | 55.7 | 1.0 |
| | Bo11 | 11.5 | 19 | 5.2 | 4.8 | 0.5 | 0.23 | 2.25 | 70 | 51.0 | 0.8 |
| | Bo12 | 9.2 | 18 | 5.0 | 5.3 | 0.4 | 0.14 | 1.56 | 93 | 57.8 | 0.6 |
| Pine | AE | 22.6 | 21 | 4.2 | 3.8 | 2.2 | 1.81 | 10.47 | 8 | 47.4 | 1.3 |
| | A1 | 20.4 | 20 | 4.7 | 4.1 | 1.0 | 0.84 | 6.86 | 14 | 49.4 | 1.7 |
| | A2 | 14.7 | 20 | 4.6 | 4.4 | 0.5 | 0.38 | 4.55 | 24 | 48.8 | 1.3 |
| | Bo11 | 11.8 | 20 | 4.5 | 4.9 | 0.4 | 0.08 | 2.91 | 75 | 46.0 | 0.6 |
| | Bo12 | 9.0 | 20 | 4.5 | 5.5 | 0.3 | 0.05 | 1.31 | 100 | 49.0 | 0.4 |
| Coarse-loamy, mixed, isohyperthermic, Typic Haplustox | | | | | | | | | | | |
| Native savanna | A1 | 9.4 | 15 | 4.7 | 3.7 | 1.3 | 0.90 | 4.64 | 37 | 19.5 | 0.8 |
| | A2 | 6.2 | 15 | 4.9 | 4.0 | 0.5 | 0.44 | 2.30 | 20 | 21.3 | 0.6 |
| | BoA | 5.2 | 16 | 4.9 | 4.2 | 0.4 | 0.26 | 1.67 | 23 | 21.1 | 0.4 |
| | Bo11 | 4.2 | 18 | 5.0 | 4.4 | 0.4 | 0.22 | 1.13 | 27 | 22.0 | 0.3 |
| | Bo12 | 3.2 | 18 | 5.1 | 4.7 | 0.3 | 0.16 | 1.04 | 44 | 24.3 | 0.3 |
| Crop | Ap | 6.6 | 17 | 5.9 | 5.6 | 3.6 | 2.05 | 2.93 | 100 | 14.8 | 0.6 |
| | A | 4.9 | 16 | 5.3 | 4.8 | 0.5 | 0.94 | 2.45 | 97 | 15.4 | 0.6 |
| | BoA | 4.3 | 18 | 4.7 | 4.3 | 0.4 | 0.46 | 1.66 | 63 | 15.1 | 0.4 |
| | Bo | 3.5 | 19 | 5.1 | 4.8 | 0.4 | 0.30 | 1.16 | 87 | 17.1 | 0.3 |
| Pasture | Ap | 7.7 | 17 | 5.4 | 4.5 | 1.0 | 1.29 | 4.18 | 91 | 16.4 | 0.8 |
| | A | 6.3 | 17 | 5.4 | 4.4 | 0.6 | 0.65 | 3.47 | 77 | 15.4 | 0.7 |
| | BoA | 5.4 | 18 | 5.3 | 4.3 | 0.5 | 0.44 | 2.58 | 50 | 16.7 | 0.5 |
| | Bo11 | 4.9 | 17 | 5.1 | 4.4 | 0.4 | 0.21 | 2.20 | 29 | 16.9 | 0.4 |
| | Bo12 | 3.6 | 19 | 5.4 | 4.7 | 0.4 | 0.08 | 1.45 | 38 | 19.2 | 0.3 |
| Eucalyptus | A | 7.4 | 17 | 5.0 | 4.2 | 0.7 | 0.45 | 3.19 | 31 | 17.8 | 0.6 |
| | BoA | 5.0 | 18 | 5.1 | 4.4 | 0.4 | 0.21 | 2.04 | 33 | 17.2 | 0.5 |
| | Bo11 | 4.3 | 19 | 5.1 | 4.5 | 0.3 | 0.18 | 1.41 | 39 | 20.7 | 0.4 |
| | Bo12 | 3.4 | 21 | 5.2 | 4.9 | 0.3 | 0.08 | 0.89 | 63 | 21.0 | 0.3 |

a. SOC = soil organic carbon; $CEC_e$, $CEC_p$ = effective and potential cation-exchange capacity, respectively; BS = base saturation; $Fe_d$, $Fe_o$ = dithionite- and oxalate-extractable iron oxides, respectively.

## *Physical properties*

Clay contents of surface soil were close to 70% in all clayey soils and increased slightly with depth, reaching 75% below 80 cm (Table 2). In the loamy soils, clay contents of the topsoil were around 18% and reached 19% to 24% in the subsoil. Concomitantly, the silt and sand contents decreased.

Flocculation augmented slightly with depth. In the clayey soils, it was followed by an abrupt elevation to

100% in at least some part of the B horizon. When values were plotted against ΔpH ($pH_{KCl} - pH_{H_2O}$), flocculation was found to occur about the point of zero net charge (PZC), that is, where positive and negative charges are equal (Figure 1). At PZC, soil colloids need the least amount of energy to come close enough to each other to attach and then flocculate (Bartoli et al. 1992). For the studied soils, PZC was close to $pH_{KCl} = 5$. Flocculation may be controlled by SOM in oxide-dominated soils (Gillman 1974). At a certain depth of the soil, SOM barely neutralizes the positive charge of the oxyhydroxides, leading to flocculation, while above and below net charge is either negative or positive and, hence, the soil remains dispersed. In fact, the relationship between SOC and $pH_{KCl}$ was very close, after excluding the crop sites where the topsoil pH was raised through regular liming ($r = -0.81^{***}$ and $r = -0.79^{**}$ for the clayey and the loamy soils, respectively). If the negative charge is lost to reduced SOM, then the PZC is likely to be closer to the soil surface than before. Whether this has consequences on soil structure and pore-size distribution needs further investigation.

Bulk density was always higher in the loamy than in the clayey soils (Table 2). Under natural conditions, it increased slightly with depth and subsequently decreased again. Land-use change led to higher densities in the surface soil, while in the subsoil, differences were generally small. This effect was most accentuated at crop sites, reflecting the impact of regular seedbed preparation. The pore volume (PV) was influenced inversely. Hence, PV was significantly lower in the loamy soils and clearly reduced because of cropping, even after summarizing to a 1-m depth (Table 4). The differences between the substrate were mainly a function of a higher microporosity (pF > 4.2) in the clayey soils, whereas macroporosity (pF < 1.8) and mesoporosity (pF = 1.8-4.2) were similar in both soil substrates. The

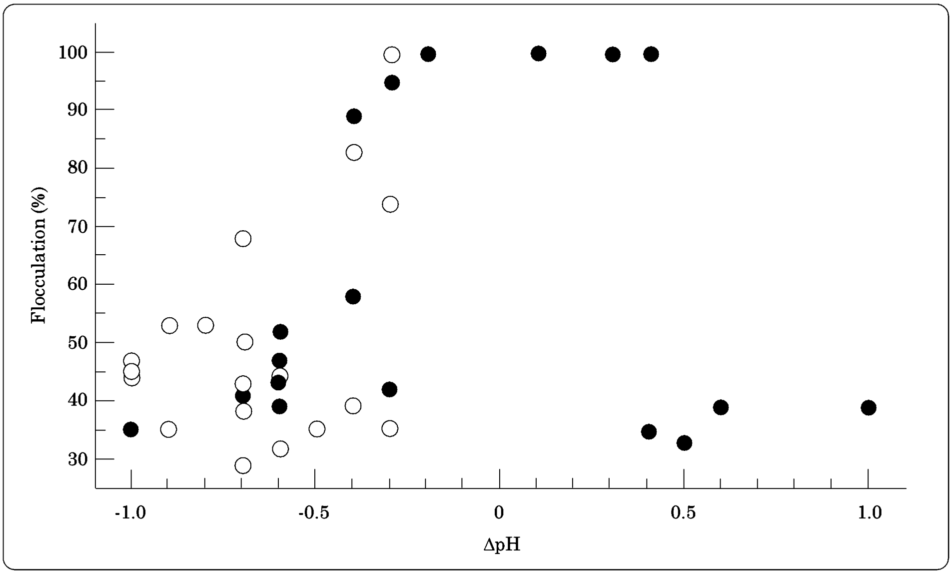

Figure 1. Plot of ΔpH ($pH_{KCl} - pH_{H_2O}$) versus the proportion of flocculated clay in clayey (●) and loamy (○) Oxisols in the savannas of the Uberlândia region, central Brazil.

Table 4. Total pore volume and pore volume at three tensions (with ±95% confidence intervals; n = 4) calculated to a 1-m depth of differently managed clayey and loamy Oxisols in the savannas of the Uberlândia region, central Brazil.

| Oxisol<br>Treatment | Total pore volume (mm/m) | Pore volume at pF (mm/m) | | |
|---|---|---|---|---|
| | | <1.8 | 1.8-4.2 | >4.2 |
| Very fine Anionic Acrustox | | | | |
| Native savanna | 738 ± 18 | 347 ± 28 | 114 ± 20 | 277 ± 7 |
| Crop | 685 ± 18 | 244 ± 38 | 154 ± 28 | 287 ± 12 |
| Pasture | 735 ± 28 | 309 ± 32 | 141 ± 27 | 285 ± 11 |
| Pine | 733 ± 29 | 339 ± 43 | 120 ± 18 | 274 ± 11 |
| Average | 723 ± 25 | 310 ± 47 | 132 ± 19 | 281 ± 6 |
| Coarse-loamy Typic Haplustox | | | | |
| Native savanna | 548 ± 18 | 319 ± 18 | 116 ± 18 | 113 ± 6 |
| Crop | 492 ± 18 | 226 ± 31 | 151 ± 26 | 115 ± 4 |
| Pasture | 537 ± 14 | 276 ± 28 | 146 ± 22 | 114 ± 4 |
| Eucalyptus | 547 ± 15 | 299 ± 20 | 143 ± 21 | 105 ± 5 |
| Average | 531 ± 26 | 280 ± 40 | 139 ± 16 | 112 ± 5 |

plant-available water content (matric potential: pF = 1.8-4.2) was considered to be very low, while the number of rapidly draining macropores was very high in both soils. However, only the clayey soils exhibited the bimodal pore-size distribution typical of Oxisols, with a large number of macro- and micropores and a comparatively small number of mesopores (Bartoli et al. 1992; Bui et al. 1989).

Land-use effects indicated a loss of macropores and an increase of mesopores in the order native savanna < reforestation < pasture < crop, suggesting that seedbed preparation and cattle trampling enlarged plant-available water at the cost of having macropores. Liming, too, may have altered pore distribution by acting on aggregation (Castro Filho and Logan 1991; Roth et al. 1992; Westerhof et al. 1999) and flocculation (Fontes et al. 1995). By contrast, microporosity was largely unaffected by management, reflecting a soil property that depends on clay content only.

## *Chemical properties*

Soil organic carbon and N contents decreased gradually with depth and were about three times higher in the clayey than in the loamy soils (Table 3). The intimate relationship between clay content and SOC is well established and has been reviewed recently for a series of tropical soils by Feller and Beare (1997). Concomitantly, both $CEC_e$ and $CEC_p$ decreased with depth. Base saturation (BS) increased as a function of a pH that was rising, either because of liming or because the pH of oxyhydroxides became more apparent in the subsoil. Soil organic carbon was highly correlated with $CEC_p$ (Table 5), indicating that OM bears the majority of exchange sites on these highly weathered soils and is therefore of great significance for soil fertility. The correlation with $CEC_e$ was less because liming led to an exchange of Al with Ca and Mg. Hence, these cations also showed lower correlation coefficients with SOC.

Table 5. Pearson correlation coefficients (*R*) and significance levels of soil constituents versus soil organic carbon in clayey and loamy Oxisols in the savannas of the Uberlândia region, central Brazil.

| Predictors[a] | Correlation coefficients | | |
|---|---|---|---|
| | Clayey Acrustox (n = 20) | Loamy Haplustox (n = 19) | Both Oxisols (n = 39) |
| $CEC_p$ | 0.87**** | 0.95**** | 0.85**** |
| $CEC_e$ | 0.71*** | 0.63** | 0.61**** |
| Al + H | 0.66*** | 0.86**** | 0.69**** |
| Al | 0.65** | 0.70*** | 0.54*** |
| Ca | 0.40 | 0.39 | 0.36* |
| Mg | 0.42 | 0.34 | 0.46** |
| K | 0.89**** | 0.85**** | 0.70**** |
| $\log_{10}$ P | 0.69*** | 0.75*** | 0.60*** |
| N | 0.98**** | 0.99**** | 0.99**** |
| $pH_{H_2O}$ | –0.10 | –0.03 | –0.25 |
| $pH_{KCl}$ | –0.53* | –0.41 | –0.05 |
| $Fe_d$ | 0 | –0.33 | 0.74**** |
| $Fe_o$ | 0.95**** | 0.91**** | 0.96**** |
| $Al_d$ | –0.20 | –0.07 | 0.46** |
| $Al_o$ | 0.39 | 0.52* | 0.70**** |

* = $P < 0.05$; ** = $P < 0.01$; *** = $P < 0.001$; **** = $P < 0.0001$.

a. $CEC_e$, $CEC_p$ = effective and potential cation-exchange capacity, respectively; $Fe_d$, $Fe_o$ = dithionite- and oxalate-extractable iron oxides, respectively; $Al_d$, $Al_o$ = dithionite- and oxalate-extractable aluminum oxides, respectively.

$P_{Mehlich}$ was very low in all the surface soils, except at the crop sites, according to benchmark values of Sousa and Lobato (1988), and decreased only weakly beyond the A horizons (Table 3). Thus, $P_{Mehlich}$ was only well correlated with SOC after log-transformation (Table 5). This is explained by the fact that, with SOC, P is mainly controlled by the mineral phase, because of a specific sorption to oxyhydroxides (Goldberg and Sposito 1985).

Nutrient stocks per hectare and at a 1-m depth are given in Table 6. Differences between soil types were reduced because of the higher bulk density of the loamy soils and indicated that, under low fertility, stocks of cations and P were comparable between the two substrates. Management effects were generally small for SOC and N, although a loss at the crop sites and under pine may be found. Ca and Mg were the elements most strongly enriched through land-use change. As a result of liming, Al was reduced at the crop and pasture sites. Phosphorus accumulated at the crop sites only, and K showed only minor alterations after land-use change. The accumulations can be attributed to a higher pH at the fertilized and limed sites because no comparable enrichment of $CEC_p$ occurred.

$Fe_d$ and $Fe_o$ were two to three times higher in the clayey soils, because of the higher clay contents (Table 3), but whereas $Fe_d$ remained somewhat unchanged with depth, $Fe_o$ usually declined gradually. The highly significant correlation between SOC and $Fe_o$ suggests that X-ray amorphous Fe oxyhydroxides and OM are linked, possibly in the form of stable complexes (Scheffer and Schachtschabel 1992). Because ferrihydrite is usually extracted with the oxalic acid method (Parfitt and Childs 1988), the results

Table 6. Stocks of soil organic carbon (SOC), total N, $P_{Mehlich}$, and effective and potential exchangeable cations ($CEC_e$ and $CEC_p$, respectively) in clayey and loamy Oxisols, calculated to a 1-m depth,.

| Oxisol<br>Treatment | SOC | N | Mineral nutrients (kg/ha) | | | | | Cations ($kmol_c$/ha) | |
|---|---|---|---|---|---|---|---|---|---|
| | (000s kg/ha) | | P | Al | Ca | Mg | K | $CEC_e$ | $CEC_p$ |
| Very fine Anionic Acrustox | | | | | | | | | |
| Native savanna | 130 | 7.7 | 5 | 260 | 50 | 20 | 140 | 40 | 370 |
| Crop | 126 | 7.3 | 35 | 10 | 2430 | 340 | 200 | 160 | 290 |
| Pasture | 134 | 7.6 | 6 | 90 | 940 | 160 | 140 | 70 | 280 |
| Pine | 125 | 6.3 | 5 | 200 | 40 | 20 | 110 | 30 | 360 |
| Coarse-loamy Typic Haplustox | | | | | | | | | |
| Native savanna | 64 | 4.1 | 6 | 270 | 80 | 30 | 170 | 40 | 230 |
| Crop | 58 | 3.3 | 14 | 60 | 1530 | 190 | 170 | 100 | 230 |
| Pasture | 65 | 3.8 | 7 | 150 | 690 | 40 | 110 | 60 | 320 |
| Eucalyptus | 64 | 3.7 | 6 | 190 | 40 | 10 | 110 | 30 | 240 |

agree with those of Schwertmann and Taylor (1989) in that OM prevents ferrihydrite from further crystallizing to goethite or hematite. Different from all other profiles, under pine, $Fe_o$ rose from the AE to the A1 horizon, reflecting Fe mobilization and beginning podzolization. Fe mobilization and podzolization occurred as a function of leaching of organic acids from the thick moder layer that formed over the last 20 years.

## Conclusions

Soil organic matter can be considered the key component in the selected Oxisols. Not only does SOM carry the majority of exchange sites—the low-activity clays and oxides contribute only marginally—but it also participates in the formation of stable pseudosand microaggregates and controls the degree of clay dispersion. Soil physical and chemical properties thus seem intimately connected through the SOM and the specific charge characteristics of Fe and Al oxyhydroxides. The extent to which the loss of SOM may contribute to structural destabilization and alteration of the pore-size distribution and to reduced soil fertility, needs further elucidation.

After about 10 years of cropping, pore-size distribution is already significantly altered, indicating a reduced macroporosity and an increase of mesopores. This shift must be considered positive in terms of plant-water supply because the number of rapidly draining macropores is so high that a decline should not aggravate soil aeration problems. The change in pore-size distribution is attributed to soil compaction during frequent seedbed preparation. Liming may also play a role.

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# CHAPTER 5

# Distribution of Water-Stable Aggregates and Aggregating Agents in Oxisols of the Brazilian *Cerrados*

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## Abstract

The effects of land-use change on the structure of Oxisols in the Brazilian savannas (also known as the *Cerrados*) are still insufficiently understood. We therefore studied loamy and clayey Oxisols under natural savanna, crop, pasture, and reforestation to (1) quantify management-induced changes in the quantity of water-stable aggregates, (2) identify the main aggregating agents, and (3) correlate aggregation with changes in pore-size distribution. Clayey soils showed a significantly higher macroaggregation than did loamy soils. Compared with natural savanna, macroaggregation was clearly reduced under crops, whereas aggregation of soils under pasture and tree plantations was only slightly affected. In both clayey and loamy soils, polysaccharides formed the main aggregating agent. In the clayey soils, lime very effectively disaggregated the soils by weakening the electrostatic forces between positively and negatively charged soil compounds. In the loamy soils, the role of roots in binding macroaggregates was significant. Because pastures provide strong rooting and high polysaccharide production, we recommend introducing crop/pasture rotations. Management-induced disaggregation strongly affected the pore-size distribution by compacting the soils, and thus reducing macroporosity and increasing mesoporosity. Microporosity, however, was unaffected by management and differed only between the two substrates. Considering the Oxisols' typically low pore space at plant-available matrix potentials, the increase in mesoporosity may be important for annual crops during the frequent dry spells in the rainy season.

*Keywords:* Aggregate fractionation, aggregating agents, Brazilian savannas, *Cerrados*, land-use change, Oxisols, water retention

## Introduction

Increasing mechanization and expansion of cultivation during the past 3 decades have strongly increased agricultural production in the savannas of central Brazil, also known as the *Cerrados*. Production is expected to increase considerably in the near future (Alho et al. 1995; Goedert 1989). The sustainable

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management of the *Cerrado* soils, most of which are Oxisols (EMBRAPA 1981), is therefore of high ecological and socioeconomic significance.

Oxisols are known for their stable microstructure, caused by electrostatic forces between positively charged oxyhydroxides and negatively charged kaolinite and organic matter (OM) (El-Swaify 1981). The structural stability leads to extremely high drainage (a unique feature), and a low quantity of ecologically important mesopores. The Oxisols are therefore less prone to erosion than many other tropical soils, but plants may quickly suffer from drought (Bartoli et al. 1992; Driessen and Dudal 1991).

Changes in the structure of Brazilian Oxisols after land-use change have been described by Campos et al. (1995), Castro Filho and Logan (1991), Roth and Pavan (1991), Roth et al. (1991), and Westerhof et al. (1999). Their results indicated that conventional tillage practices physically broke macroaggregates into smaller units, leading to new surfaces and subsequently the loss of labile OM to mineralization flushes. Liming increases pH, thus altering electrostatic forces between soil organic matter (SOM), polyvalent cations, and pedogenic oxyhydroxides, and therefore the aggregation. The establishment of no-tillage systems or pastures frequently reduced degradation or led to structural improvement (Roth et al. 1991; Westerhof et al. 1999).

Chemical, physical, and biological effects on soil structure are closely related to each other and depend on management practices, SOM contents, and amount of lime applied, as was recently shown for clayey Oxisols by Westerhof et al. (1999). However, how these factors interact and which contribute the most remain unclear. Likewise, liming is known to affect bulk density and infiltration in Oxisols (Castro Filho and Logan 1991; Roth and Pavan 1991), but how changes in soil structure act on the pore-size distribution and thus influence drainage or plant-available water content has rarely been studied.

We attempted to address these questions for differently managed Oxisols of contrasting texture by:

1. Determining the aggregate distributions,
2. Identifying the major aggregating agents by simple and multiple regression of a series of possibly aggregating organic and inorganic compounds, and
3. Comparing the results with the water-retention characteristics of the soils.

## Materials and Methods

### *Study area and site history*

The study area has already been described in Chapter 4, page 38. An overview of the management histories is given in that chapter's Table 1.

### *Soil sampling and pretreatment*

Soil sampling was done in March 1995, at the end of the rainy season. For each treatment, three plots of 50 x 50 m$^2$ were selected at about 50 m apart from each other. For each plot, five undisturbed samples were taken from the plow layer (0-12 cm) with an Uhland soil corer. The large peds were carefully broken along fissures to pass through an 8-mm screen, and the samples then kept refrigerated at 5 °C. For chemical analyses, an aliquot of the five samples per plot was dried at 40 °C in a forced-air oven, sieved through a <2-mm mesh, visible roots removed, and the samples ground until homogenized. To determine the water-retention curve, three undisturbed soil cores per plot were taken from the 0-10 cm and the 10-20 cm layers with 100-$cm^3$ cylinders.

### *Aggregate fractionation*

Field-moist samples (40%-50% water content) were used for aggregate fractionation according to Beare and Bruce (1993). The samples were placed on the uppermost of a series of sieves and wetted by capillary action until they reached field capacity. They were then fractionated into aggregates with diameters of 2-8, 1-2, 0.5-1, 0.25-0.5, or 0.05-0.25 mm by shaking a series of sieves of increasingly finer meshes for 30 min, following EMBRAPA's method (1979). Soil passing through the <0.05-mm sieve was collected after allowing to settle for 12 h and aspirating the supernatant. All fractions were dried at 40 °C in a forced-air oven and weighed. Fractionation recovery was between 96% and 100%. For analytical analyses of the aggregate fractions, all replicates per plot were combined, visible roots discarded, and the soil ground.

### *Determining particulate organic carbon and correcting for sand content*

An aliquot of each aggregate fraction was dispersed in hexametaphosphate to retain particulate organic matter (POM), together with the >0.05-mm sand fraction (Elliott et al. 1991), then sieved. Because the low carbon content of the sand fractions did not permit direct measurement of particulate organic carbon (POC), soil passing the sieve was dried, ground, and used for its indirect determination. The POC was calculated as the difference between soil organic carbon (SOC) in the whole soil and that in the sand-free fraction.

### *Analytical methods*

Soil organic carbon and total N were determined by dry combustion (Elementar Vario EL). The pH was determined in water at a soil-to-solution ratio of 1:10. Exchangeable cations were extracted according to EMBRAPA (1979). Polysaccharides were extracted with a two-step acid hydrolysis (Amelung 1997). Noncellulosic polysaccharides (NCPs) were hydrolyzed with 1 $M$ HCl at 100 °C for 5 h, and cellulosic polysaccharides (CPs) were digested by treating the residue with 12 $M$ $H_2SO_4$. The polysaccharides were determined colorimetrically with the MBTH reagent as described by Johnson and Sieburth (1977). Glucose equivalents were divided by 2.5 to obtain the polysaccharide C content. Pedogenic Fe and Al compounds ($Fe_d$, $Al_d$) were extracted with dithionite-citrate-bicarbonate (DCB) solution (Mehra and Jackson 1960). The extraction of X-ray amorphous Fe and Al oxyhydroxides ($Fe_o$, $Al_o$) was carried out with oxalic acid reagent, following Blume and Schwertmann (1969). Cations were determined by atomic absorption spectroscopy (Shimadzu AA-660). All analyses were duplicated. The grain-size distribution was determined by the sieve-pipette method after dispersion in 0.1 $M$ NaOH, and the pore-size distribution was obtained gravimetrically by centrifuging the saturated soil cores at consecutively higher speeds and final drying at 105 °C to determine bulk soil and pore volume (EMBRAPA 1979).

### *Statistical analysis*

Statistical analyses were executed with Statistica software (Statsoft). Soil effects on the distribution of water-stable aggregates (WSA) were verified with MANOVA, using Tukey's HSD test at $P < 0.05$, whereas management effects were explained by the mean ±95% confidence interval (n = 3) only. Single and multivariate regressions were calculated to determine functional relationships between aggregation and independent variables. The Durbin-Watson test for serial correlation was applied to regressions and *d* compared with benchmark values calculated by Savin and White (1977) before accepting any equation.

## Results and Discussion

### *Physical and chemical characterization of soils*

Under native savanna, the soils' chemical characteristics were typical of *Cerrado* Oxisols (Goedert 1983), as indicated by very low nutrient and P contents and a low pH, leading to an Al-dominated exchange complex (Table 1). Differences in nutrient contents between the substrates were small. Because of the limiting conditions, plants may have lowered the nutrient concentrations in the soils to minimum threshold values. Liming and fertilization raised plant-available P and the pH, stimulating the exchange of Al for Ca and Mg, and increasing the $CEC_e$. The higher $CEC_e$ rise in the clayey soils is probably related to the higher clay content because fertilizer was applied at comparable rates for both soil types.

The considerably lower bulk density and higher pore volume of the clayey soils was caused mainly by fine pores with their higher intra-aggregate pore space (Bui et al. 1989). In contrast, macro- and mesopores were not significantly different between the substrates (Table 2). Management effects increased bulk density and thus reduced pore volume by compaction through heavy machinery, liming, or both, and were most accentuated under crops, followed by the forests and pastures. Under crops, compaction reduced the quantity of macropores, increased that of the mesopores, but had little effect on the micropores.

Soil organic carbon, NCPs, and CPs were two to four times higher in the clayey than in the loamy substrate, whereas POC showed no significant differences (Table 3). The POC consisted of fresh to strongly decomposed plant fragments and fine roots that might have an entangling effect on aggregates (Degens 1997). Because POC contents were

Table 1. Selected physical and chemical topsoil (0-12 cm) properties of differently managed Oxisols in the Brazilian savannas.[a]

| Oxisol Treatment | Texture (%) | | | $pH_{H_2O}$ | $P_{Mehlich}$ (mg/kg) | Exchange complex ($cmol_c$/kg) | | | | | BS (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Clay | Silt | Sand | | | Ca | Mg | K | Al | $CEC_e$ | |
| Very fine Anionic Acrustox | | | | | | | | | | | |
| Savanna | 67 | 7 | 26 | 4.7 | 3 | 0.05 | 0.05 | 0.22 | 0.93 | 1.25 | 25 |
| Crop | 66 | 12 | 22 | 5.6 | 19 | 2.33 | 0.34 | 0.34 | 0.11 | 3.12 | 96 |
| Pasture | 66 | 13 | 21 | 5.6 | 11 | 1.69 | 0.36 | 0.25 | 0.13 | 2.43 | 95 |
| Pine | 66 | 7 | 27 | 4.5 | 3 | 0.01 | 0.02 | 0.11 | 0.81 | 0.95 | 16 |
| Coarse-loamy Typic Haplustox | | | | | | | | | | | |
| Savanna | 16 | 0 | 84 | 5.0 | 3 | 0.06 | 0.07 | 0.19 | 0.44 | 0.76 | 42 |
| Crop | 16 | 0 | 84 | 6.0 | 9 | 1.13 | 0.21 | 0.18 | 0.08 | 1.60 | 95 |
| Pasture | 17 | 0 | 83 | 5.4 | 2 | 0.56 | 0.05 | 0.08 | 0.22 | 0.91 | 76 |
| Eucalyptus | 15 | 0 | 85 | 4.8 | 4 | 0.05 | 0.04 | 0.14 | 0.70 | 0.93 | 25 |

a. $CEC_e$ = effective cation-exchange capacity; BS = base saturation.

Table 2. Distribution (±95% confidence intervals) of macro- (>0.25 mm) and microaggregates (<0.25 mm), bulk density, and pore volume at specific matrix potentials in differently managed clayey and loamy Oxisols in the Brazilian savannas.

| Oxisol Treatment | Aggregates (%) | | Bulk density ($t/m^3$) | Pore volume (g/kg) | Pore volume at pF (g/kg) | | |
|---|---|---|---|---|---|---|---|
| | Macro- | Micro- | | | <1.8 | 1.8-4.2 | >4.2 |
| Very fine Anionic Acrustox | | | | | | | |
| Savanna | 91.2 ± 4.8 | 8.6 ± 4.9 | 0.84 ± 0.02 | 76 ± 2 | 39 ± 1 | 11 ± 1 | 26 ± 1 |
| Crop | 82.3 ± 0.9 | 17.6 ± 0.9 | 0.93 ± 0.04 | 68 ± 2 | 23 ± 3 | 17 ± 3 | 28 ± 0 |
| Pasture | 89.4 ± 0.7 | 10.5 ± 0.6 | 0.89 ± 0.06 | 73 ± 4 | 30 ± 2 | 14 ± 3 | 29 ± 0 |
| Pine | 87.6 ± 1.2 | 12.0 ± 1.3 | 0.92 ± 0.04 | 68 ± 3 | 28 ± 2 | 13 ± 2 | 27 ± 1 |
| Average[a] | 87.6 b | 12.2 a | 0.90 a | 71 b | 30 a | 14 a | 28 b |
| Coarse-loamy Typic Haplustox | | | | | | | |
| Savanna | 85.2 ± 0.6 | 14.6 ± 0.8 | 1.15 ± 0.05 | 58 ± 3 | 35 ± 3 | 11 ± 2 | 12 ± 0 |
| Crop | 70.3 ± 0.3 | 29.6 ± 0.3 | 1.38 ± 0.06 | 48 ± 2 | 19 ± 2 | 17 ± 2 | 12 ± 1 |
| Pasture | 79.8 ± 1.7 | 20.0 ± 1.7 | 1.23 ± 0.03 | 54 ± 2 | 26 ± 2 | 16 ± 2 | 12 ± 0 |
| Eucalyptus | 77.8 ± 0.5 | 22.0 ± 0.5 | 1.27 ± 0.05 | 52 ± 2 | 27 ± 1 | 14 ± 3 | 11 ± 1 |
| Average[a] | 78.3 a | 21.6 b | 1.26 b | 53 a | 27 a | 15 a | 12 a |

a. Between the two soil types, values followed by the same lowercase letter are not significantly different at the $P < 0.05$ level of Tukey's HSD test.

comparable between the two soils, they represented a much higher proportion of SOC in the loamy than in the clayey soils. The NCPs were mainly of microbial origin, while the CPs were mostly plant derived (Guggenberger et al. 1994) and were determined because of their aggregate-bonding properties (Chenu 1993). The NCPs corresponded to 81%-86% of total polysaccharides, and both the NCPs and CPs were highly correlated to SOC ($r > 0.92^{***}$). Total polysaccharide contents ranged from 15%-22% of SOC, a figure that is comparable with topsoil polysaccharide contents of the Great Plains (Amelung et al. 1997), thus indicating that no pronounced differences exist between the quantity of polysaccharides in tropical Oxisols and that in temperate Mollisols. Management effects on SOC, NCPs, and CPs were restricted to the pine plantation on the clayey soil and crops on the loamy substrate. The POC was lowest under both crop treatments.

Pedogenic oxyhydroxides were at least twice as high in the clayey substrate (Table 3), reflecting the close relationship between organic compounds and clay content (Feller and Beare 1997). Over 95% of Fe oxyhydroxides were in crystalline form, suggesting an advanced degree of weathering. The proportion of $Al_o$ was probably higher because DCB extracts only a small fraction of total pedogenic Al (Wada 1989). Differences in oxyhydroxide contents between the treatments presented no clear trends, possibly reflecting natural variation rather than management effects.

## *Distribution of water-stable aggregates*

Overall, macroaggregates (diameter >0.25 mm) were slightly but significantly lower in the loamy than in the clayey soils because of the higher amounts of soil compounds per unit volume in the clayey substrate (Table 2). To better understand aggregate distribution, the aggregate classes 1-2 and 2-8 mm were combined, as were the 0.25-0.5 and 0.5-1 mm classes because they had similar

ribution (in g/kg) of soil organic carbon (SOC), organic compounds, and pedogenic oxides, with ±95% confidence intervals, in differently managed cl
ny Oxisols of the Brazilian savannas. The values in brackets represent the proportion (%) of organic compounds to SOC and of oxalate- to dithionit
actable oxyhydroxides.[a]

| | SOC | C/N ratio | POC | NCPs | CPs | $Fe_d$ | $Fe_o$ | $Al_d$ |
|---|---|---|---|---|---|---|---|---|
| onic Acrustox | | | | | | | | |
| | 23.5 ± 0.3 | 17.8 ± 0.8 | 2.3 (9.8) | 3.8 (16.2) | 0.76 (3.2) | 46.6 ± 3.6 | 2.1 (4.5) | 10.1 ± 3.6 |
| | 22.9 ± 0.4 | 16.6 ± 0.2 | 1.4 (6.1) | 3.6 (15.7) | 0.60 (2.6) | 50.8 ± 1.3 | 1.6 (3.1) | 17.0 ± 1.8 |
| | 24.6 ± 0.9 | 17.8 ± 0.2 | 3.1 (12.6) | 4.5 (18.3) | 0.84 (3.4) | 53.5 ± 2.2 | 1.9 (3.5) | 16.2 ± 3.5 |
| | 21.5 ± 1.2 | 20.0 ± 0.6 | 2.9 (13.5) | 2.5 (11.6) | 0.53 (2.5) | 48.0 ± 2.2 | 1.6 (3.3) | 12.1 ± 2.9 |
| Typic Haplustox | | | | | | | | |
| | 9.8 ± 0.4 | 15.9 ± 0.6 | 3.8 (38.8) | 1.6 (16.3) | 0.38 (3.9) | 16.0 ± 0.5 | 0.8 (5.0) | 3.9 ± 0.6 |
| | 7.1 ± 0.3 | 16.8 ± 0.3 | 1.5 (21.1) | 1.1 (15.5) | 0.22 (3.1) | 15.6 ± 1.0 | 0.7 (4.5) | 4.8 ± 0.7 |
| | 9.3 ± 0.7 | 17.5 ± 0.8 | 2.6 (28.0) | 1.5 (16.1) | 0.32 (3.4) | 19.3 ± 0.7 | 0.8 (4.1) | 3.9 ± 0.3 |
| | 10.2 ± 0.2 | 18.9 ± 0.1 | 2.5 (24.5) | 1.6 (15.7) | 0.35 (3.4) | 17.2 ± 0.6 | 0.8 (4.7) | 6.0 ± 0.5 |

ticulate organic carbon; NCPs, CPs = noncellulosic and cellulosic polysaccharides, respectively; $Al_d$, $Fe_d$ and $Al_o$, $Fe_o$ = dithionite- and oxalate-extrac
oxides and hydroxides of aluminum (Al) and iron (Fe).

distribution patterns. A higher number of macroaggregates (i.e., 1-8 mm) were found in the clayey soils, whereas the small macroaggregates (i.e., 0.25-1 mm) showed comparable proportions in both soils (Figure 1). The 0.05-0.25-mm fraction was always clearly higher in the clayey substrate, whereas the <0.05-mm fraction was generally lower in the loamy soils.

Management effects indicated that, compared with native savanna, all treatments tended to lose macroaggregates (Table 2). However, the reduction was expressed only under crops. Concomitantly, a land-use-specific aggregate distribution formed over time (Figure 1). Small macroaggregates increased at the expense of large macroaggregates under pine, and microaggregates increased considerably under crops with regular tillage.

The loss of macroaggregates under crops can be attributed to tillage, liming, and subsequent loss of OM (Campos et al. 1995; Caron et al. 1996; Castro Filho and Logan 1991; Westerhof et al. 1999). In contrast, macroaggregate distribution under pine is probably related to a strongly reduced rooting intensity in the topsoil that otherwise could have held large macroaggregates together. Under pine, most fine roots shifted from the first centimeters of the mineral soil into the thick moder horizon above. Such a shift is typical of pine reforestations in the *Cerrados*, probably because nutrient availability is higher in the organic layer than in the mineral soil and because the OM may complex toxic Al (Puhe 1994).

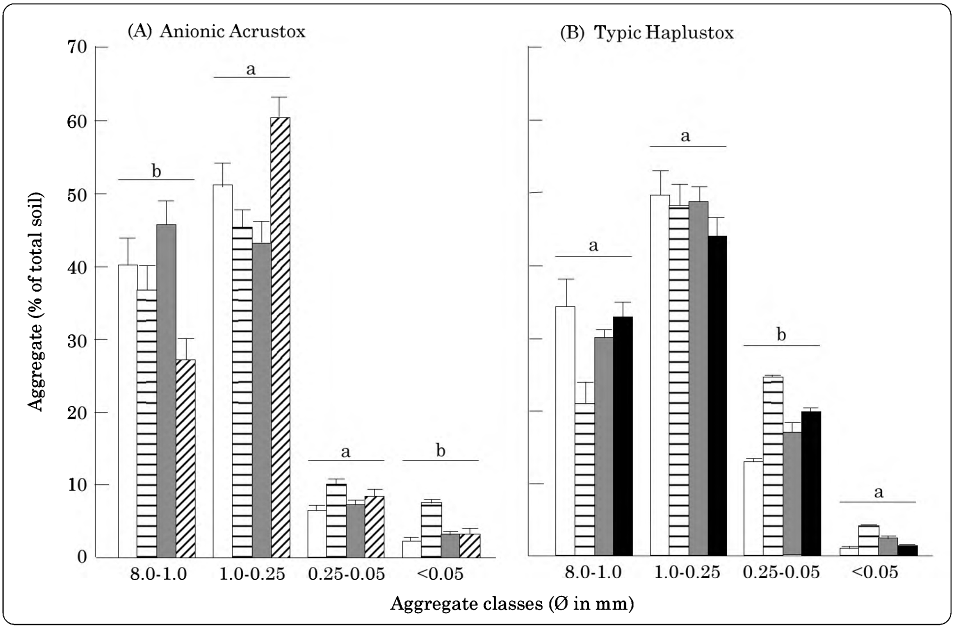

Figure 1. Management effects on the distribution of water-stable aggregates (with ±95% confidence intervals) in clayey (A) and loamy (B) Oxisols of the Brazilian savannas. The same lowercase letter above an aggregate class indicates that differences between the soil types are not significant with Tukey's HSD test at $P < 0.05$. ( □ = native savanna; ▤ = crop; ■ = pasture; ▨ = pine; ■ = eucalyptus.)

### Binding agents of aggregation

The influence of several soil compounds on aggregation was studied, using regression analyses. The results indicated that, in the loamy substrate, aggregation correlated significantly with all organic compounds, Ca, Mg, Al, and pH. In contrast, in the clayey substrate, aggregation correlated significantly with only POC, $Fe_o$, and Ca (Table 4). For both soil types, all correlations, except for Ca, Mg, and K, were significant. However, SOC, $Fe_d$, $Al_d$, and $Al_o$ were only well correlated because of the strongly contrasting contents between the two substrates. These discrepancies obliged us to calculate multiple regressions for each substrate and for both soil types together to evaluate the most important aggregating agents. The best fits of macroaggregation versus independent variables that presented an acceptable serial correlation according to Savin and White (1977) are presented below:

$$MA_{loam} = 11.33\,(NCP + CP) + 2.43\,POC + 52.08$$

$$R^2 = 0.88$$

$$MA_{clay} = 3.07\,(NCP + CP) - 0.02\,Ca + 77.77$$

$$R^2 = 0.93$$

$$MA_{both} = 3.30\,(NCP + CP) - 5.77\,pH + 2.14\,POC + 97.60$$

$$R^2 = 0.93$$

where MA = macroaggregation

These equations indicate that polysaccharides played an important role for aggregation in both soils. According to Dorioz et al. (1993), extracellular polysaccharides are especially effective in gluing soil particles together at the microaggregate (5-200 µm) level, although packing effects may also influence macroaggregation up to 1000 µm. However, because, in the studied Oxisols, more than 70% of the polysaccharides were bound to the clay fraction (Neufeldt 1998), they most probably act on microaggregation and are at least temporarily protected from

Table 4. Pearson correlation coefficients and significance levels of bulk-soil constituents versus macroaggregation in clayey and loamy Oxisols of the Brazilian savannas.

| Predictors[a] | Correlation coefficients | | |
|---|---|---|---|
| | Clayey Acrustox (n = 12) | Loamy Haplustox (n = 12) | Both Oxisols (n = 24) |
| SOC | 0.291 | 0.768** | 0.779*** |
| NCPs + CPs | 0.327 | 0.887*** | 0.768*** |
| NCPs | 0.275 | 0.884*** | 0.755*** |
| CPs | 0.553 | 0.868*** | 0.830*** |
| POC | 0.615* | 0.827*** | 0.448* |
| $Al_d$ | –0.571 | 0.419 | 0.500* |
| $Al_o$ | –0.424 | 0.117 | 0.669*** |
| $Fe_d$ | –0.280 | 0.226 | 0.706*** |
| $Fe_o$ | 0.684* | 0.380 | 0.790*** |
| pH | –0.520 | –0.786** | –0.605** |
| Ca | –0.666* | –0.758** | –0.021 |
| Mg | –0.520 | –0.096 | 0.180 |
| Al | 0.655 | 0.477 | 0.462* |

* = $P < 0.05$, ** = $P < 0.01$, *** = $P < 0.001$.

a. SOC = soil organic carbon; NCPs, CPs = noncellulosic and cellulosic polysaccharides, respectively; POC = particulate organic carbon; $Al_d$, $Fe_d$ and $Al_o$, $Fe_o$ = dithionite- and oxalate-extractable pedogenic oxides and hydroxides of aluminum (Al) and iron (Fe).

decomposition. A minor contribution to aggregation may also come from ion exchange and complexation of polysaccharides (Cheshire 1979).

The POC was important for aggregation in the loamy substrate only, possibly because of its higher proportion than in the clayey soils. However, POC corresponded to only 10% of $R^2$, indicating that its contribution was small. Gijsman (1996) also drew similar conclusions for Colombian Oxisols. In contrast, Ca in the clayey substrate corresponded to almost half of the variation, correlating strongly with the pH ($r = 0.89$) and Al ($r = -0.90$) after log-transformation and correction for valence, respectively. After bonding by polysaccharides, the increase of pH and subsequent cation exchange after liming seem to dominate disaggregation in the clayey substrate. For both soils together, the best fit included polysaccharides, pH, and POC, which contributed to 59%, 29%, and merely 6% of the $R^2$ change, respectively (Figure 2).

These results may have strong implications for management practices. They suggest that aggregation in the loamy soils depends to a greater extent on the enmeshing of aggregates by roots so that no-till systems or crop/pasture rotations may be able to reverse tillage-induced disaggregation (Campos et al. 1995; Gijsman 1996). Chemical disaggregation in the clayey substrate is probably inevitable because liming is essential to successful agriculture under the low pH and nutrient conditions of native savanna. However, according to Castro Filho and Logan (1991) and Roth et al. (1991), liming will stabilize Oxisol aggregates if application rates are sufficiently high. Westerhof et al.

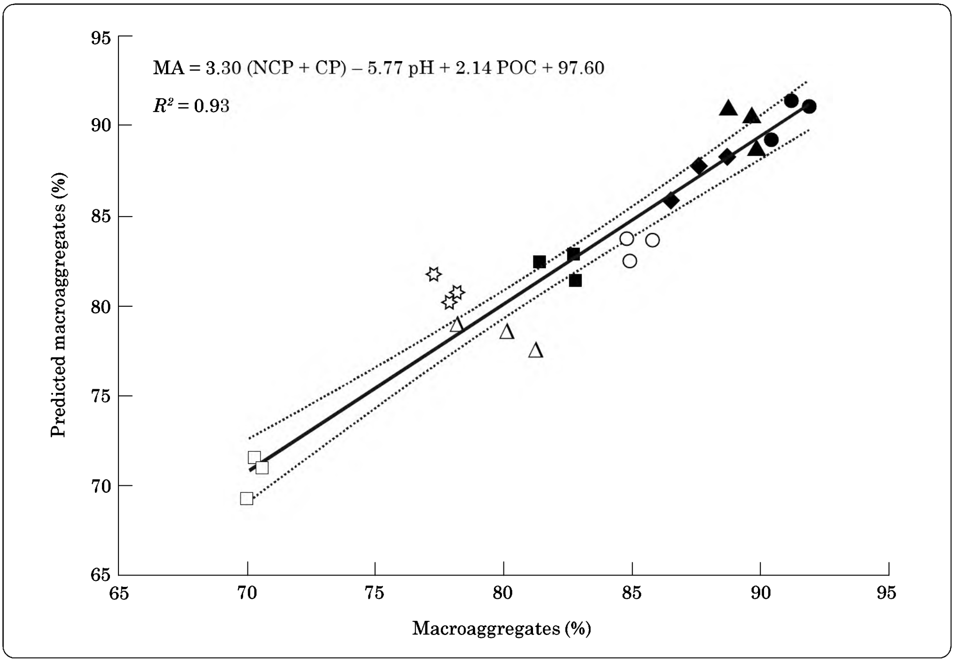

Figure 2. Predicted versus observed percentages of macroaggregates (with ±95% confidence intervals) in clayey (solid symbols) and loamy (open symbols) Oxisols of the Brazilian savannas. (●, ○ = native savanna; ■, □ = crop; ▲, △ = pasture; ◆ = pine; ✡ = eucalyptus.)

(1999) found that liming had disaggregating effects only when SOM contents were low. This would explain why liming has little effect on pastures, which have high polysaccharide contents. The structural improvement of Oxisols after introducing pastures to conventionally tilled cropland may therefore be related principally to the increase of polysaccharides, thus justifying the use of crop/pasture rotations to reduce soil slaking.

### *Effects of disaggregation on pore-size distribution*

Castro Filho and Logan (1991) and Roth and Pavan (1991) explained the reduced pore volume after land-use change in Brazilian Oxisols to liming. However, in our study, soil compaction by heavy machinery or cattle trampling could also contribute to reduced pore volume. Because macroaggregation was highly correlated to pore volume in the soils ($r = 0.892^{***}$), management-induced disaggregation probably led to soil compaction.

The loss of pore volume mainly occurred among the macropores (∅ > 50 µm), as indicated by the close correlation between macroaggregates and macroporosity ($r = 0.796^{***}$). This corresponds to the results of Roth et al. (1991), who detected reduced macroporosity after conventional tillage and no-tillage were introduced to an Oxisol in southern Brazil. Sutherland et al. (1996) showed, through regression analyses of aggregate classes, that the increase of the 0.05-0.25-mm fraction was mainly responsible for the loss of macroporosity, probably by detachment and subsequent transport of aggregates during heavy rains. However, they also found that the 0.25-2-mm aggregates were mainly responsible for soil sealing in an Oxisol in Hawaii, USA.

The number of mesopores (∅ = 0.2-50 µm) significantly correlated with the <0.05-mm fraction ($r = 0.608^{**}$), suggesting that, after land-use change, the diameter of some macropores was reduced to that of small macroaggregates. Roth et al. (1991) found a comparable increase in the number of mesopores after land-use change, and an experiment by Curmi et al. (1994) confirmed that mechanical compaction of an Oxisol derived from basalt reduced the number of interaggregate pores of 1-100 µm diameter. Considering the low pore space at plant-available matrix potentials in Oxisols (Bartoli et al. 1992), the increase of mesopores could prevent annual crops from suffering drought during dry spells in the rainy season (*veranicos*); these have more than a 30% chance of occurring in the study region (Assad et al. 1994). However, Moraes et al. (1995) determined that soybean root development in an Oxisol was strongly reduced through mechanical compaction.

Micropores (∅ < 0.2 µm) were not functionally correlated with any aggregate class because they were not affected by management practices. Likewise, Curmi et al. (1994) found that compaction had no effects on intra-aggregate pores of <1-µm diameter because their number is determined only by soil mineralogy (Bui et al. 1989).

Although these results indicate strong effects of disaggregation on water retention after land-use change, further study is needed to determine whether compaction has net positive effects for cropping systems by increasing plant-available water or net negative effects by reducing pore space.

## Conclusions

In the Brazilian savannas, Oxisols of both clayey and loamy texture are characterized by high macroaggregate stability under savanna conditions. Land-use change to cropping clearly leads to increased microaggregation, which is not so clear under pasture and eucalyptus. Change to pine leads to a management-specific increase of small macroaggregates at the expense of large macroaggregates as the fine-root maximum shifts from the mineral topsoil to the thick moder horizon lying above.

Aggregation in the clayey soils is caused mostly by the bonding of mineral particles with polysaccharides and the action of electrostatic forces between polyvalent metal cations and negatively charged OM and kaolinite. Reduction of polysaccharides and liming are therefore the most important disaggregating agents. In loamy Oxisols, after bonding with polysaccharides, the binding of larger aggregates by roots is of greatest significance. To reverse disaggregation, crop/pasture rotations are recommended, especially for loamy soils, which would benefit from the pastures' strong rooting and polysaccharide production.

Compaction after land-use change is induced by disaggregation and leads to a reduced number of macropores and an increased number of mesopores. In contrast, micropores are controlled only by soil texture. However, whether the increase of the usually low pore space at plant-available matrix potentials is positive for annual crops requires further research.

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# CHAPTER 6

# Aggregation Studied by Laser Diffraction in Relation to Plowing, Soil Organic Matter, and Lime in the Brazilian *Cerrados*

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## Abstract

In the *Cerrados*, a large savanna region in Brazil, the effects of different land use on aggregation in Oxisols were studied, using laser diffraction grain-size analyses. The topsoil of plowed systems had significantly fewer macroaggregates (194-2000 µm) and a significantly larger fraction of microaggregates and primary particles (<76 µm) than did pastures and native savanna. In plowed systems that were low in soil organic carbon (SOC), lime negatively affected aggregate stability. Lime addition had no effect on topsoil aggregation in land-use systems that were irregularly plowed and generally had a higher SOC content. For all the studied topsoils, $pH_{KCl}$ was positively correlated with the amount of clay dispersed after 3 h of shaking in water. Soil organic carbon did not influence clay dispersion in the range of soils studied. In continuous cropping systems in the *Cerrados*, a combination of mechanical stress, low SOC, and liming will increase the number of small aggregates and primary particles and hence contribute to destabilizing the soil structure.

*Keywords:* Aggregates, Brazilian savannas, *Cerrados*, laser diffraction grain-size analyses, lime, Oxisols, water-dispersible clay

## Introduction

In the *Cerrados*, a large savanna region in Brazil, Oxisols have a stable microstructure caused by strong aggregation of negatively charged kaolinite and positively charged gibbsite and goethite (Bartoli et al. 1992; Goedert 1983; Sánchez 1976). However, arable land-use systems frequently degrade soil structure, which, together with the high rainfall intensities common in the *Cerrados*, can lead to severe loss of soil through water erosion (Goedert 1983; Sánchez 1976). Land use influences the infiltration of water into the soil by its effect on soil cover, aggregation, and amount of water-dispersible clay (WDC). A negative linear relationship between WDC and infiltration rates was established for the surface soil of an Oxisol in the State of Paraná in southern Brazil (Roth and Pavan 1991). In that experiment, liming caused an increase in WDC that

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probably clogged pores. Similarly, Koutika et al. (1997) have reported an increase of both negative surface charge and WDC in the topsoils of eastern Brazilian Oxisols. According to Oades and Waters (1991), the breakdown of aggregates (>250 µm) in Oxisols leads directly to the release of clay-size particles (<2 µm).

Changes in aggregation and WDC in organic-rich horizons of Oxisols and other soils rich in variable-charged clay particles have been attributed to various factors: (1) a disruption of aggregates by mechanical stress caused by plowing or cattle trampling (Fontes et al. 1995; Koutika et al. 1997); (2) losses of soil organic matter (SOM) that could act as a cementing agent (Bartoli et al. 1992; Castro Filho and Logan 1991; Muggler et al. 1997; Tisdall and Oades 1980); and (3) liming, which causes two processes. One is the increase of soil pH. The higher pH decreases the positive charge of sesquioxides and increases the negative charge of SOM, thus leading to an increased repulsion between soil particles when the pH rises above the point of zero net charge in the soil. The second process is the substitution of $Al^{3+}$ with $Ca^{2+}$, which weakens intra-aggregate bonds (Gillman 1974; Roth and Pavan 1991; Seta and Karanthanasis 1996).

The factors mentioned above are related. For example, disruption of aggregates by plowing may cause mineralization of previously protected organic matter (Elliott 1986).

Measurements of clay dispersion can be made by shaking the soil in water and determining the clay fraction by pipette (EMBRAPA 1979). Clay in the runoff of research plots has also been measured (Roth and Pavan 1991). These methods give no information about the size of aggregates that were disrupted.

However, studies dealing with aggregate stability and aggregate distribution involve wet-sieving with a set of sieves of decreasing mesh size (Beare and Bruce 1993; Tisdall and Oades 1980). By doing so, aggregate classes are defined by the mesh size of the sieves used. These classes are unlikely to reflect the natural aggregate classes. Recently, Muggler et al. (1997) used laser diffraction grain-size analysis to study aggregation in Brazilian Oxisols. The large number of particle-size classes obtained by laser diffraction allows for the recognition of subtle changes in aggregation or particle-size distribution that occur during changes in land use or weathering (Buurman et al. 1997; Muggler et al. 1997).

We studied changes in Oxisol topsoil aggregation and clay dispersion as caused by different land uses in the Brazilian *Cerrados*, using both laser diffraction grain-size analysis and the traditional sedimentation Robinson pipette method. The relative effects of plowing, liming, and differences in SOM content on soil aggregation and WDC are discussed.

## Materials and Methods

### *Site description*

The research was conducted on selected plots of a long-term field experiment located at the EMBRAPA-CPAC research institute in Planaltina (Federal District, Brazil). The project was started in 1991 when part of virgin *Cerrados* was converted into pasture and cropland. The plots are located at 1200 m above sea level at 15°35'S and 47°42'30'W in a well-drained savanna. Mean annual rainfall is between 1400 and 1600 mm, 90% of which falls between October and April, with November, December, and January being the wettest months (>200 mm per month) (Jones et al. 1992). The mean annual temperature of 21 °C is fairly constant throughout the year, with June and July being the coolest months (average of 16 °C/13 °C, day/night) and September being the warmest month (average of 30 °C/16 °C, day/night) (Ussud 1994). The soil, a clayey Oxisol, is classified as a Typic Acrustox (Soil Survey Staff 1975) or as a Red-Yellow Latosol (Brazilian system, Macedo and Bryant 1987). Soil mineralogy is dominated by variable charge clays: about 40% gibbsite, 30% kaolinite, and 6% goethite, with the remainder of the fraction being <2-mm quartz (Macedo and Bryant 1987).

The land-use systems studied (0.2 ha for each treatment) were:

1. Native savanna;
2. Continuous legume-based pastures (P): *Andropogon gayanus* (grass) + *Stylosanthes guianensis* (legume), receiving conventional fertilizer (F2) additions (P F2);
3. Continuous cropping systems (C), with a rotation of soybean and maize at low (F1) and conventional (F2) fertilizer addition rates (C F1 and C F2, respectively);
4. Legume-based pasture/crop rotations (*Andropogon gayanus* + *Stylosanthes guianensis* and soybean/maize rotation) at low (PC F1) and conventional (PC F2) fertilizer additions rates. Both treatments were managed as pastures until May 1995, when they were plowed.

At establishment in 1991, dolomitic lime was applied at rates of 3.4 metric tons per hectare for F1 treatments and 5.8 t/ha for F2 treatments. The pastures and cropped fields also received low amounts of N, P, and K fertilizers and micronutrients. In May 1995, the legume-based pastures PC F1 and PC F2 were plowed. Early November 1995, maize was planted on all land-use systems, except P F2 and native savanna.

Soil samples were taken from the plow layer (0-10 cm) in January 1996. Four samples, each consisting of four subsamples, were taken from each plot, using a soil auger. Soils were stored in plastic bags at 4 °C for a few days until sieving (<2 mm) and air drying (40 °C).

### *Soil organic carbon, exchangeable cations, effective cation-exchange capacity, pH, and charge of soils*

Total carbon was measured on an Elementar Vario EL element analyzer. Because soil pH was low, total C was considered to represent SOC. Exchangeable cations were determined by extraction with an unbuffered $NH_4Cl$-$BaCl_2$ solution (Amacher et al. 1990). This extraction gives results similar to those of the $NH_4OAc$ extraction for exchangeable bases and the KCl extraction for exchangeable aluminum, but is more rapid (Amacher et al. 1990). Na, K, Ca, Mg, and Al were measured, using atomic absorption spectroscopy. The effective cation-exchange capacity at soil pH ($CEC_e$) was calculated as the sum of Na, K, Ca, Mg, and Al extracted by $NH_4Cl$-$BaCl_2$ solution (Amacher et al. 1990). Exchangeable H extracted by 1 *M* KCl was negligible: at <0.015 $cmol_c$/kg soil for native savanna and almost zero for the limed systems, and was not included in the calculations.

Soil pH was measured in a 1:2.5 soil-water or soil-1 *M* KCl suspension ($pH_{H_2O}$ or $pH_{KCl}$, respectively). The net charge of the soil was calculated by $pH_{KCl}$-$pH_{H_2O}$

(ΔpH); ΔpH > 0 indicates a net positive charge and pH < 0 indicates a net negative charge but gives no quantitative value of the net soil charge (Van Raij and Peech 1972).

### *Textural analyses, water-dispersible clay, and clay dispersion*

For textural analyses, 20 g soil (<2 mm) were mixed with 100 mL distilled water. To this mixture, 10 mL NaOH (0.1 *M*) was added as a dispersant (EMBRAPA 1979). The bottles were shaken manually and the soil solution mixture was left to react for 12 h. The bottles were then shaken for 3 h on a reciprocal shaker at 130 rpm. The coarse-sand fraction (0.2 to 2.0 mm) was sieved out, and silt (0.05-0.002 mm) and clay (<0.002 mm) were separated by sedimentation, using Stoke's law. Fine sand (0.2-0.05 mm) was calculated by difference. Coarse and fine sand were summed into the sand fraction (0.05 to 2.0 mm).

Water-dispersible clay was determined, following the same procedure but without adding 10 mL NaOH (EMBRAPA 1979). It is important to note that clay particles that dispersed during shaking can flocculate during sedimentation and will be retrieved in other fractions. Thus, this measurement better quantifies the clay fraction that remains after dispersion and reflocculation during sedimentation than the total dispersed clay after shaking in water.

To correct for total clay content of the soil, we calculated clay dispersion as:

$$\text{Dispersion (\% of total clay)} = 100 * \text{water-dispersible clay} * \text{clay}^{-1}$$

### *Measurement of aggregation by laser diffraction grain-size analyses*

Changes in grain-size distribution of the soil on stirring and wetting were determined by laser diffraction, using a Coulter LS230 laser grain sizer with a range of 0.04-2000 µm.

Air-dried soil was gently pushed through 2-mm sieves before analysis, and large roots and other fresh organic material were removed by hand. A 5-g sample was added to the machine's water reservoir, which contained about 2 L of tap water. The water-soil mixture was circulated at high constant speed through the measurement cell. To prevent reflocculation, 50 mL of 5% sodium polyphosphate solution was added as a dispersant and, where necessary, samples were diluted during measurement as described by Buurman et al. (1997). The high circulation speed disrupted the aggregates. The distribution of grain size was measured at the following intervals: <1, 10, 20, and 30 min. By doing so, the distribution and stability of aggregates (<2 mm) according to land-use system could be compared.

A detailed description of the apparatus and practical problems of measurement are described by Buurman et al. (1997). Muggler et al. (1997) optimized the method for Brazilian Oxisols, and we used their calculation model and similar apparatus.

Figure 1 shows a typical result of grain-size analyses after <1 and 30 min. After <1 min, a continuous distribution of aggregates was found with most of the volume fraction of the soil between 76 and 2000 µm (line 1, Figure 1). After 30 min, the number of particles (size <76 µm) increased and

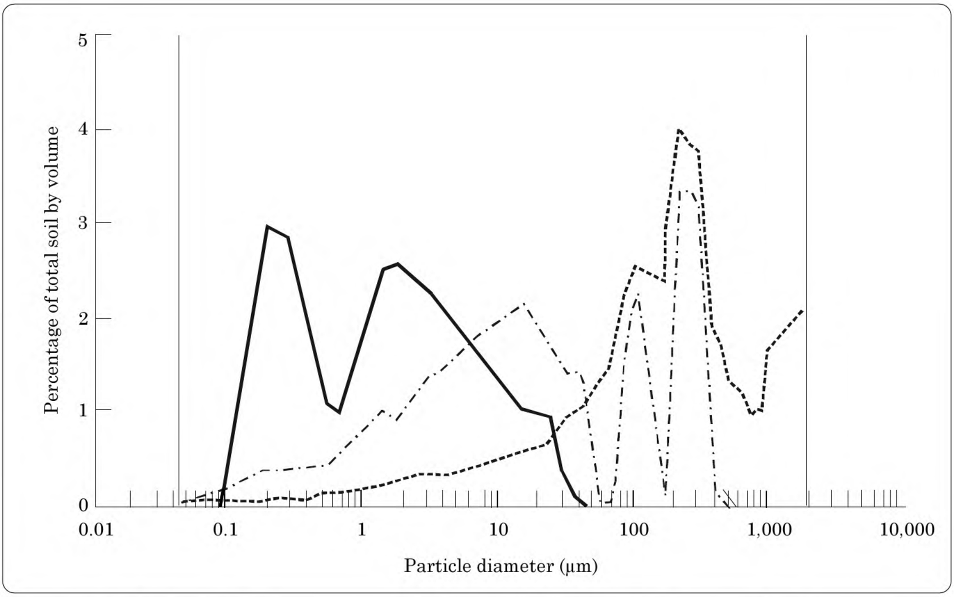

Figure 1. Grain-size distribution as measured by laser diffraction: without disruption (line 1 = ----), after 30 min circulation in the grain sizer (line 2 = - · —), and after ultrasonic dispersion (line 3 = ——) of a native savanna soil sample (0-10 cm). Samples are of Oxisols from the Brazilian savannas.

the aggregate distribution showed more distinct peaks; the most pronounced between 76 and 194 µm. The >1041-µm fraction disappeared completely after 30 min of circulation (line 2, Figure 1). This pattern typically occurred for all land-use systems, and the soil could be separated into the size classes 1041-2000, 194-1041, 76-94, and <76 µm. By integrating the area under the curve between two limits (e.g., 194 and 1041 µm) the amount of soil could be quantified in each size class. Sonification for 10 min with an energy input of 20 W caused the loss of all fractions below 76 µm (line 3, Figure 1). All primary particles of the soils were therefore more than 76 µm.

In the following text, the fraction below 76 µm is called the microaggregate and the primary particle fraction; the aggregates at 76-194 µm are mesoaggregates; and the fractions at 194-1041 and 1041-2000 µm are together considered as macroaggregate fractions.

The macroaggregates that survived the 30 min of circulation are regarded as stable, and those that were disrupted (the difference between macroaggregates at <1 min and stable macroaggregates after 30 min) as labile.

### *Statistics*

The effect of land use on aggregate classes was studied by using analysis of variance for a randomized complete block design (Little and Hill 1978). Where the analyses showed significant differences, Duncan's multiple range test was conducted to separate land-use systems (Little and Hill 1978).

# Results

## *Soil organic carbon, exchangeable cations, effective cation-exchange capacity, pH, and charge of soils*

Five years of land use had significant effects on SOC, pH, exchangeable cations, and $CEC_e$ in the upper layer of the soils studied (Table 1). Soils under pastures had higher SOC than did soils under crops. Liming caused a significant decrease in exchangeable Al and a significant increase in exchangeable cations (mostly Ca and Mg), $CEC_e$, and pH under all land-use systems, when compared with the native savanna control. The net charge of the soil was negative for all land-use systems ($\Delta pH < 0$). The higher $CEC_e$ caused by liming is explained by the increase in net negative charge of the soil with rising pH.

## *Textural analyses, water-dispersible clay, and clay dispersion*

The land-use systems PC F1 and P F2 were somewhat more clayey than C F1 or C F2. No significant effect of land use on the amount of WDC and clay dispersion was found, mostly because of high spatial variability within the plots. However, a significant positive correlation between $pH_{KCl}$ and dispersion was found ($r = 0.64$; n = 22; $P < 0.01$). The $pH_{KCl}$ was better correlated with clay dispersion than was $pH_{H_2O}$ or exchangeable cations. No significant correlation between dispersion and SOC was found.

## *Effects of increased disruption on aggregate size distribution*

In Figure 2, the distribution of the size classes measured by laser diffraction is shown. After <1 min circulation, over 50% of soil from all land-use systems was in the macroaggregate fraction. After 10 min of circulation, the macroaggregate fraction decreased to about 30% and the microaggregate and primary particle fraction increased to between 40% and 60%. After 20 and 30 min, the macroaggregates decreased to about 20% of total soil volume and the microaggregate and primary particle fraction increased to about 60%. The proportions of mesoaggregates were relatively unaffected.

## *Effect of plowing on aggregation*

Systems that were plowed regularly had significantly ($P < 0.05$) lower amounts of macroaggregates after <1 min circulation than did the native savanna, pasture, and rotations (51%, compared with 56%-59% by volume). This resulted in significantly ($P < 0.05$) higher amounts of soil in the microaggregates and primary particle fraction (23%-24%, compared with 20%-21% by volume). The difference between regularly plowed and other systems decreased or vanished with increasing circulation time, which indicates that the land-use system mainly influenced the labile macroaggregate fraction. The proportion of soil in the mesoaggregate fraction was not influenced by plowing. The pasture (P F2), rotations (PC F1 and PC F2) that were plowed only once, and the native savanna did not differ from each other.

## *The effect of soil organic carbon, exchangeable cations, and effective cation-exchange capacity on selected parameters for aggregation*

The <76-µm and macroaggregate fractions were most influenced by d soil properties[a] under different land-use systems (0-10 cm upper layer, n = 4) on Oxisols in the savannas of central Brazil.

| SOC (mg/g) | Exch. cat. (cmol$_c$/kg) | | CEC$_e$ (cmol$_c$/kg) | pH | | Texture (g/100 g) | | | WDC (g/100 g) | Cl |
|---|---|---|---|---|---|---|---|---|---|---|
| | Bases | Al | | KCl | Water | Sand | Silt | Clay | | |
| 29.6 a | 1.77 a | 0.02 c | 1.79 a | 4.85 b | 5.60 a | 25 b | 13 a | 63 ab | 35 a | |
| 24.9 bc | 0.56 c | 0.21 b | 0.77 c | 4.33 cd | 4.97 b | 36 a | 6 b | 58 bc | 29 a | |
| 23.1 c | 1.16 b | 0.09 c | 1.25 b | 4.73 b | 5.38 a | 38 a | 7 b | 56 c | 31 a | |
| 25.2 bc | 0.77 bc | 0.20 b | 0.97 bc | 4.60 bc | 5.43 a | 27 b | 7 b | 66 a | 33 a | |
| 27.1 ab | 1.78 a | 0.03 c | 1.81 a | 5.17 a | 5.50 a | 33 ab | 9 ab | 57 bc | 30 a | |
| 25.0 bc | 0.10 d | 0.37 a | 0.47 d | 4.20 d | 4.78 b | 31 ab | 9 ab | 61 bc | 28 a | |

values in the same column indicate significant differences between land-use systems (Duncan's multiple range test, $P < 0.05$). SOC = soil organic c
ve cation-exchange capacity; WDC = water-dispersible clay.
ised pastures; C = continuous crops; PC = rotation; F1 = low fertilization and with 3.4 t/ ha lime; F2 = conventional fertilization and with 5.8 t/ha li

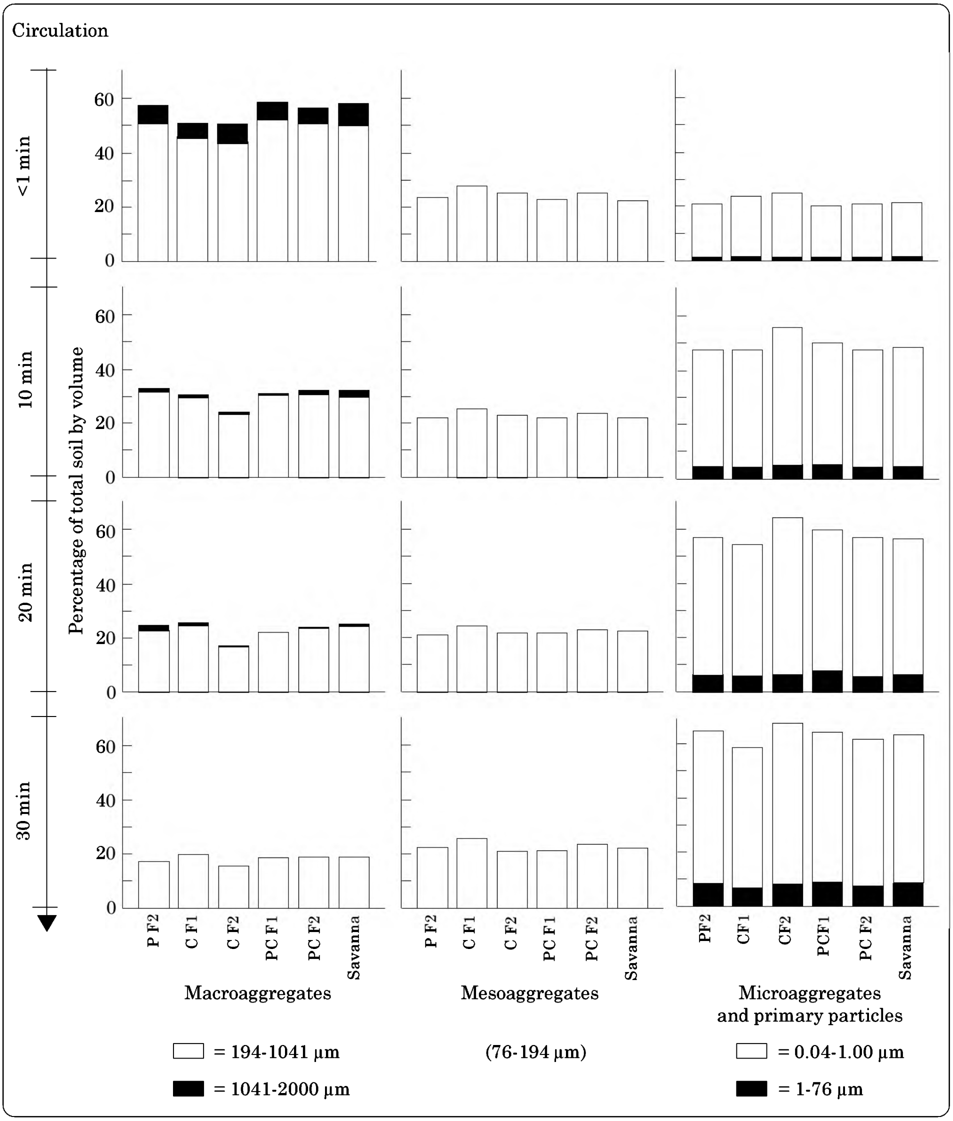

Figure 2. The effect of circulation time in the grain sizer on the aggregate size distribution of soil from a legume-based pasture (P F2), cropped fields (C F1 and C F2), legume-based pasture/crop rotations (PC F1 and PC F2), and native savanna, using samples from Oxisols of the Brazilian savannas. For statistics, see page 68 of text.

aggregate disruption and were chosen as parameters for aggregation. Because the effect of plowing overshadowed all other influences, analyzing all land-use systems together did not give information about the effect of soil chemical parameters on soil aggregation.

To overcome this problem, two groups were made: group A was plowed regularly and had a lower SOC content than group B (23.9 ± 1.4 mg/g versus 27.2 ± 2.2 mg/g). Group A contained C F1 and C F2 (n = 7) and group B contained native savanna, P F2, and PC F2 (n = 11). The rotation PC F1 was excluded because of its higher clay content (Table 2). In group A, exchangeable bases and $\text{CEC}_e$ were positively, and exchangeable Al negatively, correlated with the amount of soil in the microaggregate and primary particle fractions after 10, 20, and 30 min of disruption (Table 2, Figure 3). Furthermore, a positive correlation of labile macroaggregates with $\text{CEC}_e$ was found in group A. The stable macroaggregates tended to decrease with increasing $\text{CEC}_e$ (Figure 3). The correlation between parameters for soil aggregation and the $\text{CEC}_e$ stresses the importance of charge for aggregation in group A. In group B, no significant correlations were found between soil chemical parameters and aggregation.

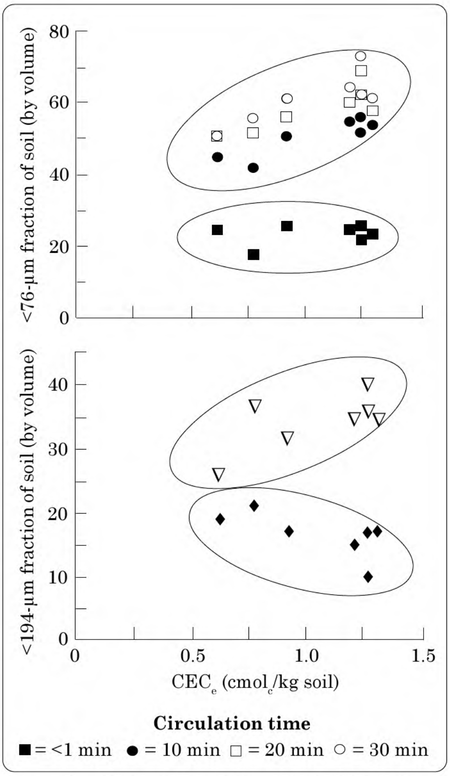

Figure 3. Scatter plot of the relationship of the volume of small particles (<76 µm) and labile (∇) and stable (♦) macroaggregates (>194 µm) with the effective cation-exchange capacity ($\text{CEC}_e$). Samples were taken from Oxisols of the Brazilian savannas.

## Discussion and Conclusions

### *The effect of land use on clay dispersion*

Plowing had no effect on the amount of WDC in our experiment. Shaking in water for 3 h probably erased the effect of plowing. This is corroborated by the results of the laser diffraction, which showed that plowing only influenced labile macroaggregates.

Even after 5 years of different land uses, SOC content probably did not change sufficiently to influence surface charge. Although the decrease of 1.9 mg/g (7.6% of SOC in native savanna) under crops caused a slight increase in the point of zero net charge (PZC), in this experiment, no significant increase of the PZC under crops was found. The PZC of native savanna, measured according to Van Raij and Peech (1972), ranged from 4.10 to 4.50 (n = 4) and that of the cropped fields (C F2) from 4.15 to 4.60 (n = 4). Note, however, that this does not mean that SOC is not important for clay flocculation.

In contrast, changes in soil pH caused by liming were sufficient to have a significant effect on the dispersion-reflocculation processes of clay.

### *The effect of land use on aggregation as measured by laser grain-size analyses*

Regular plowing decreased the macroaggregate fraction and increased the microaggregate and primary particle fractions. A parallel study of the plots, using a wet-sieving method, showed that plowing significantly

elation coefficients and ranges[a] for selected parameters for soil aggregation in groups A and B, with soil organic carbon (SOC), pH, exchangeable c
tive cation-exchange capacity (CEC$_e$). Samples are of Oxisols from the Brazilian savannas.

tinuous crops, plowed regularly (n = 7)

| e or: | Percentage of total soil by volume | SOC (mg/g) [22.1-26.5] | Exchangeable cations (cmol$_c$/kg) | | CEC$_e$ (cmol$_c$/kg) [0.62-1.30] | [4. |
|---|---|---|---|---|---|---|
| | | | Bases [0.40-1.28] | Al [0.02-0.22] | | |
| tes (<76 μm) | | | | | | |
| | 18-26 | ns | ns | ns | ns | |
| | 42-56 | ns | 0.86** | –0.70* | 0.88** | |
| | 51-69 | ns | 0.80** | –0.67* | 0.82** | |
| | 52-73 | ns | 0.75** | ns | 0.78** | |
| tes (>194 μm) | | | | | | |
| | 10-21 | ns | ns | ns | ns | |
| | 26-40 | ns | ns | ns | 0.67* | |

ume-based pastures, pasture/crop rotations (plowed once), and native savanna (n = 11)

| e or: | Percentage of total soil by volume | SOC (mg/g) [20.7-32.3] | Exchangeable cations (cmol$_c$/kg) | | CEC$_e$ (cmol$_c$/kg) [0.29-2.15] | [4. |
|---|---|---|---|---|---|---|
| | | | Bases [0.10-2.15] | Al [0-0.53] | | |
| tes (<76 μm) | | | | | | |
| | 17-24 | ns | ns | ns | ns | |
| | 41-52 | ns | ns | ns | ns | |
| | 49-59 | ns | ns | ns | ns | |
| | 57-65 | ns | ns | ns | ns | |
| tes (>194 μm) | | | | | | |
| | 14-20 | ns | ns | ns | ns | |
| | 34-47 | ns | ns | ns | ns | |

correlation at $P < 0.1$; ** = significant correlation at $P < 0.05$; ns = no significant correlation.
quare brackets are ranges of values for each parameter for Groups A and B.
n of circulation.

decreased the 2 to 8-mm aggregate fraction and significantly increased the 1-2 mm and 0.25-1 mm aggregate fractions (Freibauer 1996). The 2 to 8-mm fraction contained 29%-38% by weight of soil in that study. Because the Coulter laser grain sizer had an upper limit of 2 mm, this fraction was gently pushed through a 2-mm sieve. The significant increase, caused by plowing, in the smaller size fractions, as measured by the wet-sieving procedure, was consistent with the results obtained in this study. In contrast to the results obtained by Oades and Waters (1991) for an Australian Oxisol, the breakdown of macroaggregates did not lead to an increase in clay size particles in this experiment. We found an increase in the 1 to 76-µm fraction, most of which was above the 2-µm limit for clay (see Figure 1).

Group A, the regularly plowed crop fields, had a relatively narrow range of SOC (Table 2). This may have been why no correlation of SOC with aggregation was found. From these data, we cannot conclude that SOC is unimportant to soil aggregation, but changes in SOC within this range do not influence aggregation.

The negative influence of liming on aggregation, indicated by the positive correlations of exchangeable bases and $CEC_e$ with the number of microaggregates and primary particles, became clear after long circulation in the machine. These results confirm the conclusions by Fontes et al. (1995) that liming only increases WDC after mechanical stress.

The ranges of exchangeable bases, exchangeable Al, $CEC_e$, and pH in group B were as wide, or wider, than in group A. However, no significant correlation of these parameters with soil aggregation could be found. Tessens (1984) and Castro Filho and Logan (1991) showed that soil charge did not influence clay dispersion on soils relatively high in SOM. Although the SOC values from groups A and B showed some overlap, the 95% limit of confidence for groups A and B (SOC at 22.5-25.3 versus 25.0-29.4 mg/g soil) indicates a generally higher SOC content for group B. This can also be seen when the average SOC contents for C F1 and C F2 (group A) are compared with the average SOC contents of the pastures and native savanna (Table 1).

### *The relative effects of plowing, soil organic carbon, and liming on aggregation: some implications for management*

The effect of liming became clear only when soils were mechanically disrupted and had a relatively low SOC content. However, the differences in SOC content between groups A and B are small and the differences in reaction to liming are unlikely to be caused by differences in the amount of SOM only. The importance of soil biomass for aggregation is widely known and SOM quality strongly influences the type and amount of soil biomass (Lynch and Bragg 1985). For the same plots, but on other sampling dates, SOM quality was studied, using mineralization analyses and chemical extraction of labile SOM with potassium permanganate (Westerhof 1998; Westerhof et al. 1998). These studies showed that group B also had more labile SOM that could act as a source of energy and C and N for soil biomass than had group A.

The negative effect of liming on aggregation is reflected in the positive correlation of $pH_{KCl}$ with the amount of WDC. In this measurement, the disruptive force was stronger than in the laser diffraction grain-size analysis. Overall, these data indicate that, without mechanical disruption, changes in soil chemical parameters have little effect on soil aggregation. In continuous cropping systems, characterized by a combination of mechanical stress and relatively low SOC, liming will increase the number of small aggregates and primary particles. Such an increase may eventually affect the water-infiltration capacity of the soil and thus increase water erosion. When liming is combined with management practices aimed at reducing mechanical stress and maintaining SOM levels comparable with those in native savanna, any negative effects on soil aggregation can be avoided.

## Acknowledgments

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## CHAPTER 7

# Short-Term Variation in Aggregation and Particulate Organic Matter under Crops and Pastures

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## Abstract

Short-term changes in soil aggregation, total and particulate organic C and N were studied in cropping and pasture systems of the Brazilian savannas, also known as the *Cerrados*. Furthermore, the concepts of a hierarchical aggregate structure and of the interaction of soil structure with particulate organic matter (POM) available for temperate soils were evaluated and modified for tropical Oxisols. The results showed that Oxisol peds (>2 mm) were sensitive to land use and subject to significant seasonal turnover, indicating a similar behavior as in temperate soils. Three POM fractions were distinguished: (1) free POM situated in the free soil pore space, (2) easily accessible POM, loosely bound in peds and introduced in this study, and (3) occluded POM, which was not studied. Free and easily accessible POMs were important active C pools and increased with human activity. The ratio of free to easily accessible POMs could clearly characterize the different land-use systems.

*Keywords:* Aggregation, carbon, nitrogen, particulate organic matter, pasture, soybean

## Introduction

More than 50% of the central Brazilian savanna region, also known as the *Cerrados*, are covered by Oxisols, which have been increasingly used for cattle raising, and soybean and maize production over the last 20 years (Goedert 1983). Because of the predominance of low charge clays, organic matter (OM) is important for the nutrient storage and supply capacity of these soils (Goedert 1983). Thus, to maintain the soil production potential, land-management systems that maintain the inherently good physical structure of these soils and do not decrease the level of soil organic matter (SOM) are needed (Spain et al. 1996).

Usually, continuous cropping of a native soil disrupts the peds (Ø > 2 mm), leading to loss of organic carbon and associated nutrients (Tisdall and Oades 1982). The processes involved are mineralization of the OM that was previously protected within the peds (Elliott 1986), enhanced turnover of soil organic carbon (Dalal and Mayer 1986), and low input of litter and root biomass (Oades 1984). Aggregate disruption

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caused by cultivation was described in Australia according to a model of aggregate hierarchy (Tisdall and Oades 1982). According to this model, four levels of aggregation exist: <0.2 µm → 0.2-2.0 mmm → 2-20 µm → 20-250 µm → >2000 µm. Thus, peds (>2 mm) are formed by microaggregates (<0.25 mm) and stabilized by labile organic binding agents (polysaccharides, roots, and hyphae). Microaggregates are stabilized by persistent organic binding agents and sesquioxides. Only peds are affected by land management (Tisdall and Oades 1982). The model of aggregate hierarchy was successfully applied on moderately weathered soils (Elliott 1986), but was extended to tropical soils with controversial results (Beare et al. 1994; Oades and Waters 1991).

The interactions of soil structure and OM are complex and have rarely been studied in Oxisols (Golchin et al. 1995b; Nascimento et al. 1993). Cambardella and Elliott (1993) relate the loss of structural stability in cultivated grassland soils to losses of particulate organic matter (POM), defined as the soil fraction where the average aggregate diameter is less than 2 mm and aggregate density is <1.6 g/cm$^3$. It consists mainly of large, partly decomposed, fragments of plants and roots, which may act as labile binding agents in peds, according to Tisdall and Oades (1982). Total POM can be separated into different fractions of decreasing turnover rates with increasing degree of physical protection; this should give a closer insight into the dynamics of SOM (Golchin et al. 1994a, 1994b). The share of POM in total C is closely correlated with the type of vegetation and the intensity of litter production and turnover (Beare et al. 1994; Golchin et al. 1995a). Changes in POM content and quality therefore rapidly reflect alterations in the amount, persistence, and decomposition of plant residue inputs (Gregorich et al. 1994), and changes in POM will possibly lead to changes in total SOM. Several authors have suggested that the soil content of POM is a more sensitive indicator of the influence of land use on SOM than is total C (Cambardella and Elliott 1993; Dalal and Mayer 1986) and thus for soil quality (Gregorich et al. 1994).

Seasonal changes in soil properties indicate short-term fluctuations caused by water and biological activity. Knowledge about seasonal changes can provide a better understanding of the effects of land use on processes in soil like nutrient turnover and the activity of carbon pools, and can therefore help determine sensitive parameters for degradation or enhancement of soil properties. For the *Cerrados*, few data exist on changes of soil physical properties, SOM, and associated nutrients within one growing season.

This study compares the short-term changes in soil structure, total and particulate organic carbon and nitrogen between conventional (cropping and pure-grass pasture) and improved land-use systems (legume-based pastures) in the *Cerrados*. Furthermore, the conceptual models of aggregate hierarchy (Tisdall and Oades 1982) and of the interaction of soil structure and OM available for temperate soils (Golchin et al. 1994a, 1994b) were evaluated and modified for tropical Oxisols.

## Materials and Methods

### Site location and description

The studied area is as described in Chapter 6, pages 65-66. The soil, a clayey Oxisol, is classified as fine to very fine isohyperthermic, Anionic Acrustox (Soil Survey Staff 1994), with a clay content of 52% to 65%, a pH of

4.8 ($H_2O$), an effective CEC of 0.47 cmol(+)/kg and an 80% aluminum saturation in the topsoil.

The experiment was established in 1991 on virgin *Cerrados* in a randomized complete block design, with two replicates per treatment. The studied treatments were 4 years old when samples were taken from the following systems:

1. Continuous crops with conventional tillage (CCT, soybean/ soybean/maize/soybean) and fertilization (kg/ha per year) with 22 P, 25 K, 10 micronutrients, 35 kg/ha N in 1993, and 3.4 t/ha lime in 1991;
2. Pure-grass pasture (PG, *Andropogon gayanus* Kunth);
3. Grass/legume pasture (GL, *Andropogon gayanus* Kunth with *Stylosanthes guianensis* Sw. cv. Mineirão), with initial fertilization of both pastures (kg/ha) with 40 P, 30 micronutrients, 3.4 t/ha lime); and
4. Native savanna (NS) as reference.

### *Sampling*

On each plot, six soil samples were taken from a depth of 0-12 cm at two sampling dates: (1) at the end of November 1994, one week after the rainy season began (300 mm cumulative rain); and, (2) 3 months later in February 1995 (830 mm cumulative rain of 1200 mm during the whole rainy season). Samples were taken with a Uhland auger for keeping soil aggregates intact and for sampling a defined soil volume ($\varnothing = 8.5$ cm, volume = 680 $cm^3$). The field-fresh samples were gently pushed through an 8-mm sieve and air-dried at 40 °C. Aggregates and large roots remaining on the sieve were separated, air-dried, and weighed.

### *Aggregate fractionation*

Before fractionating by wet sieving, the samples were rewetted by capillary action to prevent slaking of aggregates by entrapped air (Cambardella and Elliott 1993). The soil was spread on the uppermost sieve, which was then adjusted at the water surface to allow the capillary rise of water through the sample for 5 min. The size distribution of water-stable aggregates was determined by wet sieving (sieving for 30 min with 21 oscillations per minute and 3 cm amplitude; EMBRAPA 1979, adapted from Yoder 1936). The soil was separated into the following fractions, which were air-dried (40 °C) and weighed: peds (2-8 mm), small and large macroaggregates (MA, 0.25-1.0 and 1-2 mm, respectively), and microaggregates (MIC, 0.053-0.25 mm). The silt and clay fraction (<0.053 mm) was calculated by taking the difference between the total weight of soil before wet sieving and the sum of all other fractions. The obtained aggregate fractions were pooled for each plot for further analyses and sieved to 2 mm. The mean weight diameter (MWD) of aggregates was calculated as the sum of mean diameters within each aggregate size class, weighted by the percentage of soil within the respective class (Hillel 1980):

$$\mathrm{MWD} = \Sigma\, x_i\, w_i \qquad [1]$$

Where,

$x_i$ = mean diameter of the ith aggregate size class,

$w_i$ = relative weight of aggregates in the ith aggregate size class, and

$_i$ = number of the aggregate size class.

### *Particulate organic matter*

We adapted Golchin et al.'s (1994b) concept of POM fractions in highly structured Oxisols. The original model is based on two POM fractions: (1) free POM, which comprises POM situated in the free soil pore space and hence not associated with aggregates, and (2) occluded POM, consisting of old POM, with low turnover rates and firmly bound in stable aggregates (Golchin et al. 1994a). According to our findings (see "Results"), the soil of this study comprises more than 30% >2-mm aggregates, which may break into fragments diameters averaging <2 mm. In Oxisols, a significant amount of POM should be loosely bound to these labile peds (2-8 mm), should represent an intermediate state of physical occlusion between free and occluded POM, and may play an important role in nutrient storage in Oxisols. We, therefore, defined a third POM fraction: the "easily accessible POM". Thus, our concept differentiates between the following POM fractions according to their position in the soil and hence to their degree of physical protection from mineralization (Figure 1): (1) free POM (Golchin et al. 1994b), (2) easily accessible POM, and (3) occluded POM (Golchin et al. 1994a).

Particulate organic matter was first separated from air-dried bulk soil sieved to <2 mm. The samples were gently shaken in a 1.6 g/cm$^3$ polytungstate solution (Golchin et al. 1994b) and the floating particles decanted, washed, and air-dried (40 °C). The obtained fraction comprised all POM between soil particles sized <2 mm, that is, free POM and easily accessible POM from peds crushed during sieving. Second, POM was separated from water-stable peds after these were sieved to <2 mm (easily accessible POM, or e. a. POM). Free POM was calculated, using equation [2]:

Free POM [mg/g] = total POM [mg/g] – (e. a. POM [mg/g] * peds in soil [%] * 100) [2]

Occluded POM was not separated in this study because it was assumed to represent an old pool with low turnover

Figure 1. Concept of the three particulate organic matter (POM) fractions in soil: 1 = free POM; 2 = easily accessible POM; 3 = occluded POM.

rates (Golchin et al. 1994a). Hence, no impact from 4 years of land use could be expected.

### Element analyses

Ash contents of the POM fractions were determined by loss of weight on ignition at 550 °C for 1 h. Total C and N in bulk-soil samples, peds, MAs, and POM were determined by dry combustion with a Carlo Erba auto-analyzer. Note that large roots are excluded by definition from total C in the soil samples. Thus, parts of POM were removed before analyses for total soil C.

### Statistical analyses

The data were statistically analyzed by a two-tailed, Kruskal-Wallis, Oneway ANOVA (SPSS 1993) to compare all treatments. To test one treatment against all other treatments or to test differences among treatment groups and due to sample time, a two-tailed, Mann-Whithney, U Wilcoxon, Rank Sum, W Test (SPSS 1993) was used. Because the experiment comprised only two plots per treatment, testing two individual treatments against each other, for example, PG against GL, was impossible because the mathematical assumptions for statistical tests were not fulfilled. Where the standard deviation of measures within plots exceeded the difference of the means between the treatments, no statistical test was applied to these data. The correlation between easily accessible POM and the proportion of peds in soil was tested, using a two-tailed, rank correlation with Spearman's Rho (SPSS 1993).

Data of soil properties at the beginning of the rainy season (November 1994 samples) were used to evaluate and modify the concepts of aggregate hierarchy (Tisdall and Oades 1982) and of physical protection of POM. Simultaneously, changes in soil properties as a result of 4 years of land use since 1991 were assessed. The samples taken 3 months later, in February 1995, were compared with the November results to test the reliability of conclusions drawn from those measurements and to describe seasonal dynamics in aggregation and SOM.

## Results and Discussion

### Aggregation

More than 90% of soil aggregates in all systems under study were found in the macroaggregate and ped fractions (<0.25 mm) (Figure 2). The Oxisol under study was highly aggregated, compared with temperate prairie soils, in which the macroaggregate fractions comprised <75% of native and 45% of cultivated soils (Elliott 1986), indicating typical pseudosand structure. After 4 years of conversion of native savanna into pastures, the size distribution of water-stable aggregates remained unchanged, while under continuous cropping (CCT), water-stable aggregation was reduced, leading to a MWD of 2.0 mm in CCT, compared with one of 2.4 in the other systems. The macroaggregate fractions of CCT were enriched by 30% with large MAs (1-2 mm) and 10% with small MAs (0.25-1.0 mm). The microaggregate fractions (<0.25 mm) were similar in all systems under study. Obviously, cropping led to a disruption of peds. The fragments accumulated in the MA fractions. The original aggregates in the MA size classes seemed to be unaffected by land use. Lilienfein et al. (1996) reported a 30% reduction of peds after 10 years of continuous cropping on a comparable clayey Oxisol. Thus, degradation of soil structure appears to be most pronounced in the first years of cultivation.

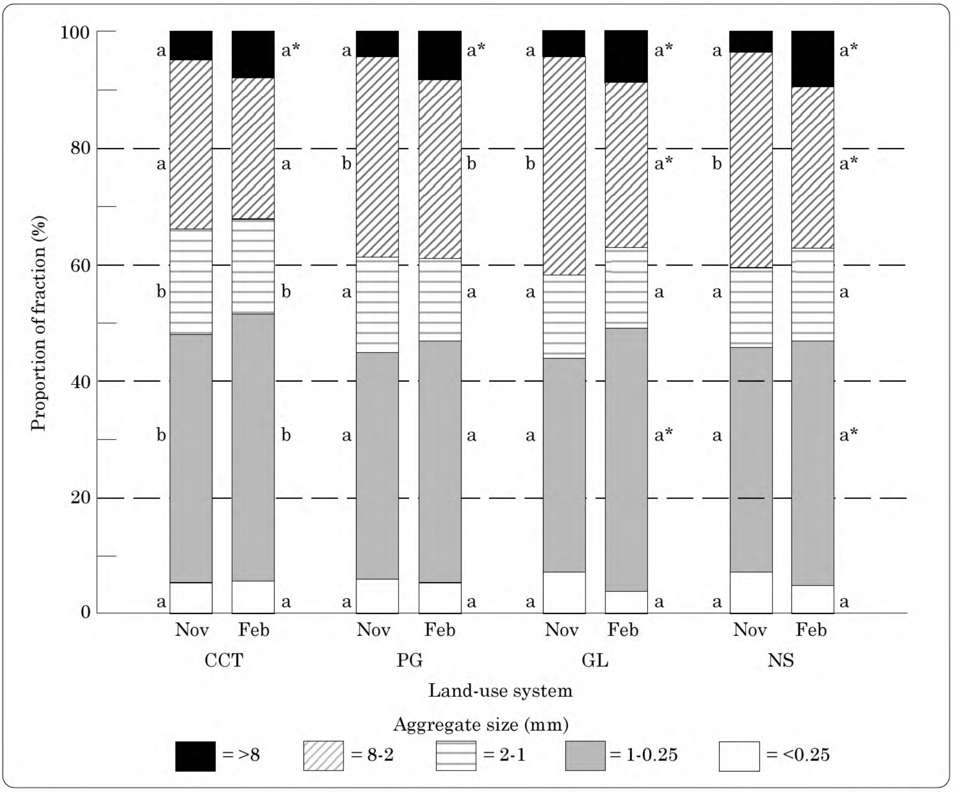

Figure 2. Size distribution of water-stable aggregates under different land-use systems in an Oxisol of the Brazilian savannas. Different lowercase letters indicate significant differences between treatments at $P < 0.05$; * = significant seasonal changes of aggregate fractions at $P < 0.05$. CCT = continuous cropping with conventional tillage; GL = grass/legume pasture; NS = native savanna; PG = pure-grass pasture.

The model of aggregate hierarchy by Tisdall and Oades (1982) was found to apply to Oxisol peds but, in contrast to temperate soils, the released particles were not of microaggregate but of macroaggregate size, which can be related to the stable pseudosand structure of Oxisols. Oades and Waters (1991) used a pooled macroaggregate fraction (>0.25 mm) only, instead of separate peds. Therefore, their method was not suitable for characterizing aggregate dynamics in Oxisols.

## *Particulate organic matter*

Soil contents of C and N were similar in all systems under study, although cultivated plots showed a tendency in C and N depletion. Pastures showed higher contents of the sum of free and easily accessible POM than did native savanna and crops. The ratio of POM-C to total soil C was also highest in pastures. The ratio of POM-N to total soil N was similar in crops and pastures, and higher than in native savanna. In all systems under study, the C/N ratio of total POM was 1.5 to two times higher than total SOM, illustrating the relatively undecomposed character of POM (Table 1; Cambardella and Elliott 1992; Golchin et al. 1994a).

In all treatments, peds were significantly ($P < 0.005$) enriched in

POM in relation to bulk soil. The enrichment factor, calculated as the ratio of easily accessible POM in peds to total POM in bulk soil, ranged from 1.2 (GL) to 1.5 (NS) for POM-C. POM-N, however, was not significantly concentrated in peds. As POM represents a binding agent of peds that is sensitive to land use (Cambardella and Elliott 1992; Tisdall and Oades 1982), our findings confirm the discussion of aggregate hierarchy above.

In all systems under study, the C/N ratio of easily accessible POM was eight units wider than that of free POM. Thus, easily accessible POM was less humified than free POM. This indicates a certain physical protection from biological attack and confirms our concept of POM fractions in Oxisols (Figure 1).

Free POM showed significantly higher contents under CCT, PG, and GL than under NS. This could be explained by the high root density of *Andropogon* in pastures (MA Ayarza 1997, personal communication) and perhaps by the incorporation of crop residues by plowing in CCT, although the free POM level in CCT was still surprisingly high. Easily accessible POM-C and POM-N were correlated with the proportion of peds in soil ($r = 0.87$ and 0.83, respectively; $P < 0.001$). Easily accessible POM, however, was spatially too variable within the treatments to allow an interpretation of the results. The ratio of free to easily accessible POM decreased accordingly: 1.6 (CCT) > 1.3 (GL) > 1.0 (PG) > 0.8 (NS). As was observed by Beare et al. (1994), under annual crops, freshly decomposed plant material accumulated in the soil pore space between the aggregates as free POM, which may be partly explained by the lower ped content. In addition, aboveground biomass is incorporated into soil by tillage, which should be found as free POM. In the native savanna, however, OM from young plants was preferentially bound within

Table 1. Characteristics of soil organic matter[a] found under different land-use systems on an Oxisol in the Brazilian savannas.[b]

| Land-use system[c] | Bulk soil | | | POM-C/$C_t$ (%) | | POM-N/$N_t$ (%) | | C/N ratio | |
|---|---|---|---|---|---|---|---|---|---|
| | $C_t$ (mg/g) | $N_t$ (mg/g) | P (mg/kg) | Free POM | e. a POM | Free POM | e. a. POM | Free POM | e. a. POM |
| November 1994 | | | | | | | | | |
| CCT | 23.1 | 1.48 | 127 b | 4.2 b | 2.6 aA | 2.2 b | 1.2 aA | 28 a | 36 a |
| PG | 27.1 | 1.62 | 116 b | 3.9 b | 4.0 aA | 1.9 b | 1.7 aA | 33 b | 42 b |
| GL | 25.8 | 1.59 | 107 b | 4.3 b | 3.1 aA | 2.4 b | 1.5 aA | 27 a | 35 a |
| NS | 25.4 | 1.57 | 99 a | 2.4 a | 3.1 aA | 1.0 a | 1.2 aA | 35 b | 42 b |
| February 1995 | | | | | | | | | |
| CCT | 23.9 | 1.52 | 124 b | 3.6 a | 1.1 aB | 1.9 b | 0.8 aB | 30 a | 33 a |
| PG | 23.2 | 1.45 | 110 b | 3.4 a | 1.8 aB | 1.4 a | 0.7 aB | 37 b | 40 b |
| GL | 27.1 | 1.67 | 113 b | 5.8 b | 1.3 aB | 3.0 c | 0.7 aB | 31 a | 33 a |
| NS | 26.3 | 1.62 | 101 a | 4.0 a | 1.6 aB | 1.8 b | 0.7 aB | 37 b | 38 b |

a. $C_t$ = total carbon; $N_t$ = total nitrogen; P = phosphorus; POM = particulate organic matter; e. a. = easily accessible.

b. Different lowercase letters indicate significant differences between land-use systems at $P < 0.05$. Different uppercase letters indicate significant seasonal changes in a given land-use system at $P < 0.05$.

c. CCT = continuous cropping with conventional tillage; GL = grass/legume pasture; NS = native savanna; PG = pure-grass pasture.

peds as easily accessible POM. Pastures showed an intermediate status with a slight predominance of free POM. In undisturbed systems, the ratio of free POM to easily accessible POM may indicate the level of litter and root input in the soil. Hence, the ratio might be a useful index to quantify the degree of protection of young POM in soil as affected by land use. Our findings suggest that a high content of free POM may not necessarily maintain the soil carbon level. The turnover of POM as a function of POM quality and accessibility and land management also needs to be considered.

The C/N ratio of POM under soybean crops and grass/legume pasture was about six units lower than in the systems without legumes (Table 1). This finding accords with the different litter quality, because the C/N ratio of soybean residues is 15 (da Silva and Resck 1997) but more than 40 for *Andropogon* (MA Ayarza 1997, personal communication). The annual N-fixing capacity of soybean grown in the *Cerrados* ranges from 60 to 178 kg/ha and, for *Stylosanthes*, from 34 to 220 kg/ha (Franco and Dobereiner 1994). At the sampling date, soybean had been cropped for 2 years and *Stylosanthes* covered about 30% of the legume-based pasture area. Even after this short period of land use, the N content of POM had considerably increased, even though N input by biological fixation had not altered the total N content in bulk soil. Hence, the POM fraction is a sensitive indicator of changes in the quality of plant residue in the soil.

Differences in POM quality, distribution, and turnover between the two pasture systems may be related to the different root systems of *Andropogon* and *Stylosanthes*. Furthermore, aboveground biomass production of grass/legume pasture (2.7 t/ha grass and 1.0 t/ha legume biomass) exceeded that of pure-grass pasture (3.0 t/ha grass biomass) by 23%, and animal liveweight gain was 45% greater, indicating the beneficial effect of legumes on soil fertility and pasture productivity (Rao et al. 1994; Thomas 1995). Probably, GL was more efficient in nutrient cycling than PG, which may be related to the synergetic effects of *Stylosanthes*, as well as to N fixation.

### Seasonal changes of aggregation

In all treatments, the >8-mm aggregate fraction was significantly ($P < 0.05$) increased by 70% (CCT) to 170% (NS) between November and February (Figure 2). Seasonal trends in the ped and MA fractions were similar in all studied systems, but not significant in CCT and PG. Two opposite seasonal processes in aggregation were evident: (1) formation of new peds (>8 mm) and of small MAs (0.25-1.00 mm) from the <0.25-mm soil fraction; and (2) disruption of peds to small MAs (0.25-1.00 mm). As the MWD of GL and NS was only 2.1 mm in February, the process of destabilization of peds was more important than aggregate formation, a finding that was consistent with those of Stefanson (1971). The 1-2-mm fraction, in which the effects of plowing were most evident (see above), showed no seasonal dynamics in aggregation and seemed to be in an equilibrium of aggregate formation and breakdown. The seasonal variation of the ped fraction may therefore efface the effect of land use apparent in the November samples.

### Seasonal changes of particulate organic matter

Total C and N concentrations were similar in bulk soil samples of

November and February samples. In general, the sum of free and easily accessible POM, POM-C, and POM-N, as well as of free POM, did not change over time, except in PG (Figure 3). Easily accessible POM was significantly ($P < 0.005$) reduced in all treatments (Table 1). The disruption of peds between November and February led to the release of 40% (CCT, NS) to more than 50% (PG, GL) of easily accessible POM, which accumulated in the free POM fraction. The loss of easily accessible POM exceeded the disruption of peds by a factor of two. Thus, peds rich in POM as a binding agent have a particularly high turnover rate.

Soil fauna was simultaneously studied on comparable CCT, PG, and NS plots at the experimental site (Rodrigues et al. 1996). The results indicated that the density and diversity of soil fauna were reduced under pasture and even more under continuous cropping. Disturbed systems showed a higher seasonal fluctuation in soil fauna than did native savanna. In the experiment plots, ants and termites were scarcely found during the November sampling, but were abundant in February. Both insect groups are known to alter considerably the soil structure and nutrient availability (Lobry de Bruyn and Cronacher 1990). To understand

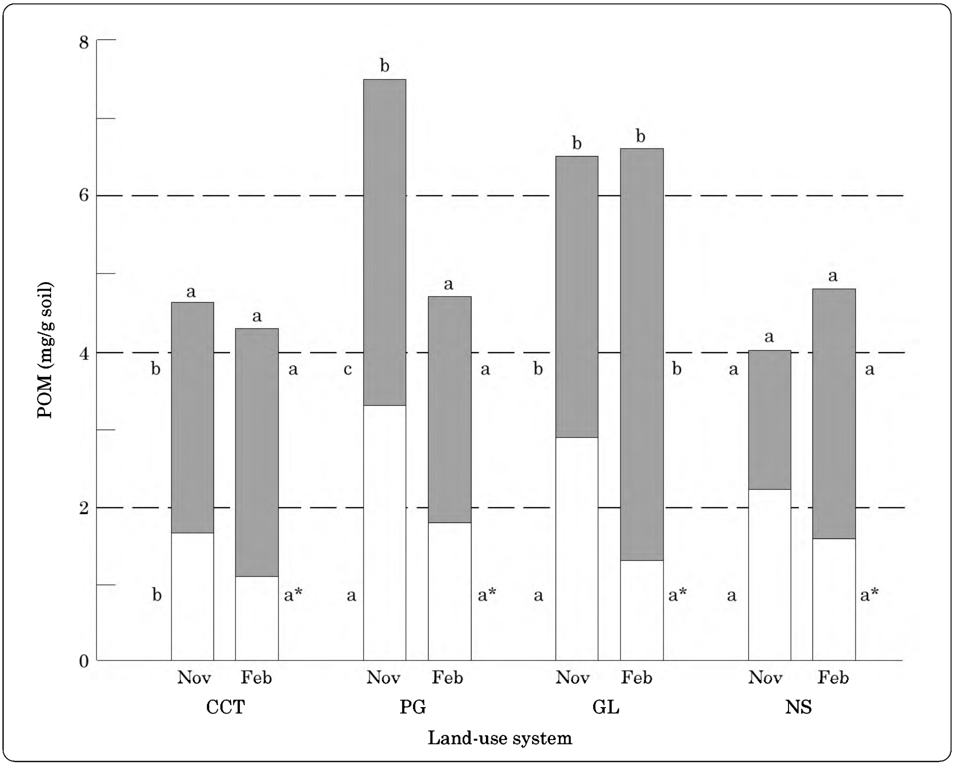

Figure 3. Free (■) and easily accessible (□) particulate organic matter (POM) (ash-free) found in different land-use systems on an Oxisol in the Brazilian savannas. Different lowercase letters indicate significant differences between treatments at $P < 0.05$; * = indicates significant changes of the POM fractions in one treatment after 3 months at $P < 0.05$. CCT = continuous cropping with conventional tillage; GL = grass/legume pasture; NS = native savanna; PG = pure-grass pasture.

the seasonal dynamics of aggregation and SOM in Oxisols of the *Cerrados*, soil macrofaunal activity must be taken into account.

## Conclusions

Despite the general opinion that aggregation in Oxisols is stable, peds of the clayey Oxisol under study are relatively fragile and sensitive to cropping. Soil from disrupted peds in continuous cropping systems accumulated in the MA fraction. The concept of aggregate hierarchy (Tisdall and Oades 1982), which was originally developed for temperate grassland soils, is, in principle, applicable to the Oxisols under study. However, the boundaries of the aggregate size classes are different to those proposed: the peds of the Oxisols are formed of small macroaggregates (0.25-2.00 mm) instead of microaggregates (<0.25 mm), as in the original model, and the Oxisol macroaggregates are stabilized by stable organic and inorganic binding agents (pseudosand structure).

Seasonal changes in aggregation were similar in all treatments but only significant in GL and NS. During the growing season, the destabilization of peds was the dominant process, leading to an increase in the small MA fraction (0.25-1.00 mm). Aggregate dynamics of grass/legume pasture was closest to the conditions of native savanna.

Easily accessible POM was found to be an important active carbon pool in Oxisols. The soil content of POM rose with human activity. In pastures and, especially, in cropping systems, plant residues accumulated predominantly in soil as free POM, which is directly available to the soil meso- and macrofauna. In native savanna, however, relatively more organic material was occluded within peds as easily accessible POM, leading, probably, to lower overall turnover rates. The distinction between free and easily accessible POM was a sensitive indicator of short-term effects of land management on C and N dynamics and availability.

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## CHAPTER 8

# Soil Organic Matter in Oxisols of the Brazilian *Cerrados*

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## Abstract

Little is known about the sustainability of cultivation systems in the Brazilian savannas, also known as the *Cerrados*, despite its increasing significance for that country's agriculture. To characterize management effects and follow alterations of organic compounds in different fractions, we studied whole-soil samples and particle-size separates from clayey and loamy Oxisols under crops, pastures, reforested sites, and savanna. We assessed soil organic carbon (SOC), polysaccharides, and CuO oxidation products (VSC-lignin). Few changes were found in SOC contents of topsoil (0-12 cm) under different land uses after 10-20 years. But organic carbon clearly diminished under continuous cropping on the loamy soil and under reforestation with pine on the clayey soil. Management effects on SOC were more apparent in sand fractions, suggesting that particulate organic matter (POM) was affected most. In the clay fraction, only minor effects were noted. Carbon-normalized polysaccharide contents were enriched under pastures and depleted under pine, but generally followed a similar distribution to that of SOC. Overall, both polysaccharides and VSC-lignin were closely related to soil porosity. Plant-derived polysaccharides and lignin contents were probably regulated by water availability to soil microbes, so that decomposition was usually more advanced in the clayey soils. Ten years of continuous cropping lowered litter inputs, thus reducing POM, whereas humified organic matter (OM) was unaffected. Planting eucalyptus or well-managed pastures, which produce high amounts of POM, would thus rapidly reverse soil degradation. Continuous cropping does eventually reduce the humified fraction and results in a substantial loss of soil fertility, which is only slowly reversible. In the loamy soils, rotation with a SOC-productive system, such as pastures or eucalyptus, was needed earlier because of their higher proportion of POM. Depletion of SOC under pine occurred because new litter was not incorporated into the mineral soil, forming a thick moder layer as decomposition continued. After felling trees, the organic layer could be rapidly incorporated into the mineral soil, thus replenishing lost OM. However, the acid litter may reduce soil organic matter quality.

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*Keywords:* Brazilian savannas, *Cerrados*, Oxisols, particle-size fractionation, polysaccharides, soil organic matter, VSC-lignin

## Introduction

Dynamics of soil organic matter (SOM) in the soils of the Brazilian *Cerrados* are of growing interest because of the recent rapid increase of cultivation in these savannas and questions concerning their sustainability under intensive land use (Alho et al. 1995; Goedert 1983; Villachica et al. 1990). As most soils of the *Cerrados* are highly weathered and nutrient poor, the significance of SOM for soil fertility and structural stability is even greater than in temperate soils (Tiessen et al. 1994). According to Resck et al. (1991) and Silva et al. (1994), under cultivation, soil fertility is reduced by management-induced SOM losses. Depletion seemed to be intimately related to both clay content and seedbed preparation. This was recently verified by Feller and Beare (1997), who studied a series of tropical soils. However, other studies from the *Cerrados* reported only minor effects of land use on SOM contents (Mendonça and Rowell 1994; Nascimento et al. 1991). Possibly, cultivation was not carried out long enough to show significant effects, but chemical or physical protection from decomposition could also be relevant (Oades et al. 1989).

Effects of land use on SOM are often not satisfactorily explained because SOM contents of whole-soil samples are not strongly heterogeneous and the different turnover rates of organic substrates are not taken into account. To overcome this problem, separation of soil into primary organo-mineral complexes by particle-size fractionation has been successfully used for the past 15 years to study OM transformation in soils (Christensen 1992). The OM associated with sand is essentially particulate, that is, it consists of fine roots and plant fragments, and is more labile than clay- or silt-bound SOM. In temperate soils, silt-associated SOM is believed to be the most recalcitrant fraction, whereas the turnover rate of clay-associated OM is intermediate (Christensen 1987). However, SOM pools in temperate soils may not correspond to highly weathered soils of the tropics. For example, Gijsman et al. (1996) could not simulate the SOM dynamics of Colombian Oxisols with the CENTURY model, which was designed for temperate grasslands. Incorrect assumptions concerning the turnover rates of the different SOM fractions or a different SOM composition may have caused these difficulties.

Therefore, we must characterize the transformation processes of organic substrates during decomposition and humification, and the factors influencing these processes. Information on changes of the dominant organic substrates in soil, that is, polysaccharides, lignin, and lipids, will eventually improve the understanding of OM dynamics. This should lead to more accurate models and improved prediction in SOM dynamics.

Kögel-Knabner (1992) concluded that the humification process in soil can be divided into microbial resynthesis of plant-derived polysaccharides, selective preservation of lignin, and direct transformation of lipids. Guggenberger et al. (1994) found high contents of plant-derived sugars in the sand-sized separates of temperate soils and an accumulation of microbially metabolized sugars in the clay. Products from lignin degradation were continuously depleted and showed higher side-chain oxidation with decreasing particle size, indicating that lignin was not redistributed and progressively degraded from sand to clay. Similar trends were obtained in highly weathered tropical soils (Guggenberger et al. 1995). However, management effects on organic compounds are still poorly understood and no information is available on how abiotic factors, in particular, soil texture and pore size distribution, affect SOM decomposition and humification.

We aimed to characterize changes of SOM in different land-use systems of the Brazilian *Cerrados*. Particle-size fractionation was employed to study management effects on SOM fractions of different turnover rates.

## Materials and Methods

### *Study area and site history*

The study area has already been described in Chapter 4, pages 38-40. An overview of the management histories of all the sites is given in that chapter's Table 1. A summary of selected physical and chemical properties of the topsoil under different management systems is also given in Tables 1 and 2 of Chapter 5 (pages 54-55).

### *Soil sampling and pretreatment*

Soil sampling was done in March 1995, at the end of the rainy season. For every treatment, three plots of 50 x 50 $m^2$ were selected, at distances of about 50 m from each other. For each plot, five undisturbed subsamples were taken from the plowing layer (0-12 cm) with an Uhland soil corer and combined, giving a total of three samples per treatment. At field moisture, the soil was carefully broken along fissures to pass through an 8-mm screen, and large roots were discarded. The samples were dried at 40 °C in a forced-air oven and sieved through a <2-mm screen. Visible roots that passed through the sieve were manually picked out and discarded. For chemical analyses of whole-soil samples, an aliquot of fine earth was ground with a mortar and pestle to pass through a 0.1-mm sieve.

### *Particle-size fractionation*

For separation into primary particles, 30 g of oven-dried fine earth were first shaken in 100 mL of deionized water for 3 h with three marbles and subsequently dispersed completely by sonication. Shaking was necessary because macroaggregates (>250 µm) frequently resist the sonication treatment proposed by Christensen (1987). After shaking, the suspension was poured through a 250-µm sieve and the coarse-sand fraction dried overnight at 40 °C. The remaining suspension was exposed to 1500 J/mL ultrasonic energy. Calibration of the probe type disintegrator (Branson W-450) followed North's method (1976). After sonication, the clay fraction (<2 µm) was separated from fine sand and silt by repeated centrifugation until the supernatant was clear, when it was freeze-dried. The 20-50 and 50-250-µm sand fractions were retained after gently forcing any persisting sonic-stable aggregates through the respective sieves with a rubber policeman, frequently liberating more clay, which then had to be separated by centrifuging again. The remaining silt fraction (2-20 µm) was freeze-dried. The 50-250 and 250-2000-µm sand fractions were combined before analysis because of the visible similarity of their respective particulate organic matter (POM). Subsequently, an aliquot of the 50-2000-µm fraction was ground to <0.1 mm for maximum homogeneity. Fractionation was done three times and all separates weighed. For comparison, particle size was determined by the conventional sieve-pipette method (EMBRAPA 1979).

### Scanning electron microscopy

The morphology of OM in particle-size separates was studied, using a JEOL 840 A Scanning Electron Microscope (SEM) at 15 kV accelerating voltage. An Everhart Thornley scintillation detector was used as collecting device to take SEM micrographs.

### Analytical methods

Soil organic carbon (SOC) and total N were determined by dry combustion (Elementar Vario EL). Analytical precision of the apparatus was better than 0.2 mg/g soil for C and 0.02 mg/g soil for N for repeatedly measured samples. Noncellulosic and cellulosic polysaccharides (NCPs and CPs, respectively) were measured colorimetrically with a modified MBTH method (Beudert 1988) after sequential acid hydrolysis (Miltner 1997). The method's coefficient of variation was better than 10% for an external standard. The polysaccharide-C content was determined by dividing glucose equivalents by 2.5. Phenolic lignin degradation products were extracted with the alkaline CuO oxidation method developed by Hedges and Ertel (1982) and modified for soil samples by Kögel and Bochter (1985) and Amelung (1997). Oxidation products were quantified with a gas chromatograph (HP 6890). The sum of vanillyl (vanillin and vanillic acid), syringyl (syringaldehyde and syringic acid), and cinnamyl (ρ-coumaric and ferulic acid) units was used to characterize the amount of lignin in the sample. VSC-lignin reflects phenols from reactive sites of the lignin macromolecule. Absolute lignin contents cannot be measured because the contribution of VSC-lignin to total lignin is unknown (Kögel-Knabner et al. 1991). The mass ratios of acid to aldehyde for the vanillyl units $(Ac/Al)_V$ were used to describe the degree of oxidative lignin alteration (Ertel and Hedges 1984). The S/V ratio, that is, the sum of syringyl units in relation to the sum of vanillyl units, is sensitive to changes in plant source, because the yields of lignin-derived phenols differ between plant species (Sarkanen and Ludwig 1971).

In the whole-soil samples, all analyses were done separately for each plot. In the particle-size fractions, this was done for SOC and N only. Before determining polysaccharides and VSC-lignin, the fractions of each treatment were combined.

### Statistical analysis

Statistical analyses were executed with Statistica software (Statsoft). Homogeneity of organic constituents between the three plots per treatment were verified with MANOVA, using Tukey's HSD test ($P < 0.05$). Management effects within one treatment were explained by the mean ±95% confidence interval (n = 3). Univariate regressions were calculated to determine the relationships between organic compounds and independent variables.

## Results

### Particle-size fractionation

Particle-size separation by shaking/sonication led to a recovery of 95% to 99% (Table 1). The grain-size distribution generally corresponded well to the one obtained by chemical dispersion. In the clayey soil type, sonication reduced the amount of sand and generally increased the clay content, compared with the conventional method, and the comparatively low clay contents after sonication in the pine treatment were balanced by the high amounts of silt. In the loamy soil type, about 4% of the sand fraction was redistributed into the silt fraction after shaking/sonication.

Table 1. Percentages (w/w) of clay (<2 µm), silt (2-20 µm), and sand (20-2000 µm) in Oxisols of the Brazilian savannas, as determined by shaking/sonication and by dispersion in 0.1 *M* NaOH, according to EMBRAPA (1979). Average of three plots per treatment.

| Oxisol | Shaking/sonication | | | | | NaOH dispersion | | |
|---|---|---|---|---|---|---|---|---|
| Treatment | <2 (clay) | 2-20 (silt) | 20-50 (fine sand) | 50-2000 (medium to coarse sand) | Σ | <2 (clay) | 2-20 (silt) | 20-2000 (medium to coarse sand) |
| Very fine Anionic Acrustox | | | | | | | | |
| Native savanna | 69.5 | 8.8 | 2.6 | 17.0 | 97.9 | 67 | 7 | 26 |
| Crop | 71.3 | 8.4 | 2.1 | 13.1 | 94.9 | 66 | 12 | 22 |
| Pasture | 75.5 | 7.6 | 2.3 | 12.8 | 98.2 | 66 | 13 | 21 |
| Pine | 64.6 | 15.8 | 2.5 | 15.3 | 98.2 | 66 | 7 | 27 |
| Coarse-loamy Typic Haplustox | | | | | | | | |
| Native savanna | 15.1 | 3.2 | 4.2 | 76.4 | 98.9 | 16 | 0 | 84 |
| Crop | 15.1 | 4.2 | 5.1 | 74.7 | 99.1 | 16 | 0 | 84 |
| Pasture | 15.6 | 4.4 | 5.1 | 73.3 | 98.4 | 17 | 0 | 83 |
| Eucalyptus | 13.6 | 4.1 | 4.1 | 77.0 | 98.8 | 15 | 0 | 85 |

## *Soil organic carbon*

Soil organic carbon (SOC) contents in whole soil were two to three times higher in the clayey than in the loamy soil type (Table 2). Compared with the native savanna control, SOC contents in the whole soil were most reduced under pine (clayey soil) and under crop (loamy soil). Management effects were most evident in the sand fractions (20-2000 µm) (Figure 1). In the loamy soil, the pasture was also depleted in sand-associated SOC. In contrast, under eucalyptus (loamy soil) and under pasture (clayey soil), SOC was frequently higher than under native savanna (control).

The C/N ratios were similar in both soil types and ranged from 16 to 20 in the whole-soil samples. In the particle-size separates, the C/N ratios generally narrowed with decreasing particle size. Differences between management systems were again most apparent in the sand fractions, while in the clay and silt fractions, only the pine site showed a clearly larger C/N ratio due to nitrogen-poor litter. The comparatively low C/N ratios at the crop sites were attributed to a good N supply from soybeans and additional nitrogen fertilization.

On the average, 65% and 71% of SOC were bound to the clay fraction in the loamy and clayey soils, respectively, whereas only 15% to 25% of OM in the loamy soil and 7% to 10% in the clayey soil were associated with the sand fractions (Table 3). In the 50-2000-µm fraction, the yields were comparable between the two soil types and indicated reduced POM contents under crops, pine, and pasture on the loamy soil.

## *Polysaccharides*

In whole-soil samples, NCPs represented, on the average, 16% of SOC, irrespective of soil type (Table 4). In the clayey soil, NCPs were highest under pasture and lowest under pine. Differences between land-use systems were less apparent in the loamy soils. In the sand fraction, NCPs accumulated in the loamy soil under

organic carbon contents (with ±95% confidence intervals; n = 3) and C/N ratios in whole soil and particle-size separates of differently managed cla
my Oxisols, Brazilian savannas.

| | Whole soil[a] (C at g/kg) | Particle-size separates (µm) (C at g/kg fraction) | | | | C/N ratio | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Whole soil[a] (rounded numbers) | Particle-size separates (µm | | |
| | | <2 (clay) | 2-20 (silt) | 20-50 (fine sand) | 50-2000 (medium to coarse sand) | | <2 (clay) | 2-20 (silt) | 20-50 (fine sand) |
| onic Acrustox | | | | | | | | | |
| nna | 23.5 ± 0.3 | 23.5 ± 1.3 | 46.1 ± 2.5 | 31.6 ± 1.1 | 8.8 ± 1.4 | 18 | 14 | 22 | 30 |
| | 22.9 ± 0.4 | 22.3 ± 1.4 | 48.1 ± 2.2 | 33.1 ± 2.6 | 7.2 ± 0.8 | 17 | 15 | 21 | 24 |
| | 24.6 ± 0.9 | 24.3 ± 1.5 | 52.2 ± 2.6 | 33.6 ± 1.3 | 11.4 ± 1.4 | 18 | 15 | 23 | 31 |
| | 21.5 ± 1.2 | 22.5 ± 1.4 | 39.3 ± 1.9 | 18.0 ± 2.2 | 7.4 ± 1.1 | 20 | 18 | 30 | 35 |
| Typic Haplustox | | | | | | | | | |
| nna | 9.8 ± 0.4 | 36.9 ± 2.4 | 33.8 ± 1.5 | 11.5 ± 1.7 | 1.9 ± 0.4 | 16 | 13 | 23 | 24 |
| | 7.1 ± 0.3 | 32.6 ± 1.4 | 26.5 ± 1.4 | 7.6 ± 1.2 | 1.0 ± 0.1 | 17 | 13 | 22 | 19 |
| | 9.3 ± 0.7 | 35.6 ± 1.6 | 31.9 ± 1.7 | 8.0 ± 1.5 | 1.2 ± 0.2 | 18 | 14 | 22 | 25 |
| | 10.2 ± 0.2 | 43.2 ± 2.0 | 37.5 ± 1.9 | 15.6 ± 1.9 | 2.5 ± 0.4 | 19 | 14 | 22 | 26 |

n Table 23, Chapter 5, page 56.

feldt (1998).

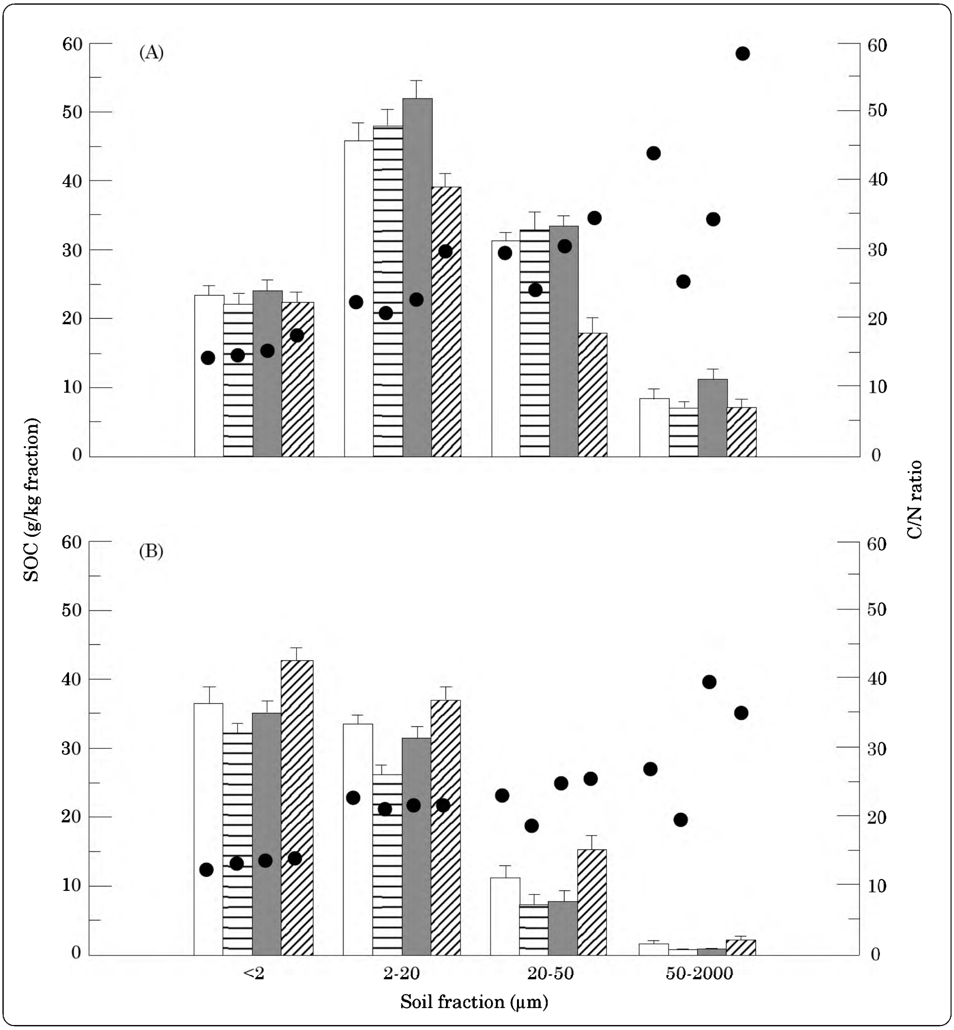

Figure 1. Soil organic contents (SOC) contents and C/N ratios (●) in particle-size separates of differently managed clayey (A) and loamy (B) Oxisols, Brazilian savannas. [▭ = native savanna; ▤ = crop; ■ = pasture; ▨ = reforestation with pine (A) or eucalyptus (B).]

pasture, whereas NCPs were depleted under eucalyptus and at both cropped sites. In the clay fraction, NCPs were enriched by about a factor of 1.2, compared with whole-soil contents in all treatments, while in the silt and the very fine sand fractions, NCPs were strongly depleted.

Cellulosic polysaccharides in whole-soil samples ranged from 2.5% to 3.9% of SOC (Table 5), corresponding to only 15% to 19% of total polysaccharide contents. Generally, CPs were enriched in the sand fractions. This proportion was significantly higher ($P < 0.001$ of Tukey's HSD test) in the loamy than in the clayey substrate and appeared to be lowest under crops planted in each soil type. Management effects were less straightforward than for NCPs. Like NCPs, CPs showed

Table 3. Yields of soil organic carbon in particle-size separates of differently managed clayey and loamy Oxisols, Brazilian savannas. Percentage of sum of separates (Σ) in parentheses.

| Oxisol<br>Treatment | Particle-size separates (µm) (C at g/kg soil) | | | | | Whole soil (C at g/kg soil) |
|---|---|---|---|---|---|---|
| | <2 (clay) | 2-20 (silt) | 20-50 (fine sand) | 50-2000 (medium to coarse sand) | Σ | |
| Very fine Anionic Acrustox | | | | | | |
| Native savanna | 16.3 (72) | 4.1 (18) | 0.8 (4) | 1.5 (7) | 22.7 | 23.5 |
| Crop | 15.9 (74) | 4.0 (19) | 0.7 (3) | 0.9 (4) | 21.5 | 22.9 |
| Pasture | 18.3 (74) | 4.0 (16) | 0.8 (3) | 1.5 (6) | 24.6 | 24.6 |
| Pine | 14.5 (65) | 6.2 (28) | 0.5 (2) | 1.1 (5) | 22.3 | 21.5 |
| Coarse-loamy Typic Haplustox | | | | | | |
| Native savanna | 5.6 (64) | 1.1 (13) | 0.5 (6) | 1.5 (17) | 8.7 | 9.8 |
| Crop | 4.9 (69) | 1.1 (15) | 0.4 (6) | 0.7 (10) | 7.1 | 7.1 |
| Pasture | 5.6 (67) | 1.4 (17) | 0.4 (5) | 0.9 (11) | 8.3 | 9.3 |
| Eucalyptus | 5.9 (60) | 1.5 (15) | 0.6 (6) | 1.9 (19) | 9.9 | 10.2 |

Table 4. Noncellulosic polysaccharide contents in whole soil (with ±95% confidence intervals; n = 3) and particle-size separates of differently managed clayey and loamy Oxisols, Brazilian savannas.

| Oxisol<br>Treatment | Whole soil (C at g/kg SOC)[a] | Particle-size separates (µm) (C at g/kg SOC)[a] | | | |
|---|---|---|---|---|---|
| | | <2 (clay) | 2-20 (silt) | 20-50 (fine sand) | 50-2000 (medium to coarse sand) |
| Very fine Anionic Acrustox | | | | | |
| Native savanna | 158 ± 6 | 190 | 114 | 61 | 142 |
| Crop | 149 ± 9 | 172 | 114 | 91 | 131 |
| Pasture | 179 ± 5 | 212 | 126 | 111 | 196 |
| Pine | 116 ± 13 | 136 | 74 | 53 | 115 |
| Coarse-loamy Typic Haplustox | | | | | |
| Native savanna | 163 ± 2 | 202 | 106 | 106 | 141 |
| Crop | 153 ± 16 | 184 | 115 | 94 | 107 |
| Pasture | 160 ± 14 | 206 | 109 | 98 | 187 |
| Eucalyptus | 154 ± 8 | 179 | 116 | 98 | 118 |

a. SOC = soil organic carbon.

lowest values under pine and enrichment under pasture in both substrates. In addition, CPs were depleted in the 50-2000-µm fraction under crop and eucalyptus. Compared with whole-soil contents, CPs were strongly enriched in both sand fractions and generally depleted in the clay and silt fractions.

Total polysaccharide contents accumulated in the clay and coarse-sand fractions, while in the silt and 20-50-µm fraction, they were strongly

Table 5. Cellulosic polysaccharide contents in whole soil (with ±95% confidence intervals; n = 3) and particle-size separates of differently managed clayey and loamy Oxisols, Brazilian savannas. Percentage of total polysaccharide contents in parentheses.

| Oxisol<br>Treatment | Whole soil<br>(C at g/kg SOC)[a] | Particle-size separates (µm)<br>(C at g/kg SOC)[a] | | | |
|---|---|---|---|---|---|
| | | <2 (clay) | 2-20 (silt) | 20-50 (fine sand) | 50-2000 (medium to coarse sand) |
| Very fine Anionic Acrustox | | | | | |
| Native savanna | 31 ± 3 (16.4) | 28 | 36 | 51 | 96 |
| Crop | 25 ± 2 (14.4) | 25 | 32 | 52 | 76 |
| Pasture | 33 ± 1 (15.6) | 27 | 33 | 62 | 108 |
| Pine | 23 ± 2 (16.5) | 21 | 16 | 30 | 67 |
| Coarse-loamy Typic Haplustox | | | | | |
| Native savanna | 38 ± 4 (19.3) | 34 | 32 | 57 | 66 |
| Crop | 31 ± 4 (16.8) | 28 | 29 | 66 | 44 |
| Pasture | 34 ± 2 (17.5) | 31 | 32 | 85 | 74 |
| Eucalyptus | 34 ± 3 (18.1) | 36 | 38 | 73 | 45 |

a. SOC = soil organic carbon.

depleted (Figure 2). In the coarse-sand fraction, a maximum of total polysaccharide contents was achieved by high contents of CPs and NCPs, whereas in the clay fraction, this maximum was obtained through NCPs only. In the loamy soil, under crop and eucalyptus, the maximum did not occur because NCPs were only weakly enriched and CPs appeared to be higher in the 20-50 µm than in the 50-2000-µm fraction.

### VSC-lignin

In the whole soil, VSC-lignin ranged from 4.4 to 12.7 g/kg SOC and was significantly higher in the loamy than in the clayey soil at the $P < 0.05$ level of Tukey's HSD test (Table 6). This difference was visible in all particle-size classes but significant only for the clay fraction. From the sand to clay fractions, VSC-lignin always decreased, on the average, from 27.7 to 3.5 g/kg SOC, respectively. In all size separates, VSC-lignin was lowest under pine, but otherwise management effects were not apparent.

The mass ratio of acids to aldehydes for the vanillyl units $(Ac/Al)_V$ rose from about 0.2 to 0.3 in the sand fractions and from 0.5 to 0.6 in the clay fractions (Figure 3), indicating increasing side-chain alteration and thus microbial lignin breakdown. However, while the ratio decreased continuously in the clayey soils, in the loamy soils, changes in the $(Ac/Al)_V$ ratio from the sand to silt fractions were small but generally higher than in the clayey soils.

The ratio of the sum of syringyl to the sum of vanillyl units (S/V) was between 0.7 and 0.9 in all treatments except under pine (data not shown), where it was 0.2 because gymnosperm lignin contains only minor proportions of syringyl units (Sarkanen and Ludwig 1971). This indicates that most of the original lignin was already substituted by pine-derived lignin.

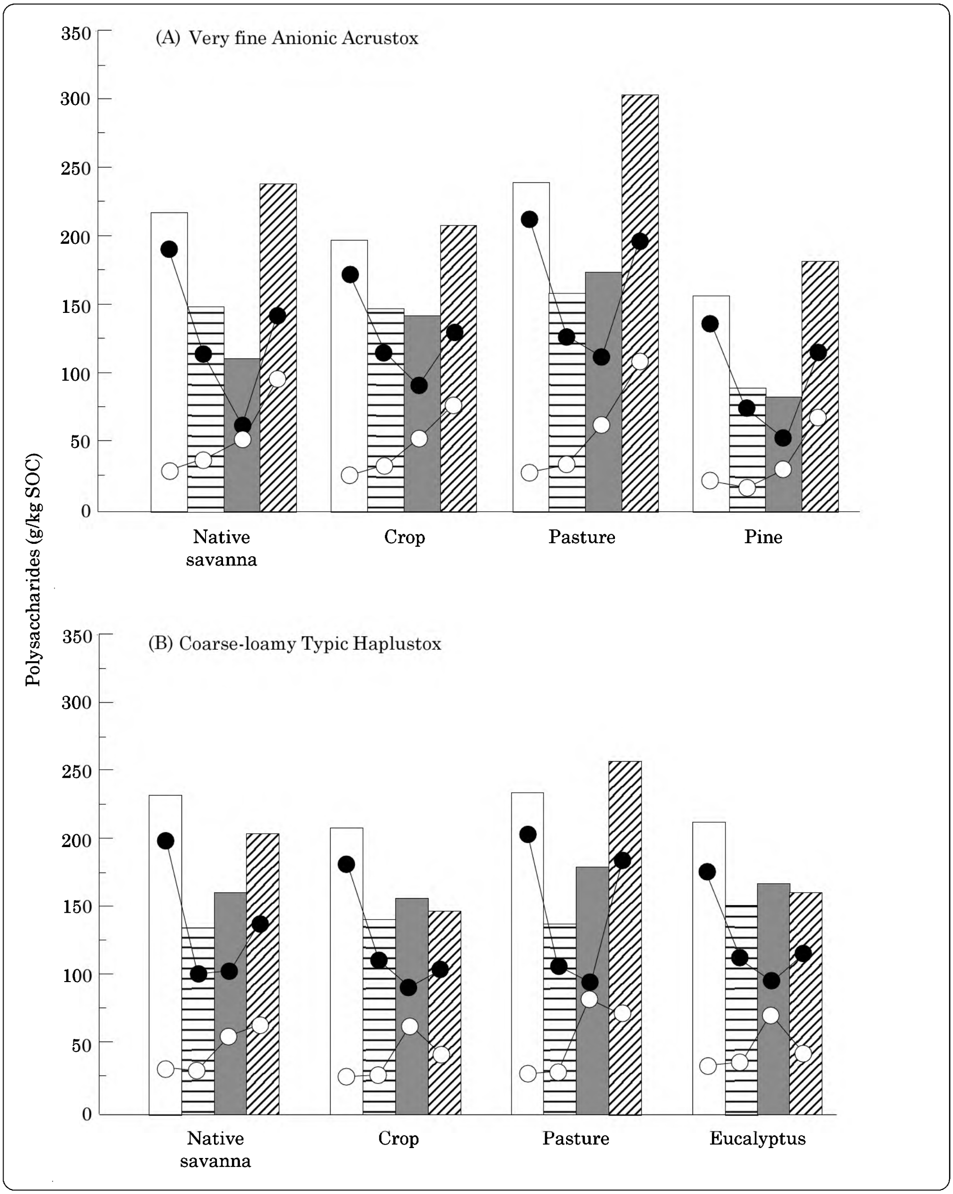

Figure 2. Total polysaccharide contents (bars) next to noncellulosic (●) and cellulosic (○) polysaccharides in particle-size separates of differently managed clayey (A) and loamy (B) Oxisols, Brazilian savannas. (SOC = soil organic carbon; □ = <2 µm; ☰ = 2-20 µm; ■ = 20-50 µm; ▨ = 50-2000 µm.)

Table 6. VSC-lignin contents in whole soil (with ±95% confidence intervals; n = 3) and particle-size separates of differently managed clayey and loamy Oxisols, Brazilian savannas.

| Oxisol<br>Treatment | Whole soil<br>(C at g/kg SOC)[a] | Particle-size separates (μm)<br>(C at g/kg SOC)[a] | | | |
|---|---|---|---|---|---|
| | | <2<br>(clay) | 2-20<br>(silt) | 20-50<br>(fine sand) | 50-2000<br>(medium to coarse sand) |
| Very fine Anionic Acrustox | | | | | |
| Native savanna | 5.5 ± 0.3 | 2.5 | 5.9 | 8.8 | 31.1 |
| Crop | 7.9 ± 1.2 | 3.0 | 11.5 | 15.3 | 25.2 |
| Pasture | 7.0 ± 0.9 | 2.8 | 9.4 | 17.7 | 37.2 |
| Pine | 4.4 ± 0.5 | 1.7 | 2.4 | 7.0 | 11.9 |
| Coarse-loamy Typic Haplustox | | | | | |
| Native savanna | 9.5 ± 1.2 | 4.7 | 8.6 | 13.4 | 31.8 |
| Crop | 12.7 ± 1.2 | 4.4 | 9.3 | 19.5 | 27.4 |
| Pasture | 8.6 ± 1.0 | 4.4 | 7.1 | 19.8 | 35.8 |
| Eucalyptus | 11.5 ± 0.6 | 4.0 | 11.3 | 14.1 | 20.9 |

a. SOC = soil organic carbon.

# Discussion

## *Factors influencing soil organic carbon and organic compounds in Oxisols of the Brazilian savannas*

The higher SOC contents in the clayey soils compared with the loamy soils can unambiguously be attributed to clay content. Feller and Beare (1997) recently showed that this relationship holds in low activity clay soils throughout the tropics and is valid in undisturbed as well as cultivated soils. For temperate soils, Christensen (1996) showed a similar relationship.

Beyond the SOC contents, the most apparent intrinsic difference between the clayey and loamy soils was the higher proportions of sand-associated OM in the loamy soils, which led to similar SOC yields in both soils. Assuming that sand-associated OM comprises primarily unprotected POM, this indicates a greater lability of the OM in the loamy soils. Similar conclusions were drawn by Silva et al. (1994) for a series of differently textured savanna soils after 5 years of cultivation. Although the OM's half-life was comparable, the sandy soils lost twice as much of their initial SOM stock as did the clayey soils. However, concurrently, the specific exchange capacity of SOM (CEC/SOC) increased in all soils, indicating that predominantly POM had been mineralized while humic matter, being rich in carboxylic groups, was less affected. Management effects are therefore likely to be most accentuated in the sand fractions, whereas the humified OM, serving as donor of exchange sites and, as such, responsible for much of the soil fertility, shows remarkable resilience. However, if the microbes are obliged to use humified matter as a food source because the input of labile plant residues is reduced for long periods of time, this might change and lead to a reduced exchange capacity and thus reduced soil fertility.

Total polysaccharide contents in the studied soils were higher than those obtained by Dalal and Henry (1988) in cultivated Australian

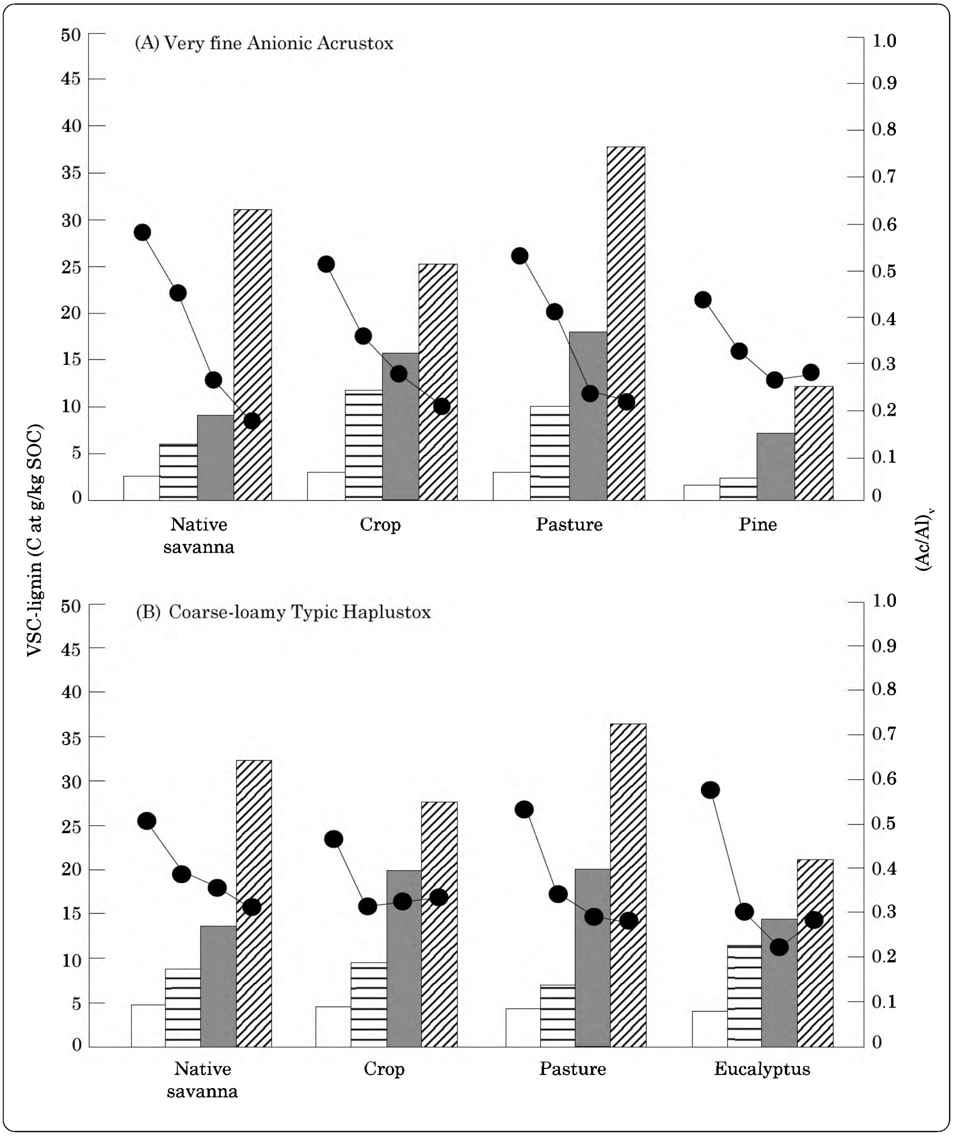

Figure 3. VSC-lignin contents and $(Ac/Al)_V$ ratios (●) in particle-size fractions of differently managed clayey (A) and loamy (B) Oxisols, Brazilian savannas. (□ = <2 µm; ▤ = 2-20 µm; ■ = 20-50 µm; ▨ = 50-2000 µm.)

Vertisols, but were comparable with differently managed German Eutrochrepts (Guggenberger et al. 1994), and were slightly lower than in Mollisols of the Great Plains (Amelung et al. 1997). In Colombian Oxisols, under native savanna and pasture, Guggenberger et al. (1995) found similar polysaccharide contents. These data suggest that similar amounts of sugars can be found independent of soil type and climate. However, Amelung et al. (1997) reported a highly significant positive correlation between carbohydrate contents and the ratio of mean annual precipitation to mean annual temperature (MAP/MAT). In the Oxisols under study, sugar contents were much lower than would be expected from their MAP/MAT ratio. Although Oxisols cannot be compared with Mollisols directly, this could be related to the water retention characteristics of the Oxisols, as there was a close negative correlation between pore volume at field capacity (pF > 1.8) and the proportion of CPs to total polysaccharides (Figure 4). Because no significant relationship existed with the fast-draining macropores nor with the litter input, cellulose decomposition must therefore be controlled by the period of time water is available to microorganisms. Therefore, the lower proportions of plant-derived sugars under crop could be seen as consequence of the tillage-induced increase in mesopores.

Values for VSC-lignin in the studied Oxisols were well within the range determined by Guggenberger et al. (1995) for Colombian Oxisols, but mostly lower than in temperate Mollisols, Inceptisols, and Entisols (Amelung et al. 1997; Guggenberger et al. 1994; Kögel-Knabner et al. 1988). These findings suggest an influence of climate or mineralogy on the decomposition of lignin. Amelung (1997) found no significant correlation between VSC-lignin and climate for a series of prairie soils. He argued that most lignin was associated with POM, which should be too young to be influenced by climatic factors.

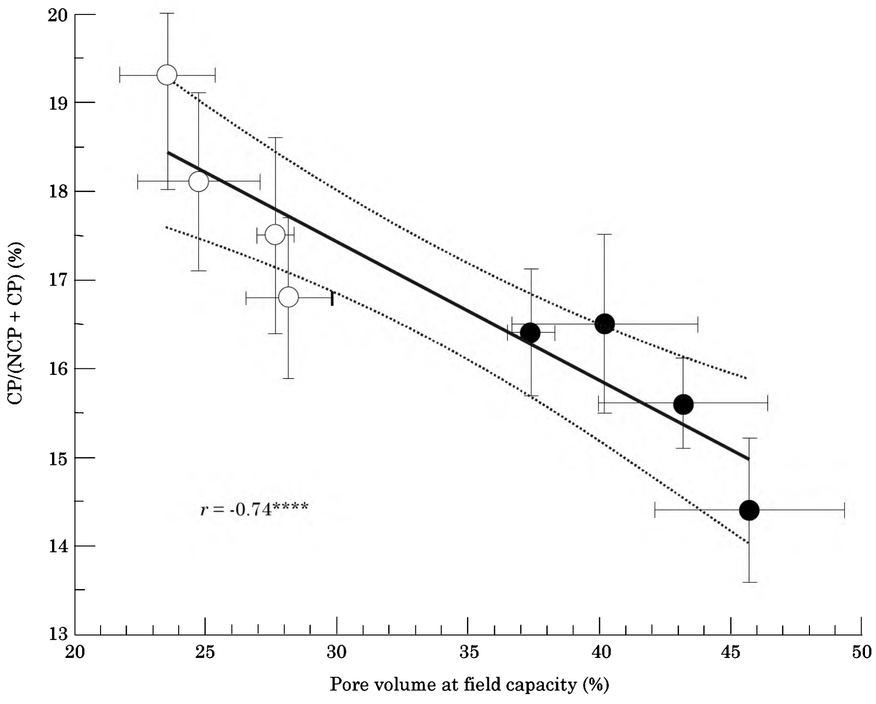

Figure 4. Plot of the proportion of cellulosic polysaccharides (CP) to total polysaccharides (NCP + CP) versus the pore volume at field capacity (pF > 1.8; pore ∅ < 50 µm), with ±95% confidence intervals, in differently managed clayey ( ● ) and loamy ( ○ ) Oxisols, Brazilian savannas. The coefficient of correlation is significant at the $P < 0.0001$ level (n = 24).

Although higher levels of VSC-lignin contents in the loamy soil indicated a certain connection to clay content, no functional relationship was found. However, total pore volume in the treatments was closely correlated to VSC-lignin (Figure 5), suggesting that lignin degradation is controlled by the water budget and, thus again, by the activity of microbes in soil. Nonetheless, the comparatively low values under pine indicate that other factors, such as the reduced litter incorporation, might be relevant too.

### *Particle-size fractionation*

The usefulness of particle-size separation by sonication has recently been reviewed by Christensen (1996), but the method's reliability depends on full dispersion into the primary organo-mineral complexes. The grain-size distribution of the studied soils was similar to that obtained by chemical dispersion and therefore considered sufficient. Higher clay contents after sonication indicated that the chemical dispersion did not fully disaggregate the soils. Probably, the clay fraction from the pine site was not fully dispersed either. In the loamy soils, higher silt contents after shaking/ sonication, compared with chemical dispersion, probably indicated a minor destruction of sand during the shaking with marbles. If it were increased, disaggregation, as found with clayey soils, followed by higher clay contents, could have been expected too.

Several authors have pointed out the limitations of applying high sonic

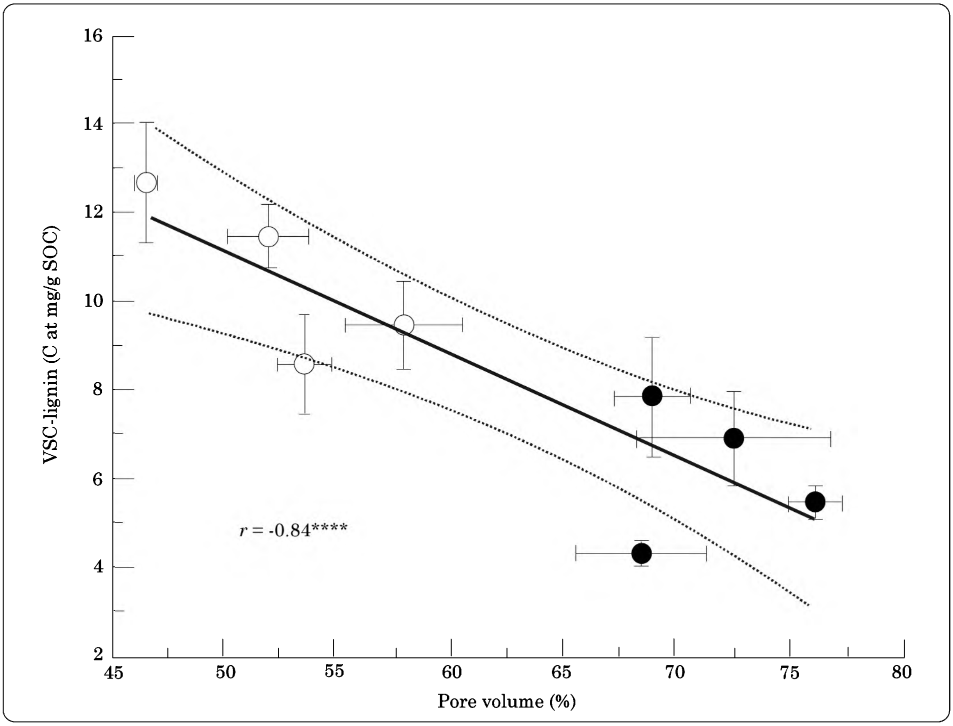

Figure 5. Plot of VSC-lignin versus the pore volume (with ±95% confidence intervals) in differently managed clayey (●) and loamy (○) Oxisols, Brazilian savannas. The coefficient of correlation is significant at the $P < 0.0001$ level (n = 24).

energy to soil samples. Elliott and Cambardella (1991) discussed the possible redistribution of OM during sonication. Redistribution of POM was avoided by sieving the coarse-sand fraction before sonication. Lysis of microbes during sonication and adhesion of their cell contents to the clay and silt fractions cannot be compared. Even so, the error that would occur must be considered as negligible because the microbial biomass never exceeded 3% of SOM in the studied soils (Renz et al. 1998). The fractionation method applied in this study can therefore be considered to be complete and reliable.

### *Alteration of organic compounds during degradation*

Researchers agree that a decrease in the C/N ratio from the coarsest to the finest fractions reflects an alteration of OM during plant decomposition and humification (Anderson et al. 1981; Christensen 1996; Tiessen and Stewart 1983). In this scheme, the nitrogen bound in the plant tissue is microbially immobilized in the soil and the carbon partly mineralized. Concomitantly, structural differences between plant tissues are replaced by similar microbial metabolites.

The distribution of NCPs and CPs within particle-size separates reflects the transformation during plant decomposition and resynthesis of microbial polysaccharides (Figure 2), in much the same way as Guggenberger et al. (1994) had described for temperate soils. Although NCPs may consist of both plant-derived hemicelluloses and microbial metabolites (Beudert 1988), they were considered as predominantly plant-derived in the 50-2000-µm fraction, because SEM micrographs showed only slightly decomposed plant structures (Figure 6A). The strong depletion of NCPs in the 20-50-µm fraction indicates that most hemicelluloses were already decomposed before reaching the silt fraction. Verifying these findings, SEM micrographs of the 20-50-µm fraction showed that only cell walls of very small plant fragments remained (Figure 6B). Because Amelung (1997) found a similar rapid depletion of hemicellulose in prairie Mollisols, we suggest that the process of breakdown is similar in tropical and temperate soils, although the time scale may be different. However, it remains unclear why CPs followed different trends in the clayey and loamy soils between the 20-50 and 50-2000-µm fraction. Selective preservation due to a different pore-size distribution may again be of importance here.

From the silt to clay fraction, CPs remained nearly unchanged. Micrographs of the silt fraction of the loamy (Figure 6C) and clayey soils (Figure 6D) showed that the particulate structure of the OM persisted in both soils, while the mineral fraction was either mainly composed of quartz or of clay in microaggregates. This suggests that the SOM in the loamy soils consisted of predominantly plant-derived structures, whereas it contained additional humified matter inside the microaggregates of the clayey soils. In the clay fraction, no more visible organic structures persisted.

The NCPs in the clay fraction must be considered as being of predominantly microbial origin (Guggenberger et al. 1994). They are enriched in the clay fraction because microbial polysaccharides are partly dissolved (Guggenberger and Zech 1994) and can therefore penetrate even the smallest pores.

Lignin alteration during plant litter degradation is caused by the breakdown of intact lignin polymers by increasing side-chain oxidation and

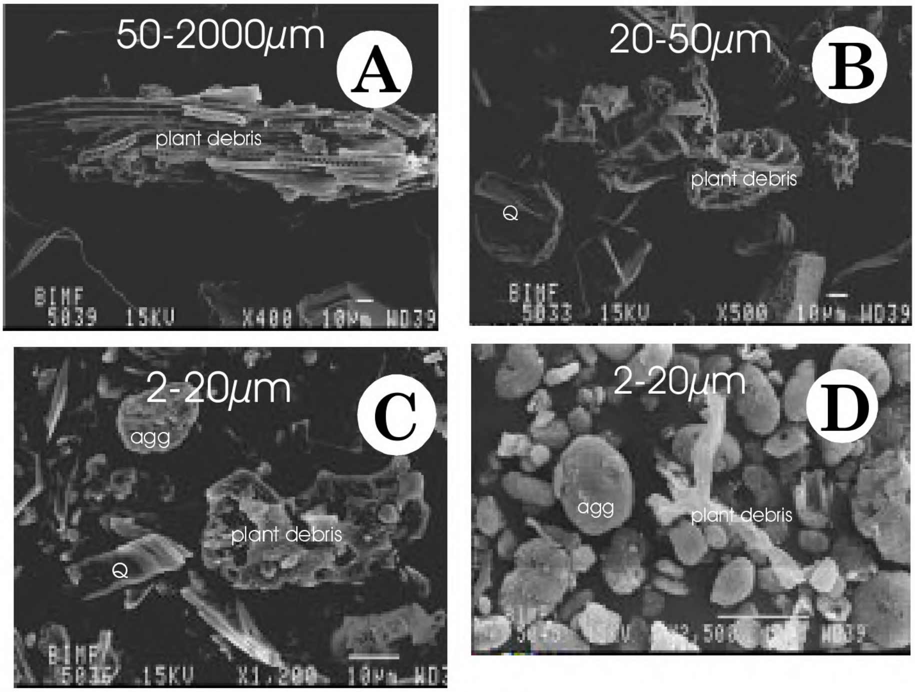

Figure 6. Scanning electron microscope micrographs of organic matter in different particle-size separates. Figures A, B, and C are from a loamy Oxisol under native savanna and Figure D is from a clayey Oxisol under native savanna, but no differences between the clayey and loamy substrates were visible in either the 50-2000 μm or 20-50 μm fraction. Q = quartz; agg = aggregate.

ring cleavage (Kögel 1986; Kögel-Knabner et al. 1988). Thus, the decrease of VSC-lignin and the increasing (Ac/Al)$_V$ ratio with decreasing particle size are indicators of lignin decomposition along a biological gradient (Guggenberger et al. 1995).

The great variability between the treatments in all but the clay fraction could be seen as a sign of highly advanced degradation. Amelung (1997) found a similarly fast decomposition of VSC-lignin after analyzing soils from a climosequence in the Great Plains. However, because the CuO oxidation procedure extracts only intact lignin subunits bound by arylether bondings and C-substituted remnants of lignin, rapid turnover of the VSC-lignin is no argument for an overall lability of soil lignin. On the contrary, according to Guggenberger and Zech (1994), aromatic structures are nearly irreversibly fixed to the mineral phase once they are adsorbed.

Because VSC-lignin content was mostly higher in the loamy soils and this depended on pore volume, it can be argued that VSC-lignin was less degraded in the loamy soils because a higher water stress reduced microbial activity. In addition, the (Ac/Al)$_V$ ratios of the loamy soils were nearly unaltered before reaching the clay, even though VSC-lignin decreased progressively from the sand to clay fraction in both substrates. Considerable side-chain alteration apparently begins only after complete comminution of the POM, thus indicating that subsequently different microbial populations are probably involved in the modification and degradation of lignin. Because most microorganisms can only be active in an aqueous environment, they are probably restricted to mesopores and so have no access to particulate lignin structures. Others may be capable of surviving higher vapor pressures and could thus be responsible for the initial decrease in VSC-lignin in the loamy soils. In the clayey soils, the increasing $(Ac/Al)_V$ ratios from the sand fraction onward may therefore reflect an earlier change of the microbial population, which could be induced by higher water contents.

### *Management effects on soil organic carbon and organic compounds*

In the clayey soils, management effects are retarded by their high contents of physically and chemically protected SOC in the clay fraction, masking changes in litter input. Therefore, at the cropped site, losses are only beginning to appear, but could lead to a stronger depletion in the future if the equilibrium of litter input and SOC turnover is constantly disturbed. However, it is doubtful if unsustainable management implemented on clayey soils could achieve the strong effects already visible at the loamy crop site.

Despite the low productivity of the pasture on clayey soil, there was a strong increase in SOC in the 50-2000-µm fraction, which is attributed to the high root density in the topsoil. Similarly, in the savannas of the Colombian Eastern Plains, soils under *Brachiaria* pastures showed much higher root densities than those of the native savanna (Rao et al. 1992). Guggenberger et al. (1995) also reported the greatest SOC accumulations in sand fractions in soils under grass-alone and legume-based *B. decumbens* pastures, compared with the native savanna. This could be related to their greater productivity, which is maintained by regular P fertilization (Rao et al. 1992). Higher microbial activities and visibly more aboveground biomass in recently recovered and fertilized grass-alone and grass-legume pastures in Brazilian savanna soils corroborate this point of view (Renz et al. 1998). An extremely low P status as a result of insufficient fertilization may have been the cause for the severe SOC loss in the loamy soil pasture through lower input of SOC into the soil (Neufeldt 1998).

The strong depletion of SOC in the surface mineral soil under pine in all but the clay fraction is not caused by a higher OM mineralization but rather a reduced litter input into the mineral soil. Inhibited litter incorporation is indicated by a thick moder layer, which was formed in only 20 years, and is typical of pine reforestation areas throughout the region (Thiele 1997). The organic layer contained a carbon stock of 22.6 t/ha, which was as large as that of the total organic carbon in the 0-12-cm soil layer (19.8 t/ha). Clearing and subsequent establishment of crop or pasture will probably lead to a quick mineralization of the organic layer. However, because the quality of the pine's OM is poor (low polysaccharide contents and high acidity), a prediction of SOM dynamics cannot be made and further research concerning the impact of pine reforestation on Brazilian savanna soils should be done.

The strong SOC enrichment in the clay fraction at the eucalyptus site cannot be explained, but clearly higher values in the sand fraction suggest a positive effect of eucalyptus on SOC contents. Because the enrichment is not restricted to the input of POM, it seems as if reforestation with eucalyptus has a positive impact on soil fertility.

The distribution of polysaccharides in relation to the control (native savanna) indicated an enrichment under pastures and a reduction under pine. Similar tendencies were apparent for VSC-lignin in the sand fractions only. Guggenberger et al. (1994, 1995) observed comparable land-use effects under temperate and tropical conditions. Because the polysaccharide contents were normalized on SOC, they reflect changes in the OM's quality and thus indicate characteristics of the different land-use systems. Assuming a rapid decomposition of plant-derived sugars and VSC-lignin, the results indicate a greater lability of pasture OM and a greater recalcitrance under pine in relation to the control (native savanna).

## Conclusions

Soil organic matter in the Brazilian savannas shows similar properties to that of other soil types and under different climatic conditions. However, lower contents of certain polysaccharides and lignin than are found in temperate soils indicate that existing concepts of SOM dynamics and turnover cannot be applied directly to tropical conditions without first receiving critical evaluation. Within the studied soils, polysaccharides and VSC-lignin are apparently strongly controlled by the soil's pore space, which is linked to the habitats of microorganisms in soil. Models attempting to simulate SOM dynamics should therefore take into account the soil's physical characteristics.

The particle-size separation represents a decomposition gradient from nearly undecomposed POM in the sand fraction to highly humified matter in the clay fraction. Both the transformation of organic compounds and management-induced SOC changes can therefore be observed more clearly in particle-size fractions than in whole-soil samples. During decomposition, plant-derived (primary) sugars are metabolized and partially resynthesized to microbial (secondary) sugars, which are then incorporated into the clay associated (i.e., humified) fraction. In contrast, VSC-lignin continuously decomposes.

Continuous cropping reduces POM, while changes in humified OM are small. Thus, a subsequent change to a land-use system with high litter input would rapidly replenish this labile pool. The cation-exchange capacity is, however, not affected as long as the recalcitrant SOC fractions are largely unchanged. Eucalyptus forests and well-managed pastures can therefore be planted on cropped fields before they lose recalcitrant SOC. This substitution is necessary earlier in loamy than in clayey soils because of their relatively higher labile POM pool. Reforestation with pine leads to the formation of a thick organic layer and a loss of POM in the mineral soil. However, to quantify future dynamics of differently managed savanna soils, the turnover rates of OM in different pools must first be calculated.

## Acknowledgments

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## Chapter 9

# Soil Organic Carbon, Carbohydrates, Amino Sugars, and Potentially Mineralizable Nitrogen under Different Land-Use Systems in Oxisols of the Brazilian *Cerrados*

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## Abstract

Intensive farming and grazing on Oxisols of the Brazilian savannas (also known as the *Cerrados*) are leading to loss of soil organic matter (SOM) and consequently to a decline in fertility and sustainability of the soils. Alternative land-use systems such as the introduction of legumes in pastures and the use of no-tillage systems can reverse this process. In this study, the effects of seven land-use systems (native savanna, forest, degraded pasture, improved pure-grass pasture, improved grass/legume pasture, conventional cropping, and no-tillage cropping) on the SOM and potentially mineralizable nitrogen ($N_{pot}$) were examined in whole-soil samples and particle-size separates. In addition, sugars and amino acids were determined for a better understanding of SOM dynamics. Compared with native savanna, soil organic carbon (SOC), cellulosic and noncellulosic polysaccharides (CPs and NCPs, respectively), amino sugars, and $N_{pot}$ decreased under forest and increased under pastures. The positive influence of improved pasture systems, especially the grass/legume pasture, was clearly recognizable. Under the no-tillage system, SOC and $N_{pot}$ levels increased, compared with conventional tillage. These differences were clearest in the sand fractions of the particle-size separates. The sugar dynamics reflected decomposition of plant tissue and subsequent accumulation of microbial sugars. The ratio of glucosamine to muramic acid increased from coarse sand to fine sand and thereafter decreased toward clay. The cause may be a stronger association of fungal hyphae with fine roots in the fine-sand fraction and an increased association of bacteria with the clay fraction. Amino sugars appeared to be an important source of $N_{pot}$.

*Keywords:* Available carbon, available nitrogen, Brazilian savannas, *Cerrados*, mineralization, permanganate, soil organic matter, water-extractable carbon

## Introduction

The loss of soil organic matter (SOM) under intensive land use is one of many factors that degrade the Oxisols of the Brazilian savannas, also known as the *Cerrados*. Intensive tillage leads to a loss of SOM through the physical

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destruction of soil aggregates and consequently to a faster release of C, N, S, and P. Traditional grazing also leads to decreased fertility and, therefore, to declining productivity (Ayarza 1994; Rao et al. 1994). Alternative land-use systems, such as grass/legume pastures, can improve both soil fertility and animal production (Rao et al. 1992; Serrão et al. 1979; Thomas et al. 1992, 1994). No-tillage systems reduce the loss of SOM because the mechanical destruction of aggregates and the subsequent mineralization of SOM is diminished (Cambardella and Elliott 1992; Holland and Coleman 1987; Lal 1976; Lamb et al. 1985).

Soil organic matter is extremely heterogeneous, ranging from only slightly decomposed plant and microbial residues to highly humified organic substances. The stability of the organic matter increases with the degree of humification and the protection from further decomposition in aggregates and in association with the mineral phase. Therefore, labile and stable pools of SOM can be separated through particle-size fractionation (Gregorich et al. 1988; Guggenberger and Christensen 1993; Tiessen and Stewart 1983). For soils of temperate regions, silt associated with SOM has been shown to be the most stable fraction, clay associated with SOM is intermediately stable, and sand associated with SOM the most labile fraction (Christensen 1992). The sand fraction with SOM consists mainly of particulate organic matter (POM), which should thus reflect effects of land-use change better than SOM in bulk-soil samples. Particulate organic matter could therefore be regarded as a sensitive indicator for changes in soil fertility (Cadisch et al. 1996).

Very often, however, the determination of SOM by itself is not sufficient because differences in SOM quality are not expressed. The sugars, especially the amino sugars (AS), can better highlight the mechanisms of litter decomposition and SOM turnover because they differ from each other in origin and chemical stability (Amelung 1997). Celluloses and hemicelluloses are among the most important constituents of plants (Molloy et al. 1977). During litter decomposition, plant-derived polysaccharides are rapidly decomposed by microorganisms, and microbial polysaccharides accumulate (Murayama 1988; Ziegler and Zech 1991).

Plant-derived sugars are mainly associated with POM in sand, whereas microbially synthesized sugars are enriched in clay (Guggenberger et al. 1994). Amino sugars in soils come from microorganisms (Stevenson 1982), in which the AS spectrum characterizes definite decomposer communities (Benzing-Purdie 1984). Glucosamine is an important constituent of fungal chitin, galactosamine is synthesized by various microorganisms, while muramic acid is produced exclusively from bacterial cell walls (Parsons 1981). Mannosamine is also believed to be of bacterial origin (Kenne and Lindburg 1983). Because of this, the ratio of glucosamine to muramic acid (GlucN/Mur) can be used to estimate the level of bacterial and fungal activity during the decomposition of plant litter.

Over 90% of nitrogen in soils is organically bound (Stevenson 1982). Only nitrate and ammonium, however, are directly plant available. Thus, a considerable amount of organically bound nitrogen becomes available only after mineralization during growth (Thicke et al. 1993). However, in soils with a low pH, the levels of mineralization of organic nitrogen is often low and, hence, is influenced by land use (Kuntze and Bartels 1979).

In this work, we attempt to determine what effects traditional and improved land-use systems have on SOM and organic compounds, and nitrogen supply. In addition, we examine the relationship between potentially mineralizable N, carbohydrates, AS, and nitrogen supply.

## Materials and Methods

### *Study area*

Two study areas, roughly 80 km apart, were chosen. Both lie at between 950 and 1000 m above sea level (masl), on Tertiary, unconsolidated, limnic deposits. The climate is typical of the savannas, with a pronounced rainy and dry season: Aw, according to Köppen (1936). Annual precipitation is about 1700 mm, 75% of which occurs between November and March. The dry season occurs between June and September. The average temperature varies from 18 °C in July to 23 °C in October. All soils are classified as very fine, allitic, isohyperthermic, Anionic Acrustox (Neufeldt 1998), and have a clay content of 60% to 80%. Some important characteristics of the topsoils are shown in Table 1.

In the first study area, near the city of Uberlândia, (19°09'S, 48°07'W, 950 masl), five different land-use systems were investigated: native savanna (NS) as control; forest (F); degraded pasture (DP); improved pure-grass pasture (PG); and improved grass/legume pasture (GL). The forest was planted in 1975 with *Pinus caribaea* ssp. *caribaea*. The seedlings were planted at 3 x 3 m, and each was fertilized with 20 g monocalcium superphosphate. The degraded *Brachiaria decumbens* pasture was put into use in 1986 and fertilized with 616 kg lime, 1 t gypsum, and 78 kg $P_2O_5$ per hectare. Part of this degraded pasture was later planted with rice and, in 1992, was improved with 1 t lime, 90 kg $P_2O_5$, 32 kg $K_2O$, and 12 kg N per hectare. After the rice was harvested, this fertilized site was divided into a pure-grass pasture with *B. decumbens*, and a grass/legume pasture with a mixture of *B. decumbens* and *Stylosanthes guianensis*.

The second study area was near Iraí de Minas (18°59'S, 47°33'W, 1000 masl). The following land-use systems were investigated: continuous cropping with conventional tillage (CCT) and with no tillage (CCN). Both

Table 1. Selected chemical and physical properties of the topsoils (0-12 cm) studied under different land-use systems in the Brazilian savannas.[a]

| Land use[b] | Bulk density (g/cm$^3$) | Color[c] (moist soil) | pH ($H_2O$) | pH (KCl) | P (µg/g) | CEC (cmol(+)/kg) | CEC$_e$ (cmol(+)/kg) | BS (%) |
|---|---|---|---|---|---|---|---|---|
| NS | 0.90 | 7.5 YR 3/4 | 4.6 | 4.0 | 1.8 | 7.54 | 1.34 | 22 |
| F | 0.92 | 10.0 YR 3/4 | 4.7 | 4.1 | 1.0 | 6.87 | 0.85 | 14 |
| DP | 1.00 | 7.5 YR 3/4 | 5.3 | 4.7 | 0.9 | 5.65 | 2.48 | 95 |
| GL[d] | 1.07 | 7.5 YR 3/4 | 5.8 | 5.1 | 2.1 | 7.81 | 1.63 | 98 |
| CCT | 1.05 | 8.8 YR 3/4 | 6.2 | 5.6 | 8.2 | 7.07 | 1.89 | 100 |
| CCN | 1.03 | 8.8 YR 3.5/4 | 5.8 | 5.3 | 9.2 | 7.01 | 1.41 | 100 |

a. CEC = cation-exchange capacity; CEC$_e$ = effective cation-exchange capacity; BS = base saturation.
b. NS = native savanna; F = forest; DP = degraded pasture; GL = improved grass/legume pasture; CCT = continuous cropping with conventional tillage; CCN = continuous cropping with no tillage.
c. Color notation according to Munsell Color Company (1975).
d. The improved pure-grass pasture was not examined, because it was located close by the GL.

treatments were cropped in rotation with maize and soybean and were conventionally tilled from 1981 until 1989. In 1990, a part of the CCT field was transformed into a CCN field. Both were fertilized with 350 kg NPK per hectare, and 1 t lime was added every 3 years. In 1996, the soybean yields were 2100 kg/ha, independently of cropping system.

### *Soil sampling, pretreatment, and particle-size separation*

All samples were taken on 2 and 3 December 1995, during the rainy season. For each treatment on each site, sampling took place in a 50 x 50 m area. Five undisturbed samples were then taken at random from the 0-12 cm layer with an Uhland auger. The samples were dried for 1 week at 40 °C in an oven and sieved through a 2-mm mesh. Roots were removed. The bulk soil was ground for future analyses.

The particle-size separation followed Christensen's method (1985), as modified by Neufeldt (1998), that is, five single samples from each treatment were combined into a mixed sample.

### *Chemical analyses*

Total C and N were measured with a CN-analyzer (Elementar Vario EL). Inorganic C was determined after burning the organic carbon at 560 °C. The soil organic carbon (SOC) content was calculated by difference. Cellulosic and noncellulosic polysaccharides (CPs and NCPs, respectively) were determined with the MBTH method (Johnson and Sieburth 1977, as modified by Miltner 1997). Amino sugars were measured, using Zhang and Amelung's method (1996). The samples were hydrolyzed for 8 h with 6 *M* HCl at 105 °C, and purified with 0.5 *M* KOH at pH 6.6-6.8. The samples were then treated with a mixture of hydroxylamine hydrochloride and 4-(dimethylamino)pyridine in pyridine-methanol in the ratio 4:1. The simultaneous quantification of glucosamine, galactosamine, mannosamine, and muramic acid was done by gas chromatography (Hewlett-Packard 6890). Potentially mineralizable nitrogen ($N_{pot}$) was determined, using Keeney's anaerobic incubation method (1982). We weighed 10 g of dried bulk soil in a tightly sealed glass container filled with 30 mL of water, then incubated in the dark for 1 week at 40 °C. The ammonium produced was then measured colorimetrically with a continuous-flow analyzer. Water-extractable ammonium from unincubated samples was also determined in the same manner. The ammonium produced during the incubation was calculated by difference. Each determination was done twice.

## Results and Discussion

### *Soil organic constituents and $N_{pot}$ in bulk-soil samples*

Taking native savanna as control, differences in SOC contents after land-use change are rather small (Table 2), but a decrease in the degraded pasture and under pine was observed. Improved grass/legume pasture had the highest soil carbon. The cropping systems showed no differences. Within the pastures, a positive influence of the improved pasture systems can be seen. Degraded pastures apparently regenerated after only 3 years. Guggenberger et al. (1995) likewise showed an increase of SOM with improved tropical pastures. The introduction of legumes in tropical pastures clearly leads to improved soil fertility (Gijsman et al. 1997; Rao et al. 1994; Thomas et al. 1997).

Table 2. Soil organic carbon (SOC), carbon-to-nitrogen ratio (C/N), cellulosic polysaccharides (CPs), noncellulosic polysaccharides (NCPs), amino sugars (AS), ratio of glucosamine to muramic acid (GlucN/Mur ratio), and potentially mineralizable nitrogen ($N_{pot}$) in bulk soil under different land uses in the Oxisols of the Brazilian savannas.

| Land use[a] | SOC (mg/g) | C/N ratio | CPs (mg/g C)[b] | NCPs (mg/g C)[b] | AS (mg/g C) | GlucN/Mur ratio | $N_{pot}$ (N at kg/ha) |
|---|---|---|---|---|---|---|---|
| NS | 25.6 ± 2.7* | 17 | 36 | 152 | 63 | 6 | 22.9 ± 0.2* |
| F | 22.1 | 25 | 30 | 124 | 38 | 6 | 4.9 |
| DP | 23.1 ± 0.8 | 17 | 38 | 189 | 79 | 6 | 29.9 ± 0.5 |
| PG | 26.0 ± 0.8 | 17 | 42 | 185 | 73 | 8 | 43.0 ± 5.0 |
| GL | 28.9 ± 1.1 | 16 | 40 | 192 | 70 | 8 | 63.3 ± 5.8 |
| CCT | 24.1 ± 1.6 | 16 | n.d. | n.d. | 67 | 9 | 17.9 ± 1.0 |
| CCN | 24.6 ± 0.7 | 16 | n.d. | n.d. | 59 | 8 | 25.9 ± 5.1 |

* = confidence limits at 95%.

a. NS = native savanna; F = forest; DP = degraded pasture; PG = improved pure-grass pasture; GL = improved grass/legume pasture; CCT = continuous cropping with conventional tillage; CCN = continuous cropping with no tillage.

b. n.d. = not determined.

The levels of CPs, NCPs, and AS in bulk-soil samples showed similar, but more marked differences to those of SOC. Compared with native savanna, all three pastures showed elevated levels, especially of NCPs and AS. Among the pastures and cropped sites, no clear differences were observed. The higher input of fresh plant material into the mineral soil of the pastures could have caused the higher content of plant-derived sugars. These results are consistent with those of Guggenberger et al. (1994). The increase in NCPs and AS is also the result of a higher microbial activity (Renz 1997). In the pine forest, all sugar separates were less than the other treatments, reflecting the low quality of the forest litter.

Potentially mineralizable nitrogen ($N_{pot}$) showed clear land-use effects (Table 2). Compared with native savanna, $N_{pot}$ was very low under pine and highest under pastures, while no differences were apparent between the cropping systems and native savanna. The influence of improved pasture systems was very clear. The legumes, with their nitrogen-fixing ability, elevate microbial activity so that more nitrogen becomes mineralized. This result is consistent with other studies, which likewise proved a higher $N_{pot}$ content in the presence of legumes (Cadisch et al. 1996; Rao et al. 1994; Westerhof 1998). In relation to the two cropping systems, the $N_{pot}$ level was somewhat higher in the no-tillage field than in the conventionally cultivated one, which might be explained by a decrease of microbial biomass under intensive tillage (Follett and Schimel 1989). The correlation of $N_{pot}$ with AS was highly significant (Figure 1). Because $N_{pot}$ represents a labile N pool, it can be said that AS are an important source of mineralizable N. This view is reinforced by Schneider (1995) and Schnier et al. (1987).

## *Particle-size separation*

Differences between particle-size distribution as determined by ultrasonic dispersion and that by dispersion in 0.1 *M* NaOH (EMBRAPA 1979) were generally small (Table 3). However, the physical particle-size separation reduced the coarse sand content and increased the silt, while fine sand and clay remained comparable. In contrast, chemical dispersion probably does not

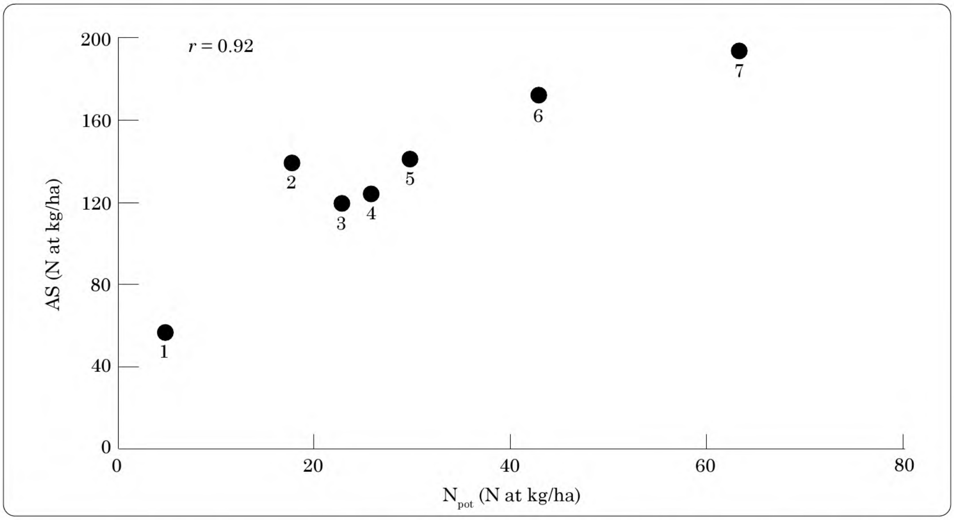

Figure 1. Correlation of amino sugars (AS) with potentially mineralizable N ($N_{pot}$) according to land use, Brazilian savannas. 1 = forest; 2 = continuous cropping with conventional tillage; 3 = native savanna; 4 = continuous cropping with no tillage; 5 = degraded pasture; 6 = improved pure-grass pasture; 7 = improved grass/legume pasture.

Table 3. Particle-size distributions (∅ in µm), according to land use after physical and chemical fractionation. Soil samples taken from Oxisols in the Brazilian savannas.

| Land use[a] | After ultrasonic dispersion | | | | | After NaOH dispersion | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 250-2000 (coarse sand) | 50-250 (medium-sized sand) | 20-50 (fine sand) | 2-20 (silt) | <2 (clay) | 250-2000 (coarse sand) | 20-250 (fine and medium-sized sand) | 2-20 (silt) | <2 (clay) |
| NS | 10 | 10 | 2 | 9 | 69 | 15 | 12 | 4 | 69 |
| F | 8 | 10 | 2 | 14 | 66 | 10 | 12 | 7 | 71 |
| DP | 5 | 8 | 2 | 9 | 76 | 10 | 10 | 9 | 71 |
| PG | 8 | 9 | 1 | 10 | 72 | 12 | 12 | 5 | 71 |
| GL | 8 | 9 | 2 | 11 | 70 | 13 | 13 | 7 | 67 |
| CCT | 2 | 5 | 1 | 6 | 86 | 5 | 16 | 22 | 57 |
| CCN | 3 | 5 | 1 | 5 | 86 | 4 | 13 | 19 | 64 |

a. NS = native savanna; F = forest; DP = degraded pasture; PG = improved pure-grass pasture; GL = improved grass/legume pasture; CCT = continuous cropping with conventional tillage; CCN = continuous cropping with no tillage.

completely destroy highly stable macroaggregates. After shaking with agate beads and sonication, the destroyed aggregates are redistributed into silt. The differences between chemical and physical separation of soil from Iraí de Minas substantiate this hypothesis: after ultrasonic dispersion, a notably higher clay content was obtained.

### *Soil organic constituents in particle-size separates*

Compared with bulk-soil samples, SOC contents in the particle-size separates were strongly depleted in the coarse and medium-sized sand fractions and highly enriched in the fine sand and silt fractions, while the clay fraction was comparable with the bulk soil (Table 4). The last finding is simply explained by the soils having a clay content of between 66% and 86%, so that the clay corresponded closely to the bulk soil. The distribution of SOC contents mostly indicates a strong similarity between the 50-250 and 250-2000-µm fractions on the one hand and the 2-20 and 20-50-µm fractions on the other. This is also visible in the comparable C/N ratios and indicates a similar degree of SOM decomposition. The higher amount of SOC in the coarse sand from the soils of Iraí de Minas is explained by the previously mentioned textural differences between the two study areas, where the coarse sand fraction from Iraí de Minas is lower than that from Uberlândia.

In all particle-size separates, SOC decreased more under forest than under native savanna. It also increased under pastures, reflecting the same trend as in the bulk soil, but the differences in the sand fractions were much clearer. The SOC levels in fine sand increased according to pasture system, being lowest under DP, higher under PG, and highest under GL. The CCN system showed higher SOC contents in the fine sand and silt fractions than did the CCT system. These results demonstrate very well that degraded pastures can be regenerated by establishing improved pasture systems and that the greatest changes occur in the POM fraction. The same is true for no-tillage systems. Similar results have been reported from soils of temperate regions (Holland and Coleman 1987; House et al. 1984; Lamb et al. 1985).

In all land-use systems, the C/N ratios clearly decreased from sand to clay, reflecting a progressive SOM decay (Table 4). The C/N ratio was again highest under forest in all particle-size separates. The GL had the lowest C/N ratio in the silt and fine sand fractions, probably because of the additional nitrogen obtained from fixation of atmospheric N.

Table 4. Soil organic carbon (SOC) and carbon-to-nitrogen (C/N) ratio in particle-size separates (∅ in µm) under different land uses in Oxisols of the Brazilian savannas.

| Land use[a] | SOC (mg/g) | | | | | C/N ratio[b] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 250-2000 (coarse sand) | 50-250 (medium-sized sand) | 20-50 (fine sand) | 2-20 (silt) | <2 (clay) | 250-2000 (coarse sand) | 50-250 (medium-sized sand) | 20-50 (fine sand) | 2-20 (silt) | <2 (clay) |
| NS | 7.9 | 7.6 | 63.1 | 60.0 | 24.7 | 56 | 69 | 33 | 23 | 18 |
| F | 5.9 | 4.7 | 41.0 | 46.5 | 21.3 | n.d. | n.d. | 48 | 33 | 20 |
| DP | 8.0 | 4.7 | 38.2 | 46.4 | 22.6 | 80 | 79 | 35 | 23 | 19 |
| PG | 9.0 | 7.8 | 64.9 | 50.1 | 25.2 | n.d. | 60 | 29 | 22 | 18 |
| GL | 9.7 | 8.9 | 74.9 | 52.6 | 27.5 | 54 | 41 | 24 | 19 | 17 |
| CCT | 14.8 | 4.6 | 58.3 | 76.8 | 21.6 | 26 | 51 | 29 | 24 | 16 |
| CCN | 12.1 | 1.7 | 80.2 | 92.4 | 21.1 | 28 | n.d. | 30 | 26 | 16 |

a. NS = savanna; F = forest; DP = degraded pasture; PG = improved pure-grass pasture; GL = improved grass/legume pasture; CCT = continuous cropping with conventional tillage; CCN = continuous cropping with no tillage.

b. n.d. = nitrogen was not detected.

The CPs decreased from coarse sand to clay (Table 5). This trend was observed in all land-use systems. The NCPs were also most abundant in coarse sand, decreasing in quantity from medium-sized sand, fine sand, to silt, and subsequently increasing again in clay. This shows that plant-derived sugars decrease with progressive litter decomposition and at the same time, microbial sugars are synthesized and accumulate in the clay (Guggenberger et al. 1994; Murayama 1988; Ziegler and Zech 1991).

In all particle-size separates, the CPs and NCPs declined under forest and increased under pasture. The CPs showed no clear differences between the three pastures, whereas the NCPs indicated a slight rise from DP over PG to GL, reflecting the increasing quality of SOM. Because sugars are easily decomposed, the improved pastures show an increasing SOM lability.

The total AS contents mostly increased from coarse sand to clay (Table 6). The distribution of AS was,

Table 5. Distribution (in mg/g C) of cellulosic polysaccharides (CPs) and noncellulosic polysaccharides (NCPs) according to particle-size separate (∅ in µm) and land use in Oxisols of the Brazilian savannas.

| Land use[a] | CPs | | | | | NCPs | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 250-2000 (coarse sand) | 50-250 (medium-sized sand) | 20-50 (fine sand) | 2-20 (silt) | <2 (clay) | 250-2000 (coarse sand) | 50-250 (medium-sized sand) | 20-50 (fine sand) | 2-20 (silt) | <2 (clay) |
| NS | 108 | 73 | 51 | 31 | 30 | 180 | 105 | 78 | 94 | 165 |
| F | 95 | 72 | 42 | 25 | 24 | 157 | 100 | 69 | 80 | 139 |
| DP | 133 | 88 | 68 | 39 | 34 | 265 | 164 | 131 | 147 | 187 |
| PG | 142 | 77 | 76 | 40 | 33 | 299 | 135 | 155 | 149 | 190 |
| GL | 142 | 79 | 79 | 45 | 31 | 292 | 163 | 166 | 162 | 191 |

a. NS = native savanna; F = forest; DP = degraded pasture; PG = improved pure-grass pasture; GL = improved grass/legume pasture.

Table 6. Distribution (in mg/g C) of amino sugars (sum of glucosamine galactosamine, mannosamine, and muramic acid) and the ratio of glucosamine to muramic acid (GlucN/Mur) according to particle-size separate (∅ in µm) and land use. Soil samples were from Oxisols of the Brazilian savannas.

| Land use[a] | Amino sugars | | | | GlucN/Mur ratio[b] | | | |
|---|---|---|---|---|---|---|---|---|
| | 50-2000 (medium to coarse sand) | 20-50 (fine sand) | 2-20 (silt) | <2 (clay) | 50-2000 (medium to coarse sand) | 20-50 (fine sand) | 2-20 (silt) | <2 (clay) |
| NS | 28 | 37 | 51 | 63 | n.d. | 60 | 15 | 5 |
| F | 19 | 19 | 33 | 50 | 21 | 30 | 9 | 6 |
| DP | 31 | 54 | 74 | 72 | 30 | 60 | 14 | 6 |
| PG | 33 | 54 | 76 | 78 | 43 | 71 | 16 | 7 |
| GL | 35 | 64 | 85 | 77 | 40 | 60 | 17 | 6 |
| CCT | 52 | 49 | 57 | 71 | n.d. | n.d. | 36 | 6 |
| CCN | 47 | 47 | 49 | 73 | n.d. | n.d. | 41 | 6 |

a. NS = native savanna; F = forest; DP = degraded pasture; PG = improved pure-grass pasture; GL = improved grass/legume pasture; CCT = continuous cropping with conventional tillage; CCN = continuous cropping with no tillage.

b. n.d. = muramic acid was not detected.

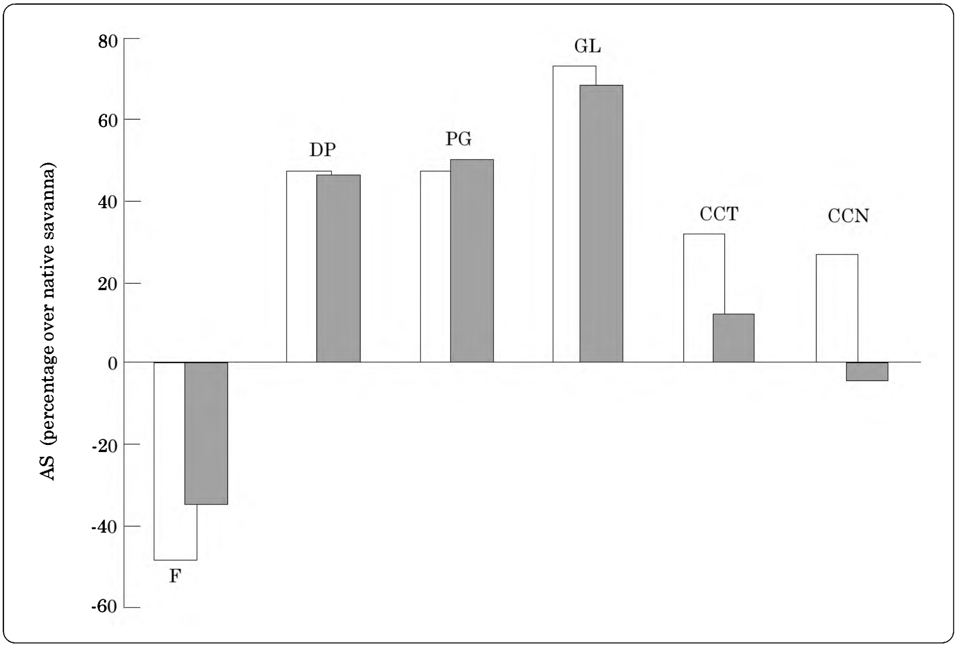

Figure 2. Percentages of amino sugars (AS) in the fine sand (☐ = 20-50 µm) and silt (■ = 2-20 µm) fractions according to land use, compared with native savanna control (0%), Brazilian savannas. F = forest; DP = degraded pasture; PG = improved pure-grass pasture; GL = improved grass/legume pasture; CCT = continuous cropping with conventional tillage; CCN = continuous cropping with no tillage.

however, different between the particle-size separates as indicated by the GlucN/Mur ratio. Glucosamine was enriched in fine sand, while the highest content of muramic acid was found in clay. Thus, the ratio of GlucN/Mur clearly increased from coarse and medium-sized sand to fine sand, and decreased again to clay. Chitin-derived glucosamine was probably enriched in the fine sand separate, because fungal hyphae are mostly associated with fine roots and >20-µm particles of decomposed plant litter (Amelung 1997; Tisdall and Oades 1982). Amino acids originating from bacteria such as muramic acid increased in the clay fraction, probably because their smaller size enables them to come in closer contact with clay particles than fungal hyphae. Dorioz et al. (1993) showed that aggregating effects of bacterial extracellular polysaccharides (ECPs) were restricted to the clay fraction, whereas fungal ECPs had greater influence on silt-sized aggregates. The muramic acid's carboxyl group, which binds strongly to the mineral phase, may also be a reason for enrichment with muramic acid (Kaiser 1996).

The effects of land use on AS were most evident in the fine sand and silt fractions, where AS were enriched under pastures and crops and reduced under pine (Table 6). In particular, AS were more enriched under GL than under DP or PG in the fine sand and silt fractions (Figure 2). Hence, the fixation of atmospheric N by the legume also results in greater microbial activity, confirming measurements of microbial activity with dimethyl sulfoxide (DMSO) and acid monophosphatase by Renz (1997).

Because microbial decomposition of SOM and subsequent recycling of nutrients are more limited by the supply of nitrogen than of carbon, the organic matter from GL can also be considered as more labile than SOM from the other pastures.

Land-use effects on the GlucN/Mur ratio were most apparent in the silt fraction (Table 6). The forest had the lowest, and both cropping systems the highest, GlucN/Mur ratios. Why fungal activity was highest under crops is not easily explained. Perhaps soil conditions under crops are more advantageous for fungi than for bacteria because more undecomposed litter is incorporated into the mineral soil (Beare et al. 1992).

## Conclusions

The results of this work show that particle-size separation is of great importance in determining short-term effects of land use on SOM. In addition, it is possible to determine the dynamics of sugars during litter decomposition and estimate the biomass of decomposer communities. The AS were shown to belong to the labile N pool, which is easily mineralized during growth.

All results show degraded pastures can be regenerated through improved pasture systems, especially when legumes are added, because SOM becomes more labile and thus increases microbial activity and nutrient recycling. For the cropping systems, 5 years of no-tillage cropping already show an enrichment of SOC in the silt fraction and an improved nitrogen supply in the bulk soil. No tillage can therefore reduce loss of SOM in Oxisols in the Brazilian savannas.

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## CHAPTER 10

# Carbon Fractions as Sensitive Indicators of Quality of Soil Organic Matter

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## Abstract

Soil organic matter quality is usually seen as a major attribute of soil quality. In this study, we extracted organic carbon with water (WEOC) or with potassium permanganate (PEOC). We assessed these extractions for their potential as sensitive indicators of the effect of land use on two important soil functions: biological activity and nutrient availability. Water-extractable organic carbon and PEOC were better correlated with C and N mineralization in the laboratory than were total and stable C, and were also more influenced by the mineralization flush that occurs at the beginning of the wet season. However, the more stable fraction also seemed to contribute to the pool of mineralizable C and N and was, within 5 years, significantly affected by changes in land use. Extraction of labile soil organic carbon with water and permanganate is an easy and valuable screening method for comparing the short-term effects of land-use systems on biological activity and nutrient availability in the soils of the Brazilian savannas.

*Keywords:* Available carbon, available nitrogen, mineralization, Oxisols, potassium permanganate, soil organic matter, water-extractable carbon

## Introduction

Soil organic matter (SOM) is a key attribute of soil quality (Boddey et al. 1997; Gregorich et al. 1994). Important soil functions influenced by SOM are nutrient storage, biological activity, and soil structure (Gregorich et al. 1994). Biological activity and nutrient storage are closely related with the mineralization and immobilization of nitrogen (N) and phosphorus (P) by the soil biomass. If the soil biomass is carbon (C) limited, the demand for energy, especially, will lead to a net mineralization of N. If available C is abundant, net immobilization of N will occur (Schimel 1986).

Water-extractable organic carbon (WEOC) has been proposed as an important source of carbon and energy for microbes (Burford and Bremner 1975; Cook and Allan 1992; McGill et al. 1986; Zsolnay and Görlitz 1994). On-farm research on pastures, cropping systems, and native savanna in the

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Brazilian savannas, also known as the *Cerrados*, showed that microbial activity and microbial biomass were highly correlated ($P < 0.0001$), with both total C and WEOC (TE Renz 1997, personal communication). However, Mazzarino et al. (1993) did not find any correlation between soil microbial biomass and WEOC, suggesting that factors other than available C were limiting the soil biomass.

Recently, oxidation of soil organic carbon (SOC) with potassium permanganate was used to separate total SOC into a labile fraction, extractable with permanganate, and a stable fraction that was not extractable (Blair et al. 1995; Lefroy et al. 1993; Loginow et al. 1987). These studies showed that the permanganate-extractable organic carbon fraction (PEOC) was more influenced by land use than were total and stable SOC. Permanganate-extractable N correlated better with N mineralization (Stanford and Smith 1978; Westerhof et al. 1999) and with N uptake by wheat (Hussain et al. 1984) and maize (Thicke et al. 1993) than did total N. The fact that N mineralization is controlled by C mineralization (McGill and Cole 1981) suggests that PEOC is, biologically, a more accessible fraction than total SOC. Water-extractable organic carbon and PEOC are relatively easy to measure and may be valuable as indicators of the effect of land use on nutrient storage and biological activity in soils.

The study attempted to evaluate the effect of time and contrasting land use on WEOC, PEOC, and total and stable SOC. The agronomic relevance of the parameters studied was examined by calculating the correlations of WEOC, PEOC, and total, stable, and nonextractable SOC with a biological index for N availability (Keeney 1982). To determine those nutrients that limit microbial activity in the various land-use systems studied, a laboratory experiment was also conducted to test the effects of adding N, P, or C on C mineralization.

## Materials and Methods

### *Site description*

The study area and its soil are described in Chapter 6, pages 65-66. The topsoils (0-10 cm) of the area contain between 55% and 62% clay, 10% and 12% silt, and 30% and 40% sand, as determined by the pipette method and chemical dispersion of aggregates with NaOH. Land-use systems studied were those described in Chapter 6, page 66. From 1991, when the project was started on native savanna, until the end of 1995, the total of fertilizer received was as follows:

| *Land-use system* | *Nutrient* | *Quantity (kg/ha)* |
|---|---|---|
| C F1 | N | 75 |
|  | P | 109 |
| C F2 | N and P | 150 and 218, respectively |
| PC F1 rotation | P | 39 at pasture establishment in 1991 |
|  | N and P | 40 and 22, respectively, in November 1995 when maize was planted |
| P F2 and PC F2 | P | 47 at establisment |
| PC F2 | N and P | 80 and 43, respectively, in November 1995 |

In May 1995, the legume-based pastures (PC F1 and PC F2) were plowed. In early November 1995, fertilizer was added and maize planted on all land-use systems, except P F2 and native savanna.

Soil samples were taken from the 0-10 cm layer in September 1995 (end of dry season), October 1995 (after the first rain in the rainy season), and in March 1996 (at the end of the growing season). On all sampling days, four samples, consisting of four subsamples, were taken with a soil auger. Soils were stored in plastic bags at 4 °C until they were sieved through a <2-mm mesh, air dried (40 °C), and sorted out for roots.

As described on page 66, exchangeable cations were determined on soils sampled in January 1996 by extraction with a $NH_4Cl$-$BaCl_2$ solution, following Amacher et al. (1990). This type of extraction gives similar results as does the $NH_4OAc$ extraction method for exchangeable bases and the KCl extraction method for exchangeable aluminum, but is quicker (Amacher et al. 1990).

### *Water-extractable organic carbon*

Five grams of air-dried soil were sieved through a <2-mm mesh and added to 100-mL PE bottles. Carbon was extracted with 12.5 mL of distilled water by end-over-end shaking for 30 min at room temperature. Extracts were centrifuged and filtered (through a <0.45-µm filter), and organic C in the extracts measured with a Shimadzu TOC-5050 analyzer.

### *Permanganate-extractable organic carbon and total soil organic carbon*

Two grams of air-dried soil were sieved through a <2-mm mesh into 100-mL PE bottles, containing about 50 mg C. Then, 75 mL of 333 m*M* potassium permanganate solution were added (Blair et al. 1995). The bottles were closed and shaken end-over-end in the dark for 1 h at room temperature. They were then centrifuged at 2000 rpm for 15 min and the potassium permanganate solution poured out. To clean the soil of remaining solution, the bottle was filled with water and centrifuged again. The water was poured out. This was repeated and, after the second washing, the soils were dried at 40 °C. Soil loss to washing and extraction was always less than 5% and mostly less than 2.5%. SOC before and after extraction was measured with an Elementar Vario EL element analyzer. Soil organic carbon in untreated soil is called total SOC (or $SOC_t$) and SOC remaining after extraction with potassium permanganate is called stable SOC (or $SOC_s$). The amount of PEOC was calculated as the difference between total and stable SOC.

### *Nitrogen mineralization potential*

The nitrogen mineralization potential was measured by Keeney's method (1982) for obtaining a biological index for N availability. Ten grams of air-dried soil, sieved through a <2-mm mesh, were put into glass containers, which were filled to the brim with water (about 30 mL), closed, and incubated for 1 week in the dark at 40 °C (Keeney 1982). The solution was then filtered through a Schleicher and Schuell white-band filter, rinsed with water, and diluted. Ammonium was measured colorimetrically. Water-extractable ammonium from unincubated soils was measured, following the same procedure, and the amount of ammonium produced calculated by difference. Potentially mineralizable nitrogen is called $N_{pot}$.

### *The effect of C, N, and P additions on carbon mineralization*

Samples (four replicates per nutrient addition) of native savanna, PC F2, and C F2 were taken in September and incubated in the laboratory. Two grams of air-dried soil were sieved through a <2-mm mesh and mixed with 6 g of sand (prewashed with acid and rinsed twice with distilled water) and 6 mL water or water-nutrient solution, following Keeney and Bremner (1967). Four blanks containing only sand were also incubated with water. The added solution contained no nutrients (i.e., water only); the equivalent of 50 or 100 kg N per hectare added as $KNO_3$; the equivalent of 50 or 100 kg P per hectare added as $K_2HPO_4$; and the equivalent of 3 and 6 mg C per gram of soil added as glucose. The amounts of N and P added represented the low and normal rates of application for N or P in agricultural systems found in the Brazilian *Cerrados*. The glucose additions are about 10% and 20% of total carbon in the soil studied. The soil-sand-water mixtures were incubated in the dark at 40 °C in closed bottles (120 mL). After 1, 3, 8, 15, 22, 37, and 53 days, samples were taken from the headspace of the bottle through a rubber septum in the lid. $CO_2$ was analyzed. After 22 days, the bottles were aerated to prevent oxygen limitation.

### *Statistical analyses*

The effects of land use and time of sampling on C fractions were tested, using analysis of variance for a randomized complete block design (Little and Hill 1978). To analyze the effect of land use on C fractions, all sampling dates were used. Where the analyses showed significance at the $P < 0.05$ level, Duncan's multiple range test was used to separate land-use systems (Little and Hill 1978). Differences between sampling dates could also occur because of spatial variability rather than because of a "real" effect of time. We assumed that spatial variability becomes negligible with a large number of samples, which is why we discuss the temporal dynamics of C fractions for the whole experiment only and not for individual land-use systems. Correlation coefficients of C fractions with $N_{pot}$ were calculated, using the average values per land-use system per sampling date (6 land-use systems, 3 sampling times; n = 18, 16 degrees of freedom).

## Results

### *Exchangeable cations and aluminum*

Exchangeable bases were 1.16-1.78 $cmol_c$/kg soil in the F2 treatments and 0.56-0.77 $cmol_c$/kg soil in the F1 treatments. Exchangeable Al was 0.02-0.09 and 0.20-0.21 $cmol_c$/kg soil for F2 and F1, respectively. Both the F1 and F2 treatments had higher amounts of exchangeable Ca and Mg, higher pH, and lower amount of exchangeable Al than did native savanna, mainly because of the lime addition (F1 = Mg at 3.4 kg/ha; F2 = Mg at 5.8 kg/ha at establishment in 1991). Native savanna had 0.37 $cmol_c$/kg soil of exchangeable Al, 0.10 $cmol_c$/kg soil of exchangeable bases, and a $pH_{H_2O}$ of 4.78. All treatments were characterized by a low cation-exchange capacity and low amounts of exchangeable bases. However, phosphorus was a limiting nutrient for plant growth, as was shown by clear visual signs of P deficiency in maize throughout the growing season and a significant correlation of crop yields with available P.

### *The effect of C, N, and P additions on carbon mineralization*

After 53 days, incubated soils that had not received nutrients had mineralized C at a rate 0.51-0.66 mg/g soil, which is about 2% of total SOC (Figure 1). The legume-based pasture had clearly higher C mineralization, compared with the cropped field (0.65-0.66 mg/g soil versus 0.53-0.57 mg/g soil). In the same period, native savanna had the lowest C respiration (0.41-0.45 mg/g soil).

Carbon mineralization in treatments that received N at the equivalent of 100 kg/ha was 81%-88% of that of the soils that were incubated without nutrient additions. Adding P at the equivalent of 100 kg/ha increased C respiration to 130%-152%, and adding C at 6 mg/g soil led to a 235%-285% higher rate of C mineralization, compared with soils having no nutrient additions. However, only about 25% of the glucose-C added was respired within 53 days. The treatments that received N or P at the equivalent rates of 50 kg/ha and additions of C at 3 mg/g soil were always intermediate between "no nutrient additions" and the higher additions. These treatments are therefore not discussed here.

### *The relation of soil organic carbon fractions with N availability and biological activity*

The correlation coefficients of WEOC ($r = 0.79$) and PEOC ($r = 0.72$) with $N_{pot}$

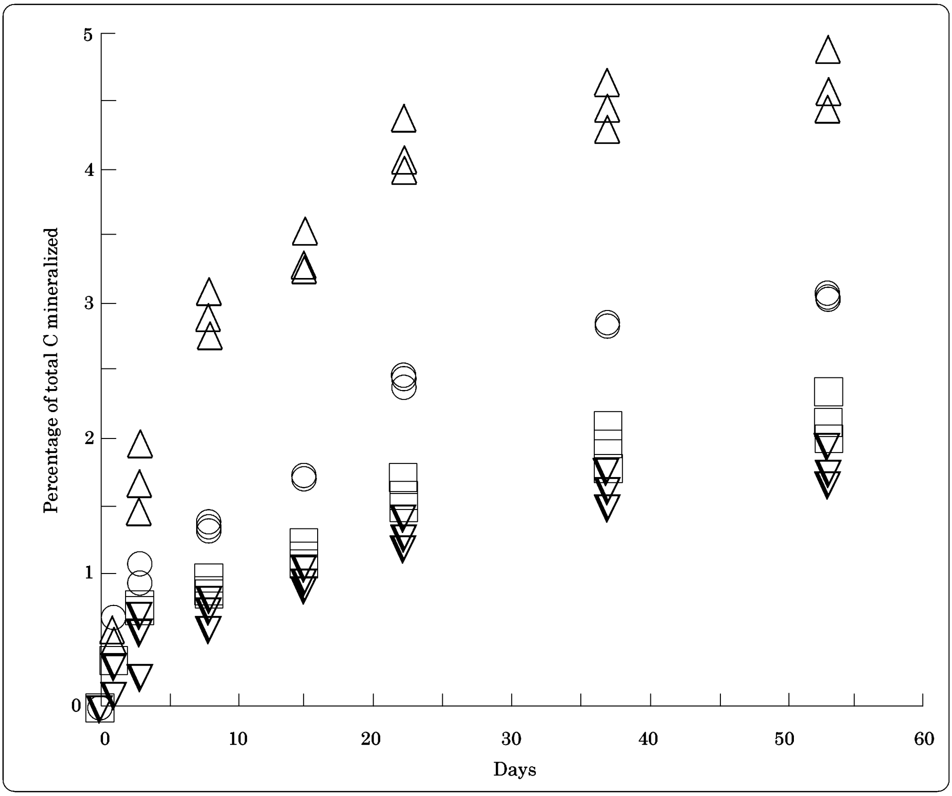

Figure 1. The effect of C, N, and P additions on the mineralization of soil organic matter in an Oxisol of the Brazilian savannas. Points are averaged values per land-use system (n = 4); ++P (○) = 100 kg/ha P; ++N (∇) = 100 kg/ha N; ++C (△) = 6 mg glucose-C per gram of soil; □ = no additions. See text for differences in mineralization between land-use systems.

were highly significant ($P < 0.001$). Stable SOC ($r = 0.55$; $P < 0.05$) and total SOC ($r = 0.70$; $P < 0.01$) had lower, but still significant, correlations with $N_{pot}$ (Figure 2).

Averaged over September, October, and March, the pasture-based systems (P F2, PC F1, and PC F2) had significantly ($P < 0.05$) higher total SOC and PEOC than did continuous crops (C F1 and C F2) and native savanna (Table 1). Furthermore, P F2 and PC F1 had higher stable SOC levels than did the other treatments. The C F2 system had the lowest total and stable SOC levels of all treatments studied. Water-extractable organic carbon was not significantly different between land-use systems. The differences in stable SOC among pasture-based systems (P F2 and PC F1 were higher than PC F2) was caused by differences in pasture quality. The P F2 and PC F1 systems had higher amounts of *Stylosanthes* than PC F2, which indicates that, in well-established pastures, legumes can lead to increases in both PEOC and the more stable SOC.

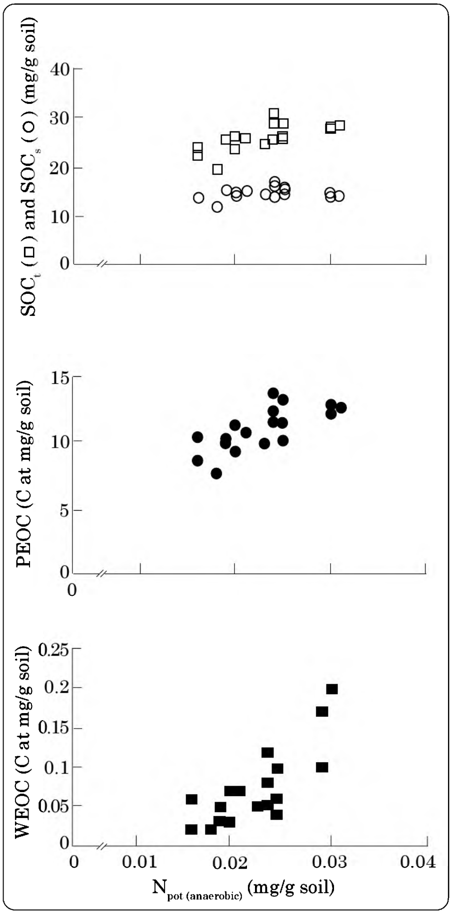

Figure 2. Scatter plot showing correlations of total soil organic carbon ($SOC_t$), not-extractable SOC ($SOC_s$), permanganate-extractable SOC (PEOC), and water-extractable SOC (WEOC) with potentially mineralizable nitrogen ($N_{pot}$). Soil samples were taken from an Oxisol of the Brazilian savannas.

Averaged over all land-use systems, total SOC decreased significantly from September to October (Table 2). On the average, 12% of total SOC in September was lost in October, ranging from 8% (PC F1) to 23% (C F2). Water-extractable organic carbon and PEOC were most influenced by time of sampling; WEOC decreased by 77% and PEOC by 23% between September and October. The decrease in WEOC and PEOC accounted for 3% and 81% of the total decrease in SOC, respectively. Stable SOC did not change significantly in this period but still accounted for about 20% of the decrease in total SOC. From October to March, the fractions returned to about the values they had in September.

## Discussion

The available C controlled microbial activity in the incubation experiment. Water content was optimal for microbial activity by mixing samples with sand, according to Keeney and Bremner's method (1967). However, when incubated soils are subjected to various wetting and drying cycles, more C is lost than when the soil

Table 1. The effect of contrasting land use on water-extractable (WEOC) and potassium permanganate-extractable (PEOC), soil organic carbon (SOC), and total and not-extractable (stable) SOC. Values are averaged from samples taken in September, October, and March from an Oxisol in the Brazilian savannas.[a]

| SOC fraction from land use[b] | Total SOC | Stable SOC (C at mg/g soil) | PEOC | WEOC |
|---|---|---|---|---|
| P F2 | 28.3 a | 16.2 a | 12.1 a | 0.07 a |
| C F1 | 24.8 bc | 14.6 c | 10.2 b | 0.06 a |
| C F2 | 23.2 c | 13.3 d | 9.9 b | 0.07 a |
| PC F1 | 28.0 a | 16.2 a | 11.8 a | 0.10 a |
| PC F2 | 27.2 a | 15.2 b | 12.1 a | 0.09 a |
| Native savanna | 25.2 b | 15.0 bc | 10.5 b | 0.06 a |

a. Values in the same column with the same letter are not significantly different (Duncan's multiple range test, $P < 0.05$).

b. P F2 = continuous legume-based pasture with conventional applications of fertilizer;
C F1 = continuous cropping system with a rotation of soybean and maize and low rates of fertilizer applications;
C F2 = continuous cropping system with a rotation of soybean and maize and conventional rates of fertilizer applications;
PC F1 = legume-based pasture/crop rotations with low rates of fertilizer applications;
PC F2 = legume-based pasture/crop rotations with conventional rates of fertilizer applications.

Table 2. The effect of time on water-extractable (WEOC) and potassium permanganate-extractable (PEOC), soil organic carbon (SOC), and total and not-extractable (stable) SOC. Values are averaged from all land-use systems studied on an Oxisol of the Brazilian savannas.[a]

| SOC fraction sampling date | Total SOC | Stable SOC (C at mg/g soil) | PEOC | WEOC |
|---|---|---|---|---|
| September 1995 | 27.2 a | 15.2 a | 12.0 a | 0.13 a |
| October 1995 | 23.9 b | 14.5 a | 9.3 b | 0.03 c |
| March 1996 | 27.5 a | 15.5 a | 12.0 a | 0.06 b |

a. Values in the same column with the same letter are not significantly different (Duncan's multiple range test, $P < 0.05$).

moisture is kept constant (Sørensen 1974; Soulides and Allison 1961). This explains why, in our incubation study, only 2%-5% of the total SOC was lost. By contrast, in the field where the soil experienced various wetting and drying cycles from the combined action of sun and rain, about 12% of SOC was lost in about 3 weeks.

Additions of P influenced microbial activity much less. This was also shown by the lower C mineralization of the cropped field (C F2), compared with the pasture/crop rotation (PC F2). The C F2 system had more available P (Olsen-$P_i$ = 7 mg/kg soil) and lower available C, compared with P F2 (Olsen-$P_i$ = 4 mg/kg soil). Adding mineral N frequently decreased C mineralization, probably because mineral N inhibited the action of ligninases (Fog 1988).

The importance of carbon availability for N mineralization is evident from the high correlations of easily accessible carbon fractions (WEOC and PEOC) with potentially mineralizable N. Apparently, labile SOM fractions also contained considerable amounts of N.

Carbon-to-nitrogen ratios were comparable: between 16 and 17 for all land-use systems studied. The PEOC and stable SOC differed slightly in the C/N ratio: 15.6-16.7 for the stable and 16.8-18.6 for the PEOC fraction. Guggenberger et al. (1995) also reported narrower C/N ratios for stable SOM fractions, compared with more labile fractions for a Colombian savanna soil. Probably, the stable fraction is more decomposed (Guggenberger et al. 1995). No consistent effect of land use on the C/N ratio was found.

Total SOC had a lower correlation with potentially mineralizable N than had either WEOC or PEOC. The stable, non-extractable SOC fraction had the lowest correlation. It is interesting to note that the more resistant a fraction becomes to chemical extraction, the less important it becomes for N availability. Similar results were found when the amounts of C mineralized from the samples with "no nutrient additions" in the incubation experiment were correlated with WEOC, PEOC, and total and stable SOC. Labile carbon fractions were better correlated with both microbial activity than were stable and total SOC. These results stress again the strong interaction between C mineralization and N availability (McGill and Cole 1981; Schimel 1986).

Five years of differing land use led to significantly lower amounts of carbon in all fractions—except the WEOC—in the cropped systems than in the pasture and pasture/crop rotations (4 years pasture, 1 year crop). Native savanna had intermediate values. The ratio of PEOC to stable carbon was comparable for all land-use systems—about 0.75—indicating that PEOC and stable SOC changed at the same rate and that the lability of the SOC was not changed (Blair et al. 1995).

Extractable carbon fractions showed high seasonal variability. For WEOC, this high variability masked significant differences between land-use systems. The high net mineralization that occurred between September and October was caused by the start of the rainy season shortly after sampling in September. The ratio of PEOC to stable SOC decreased from September (0.75) to October (0.64) for all land-use systems, indicating that the lability of the remaining SOC decreased in this period (Blair et al. 1995). Rewetting dry soils by rain or in the laboratory always caused a mineralization flush (Birch 1958; Orchard and Cook 1983; Van Gestel et al. 1993). The increase in all SOC fractions from October to March might be caused by an increase in soil biomass, and light fraction caused by input of plant biomass and root and microbial exudates. In a 12-week incubation, soil biomass provided 15%-25% of the net increase in mineral N, which shows that labile SOM fractions consist only partly of microbial biomass (Juma and Paul 1984).

In this study, we showed that WEOC and PEOC correlated better with C and N mineralization in the laboratory than did total and stable C, and are also more influenced by mineralization processes in the field. However, the more stable fractions also seemed to contribute to the pool of mineralizable C and N and were significantly affected by changes in land use within a period of 5 years. Extraction of labile SOC with water and permanganate is an easy and valuable screening method for comparing the short-term effects of land-use systems on two important soil functions: biological activity and nutrient availability.

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# CHAPTER 11

# Labile N and the Nitrogen Management Index of Oxisols in the Brazilian *Cerrados*[1]

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## Abstract

The effect of land use on the availability of soil nitrogen (N) was studied by separating total soil N into one labile and one stable fraction by oxidation and extraction of labile N with potassium permanganate. The nitrogen management index (NMI) was calculated according to Blair et al. (1995) for the carbon management index. In all systems, labile N released by potassium permanganate was a better indicator for nitrogen availability than were total and stable N. The NMI was a good indicator for N availability but gave no information on the total amount of N. In land-use system analysis, total N and labile N can be used together as a simple and rapid way to evaluate the nitrogen status of the soil. Legume-based pastures specifically increased the amount of labile N. Although soybeans had a dominant role in the continuous cropping systems studied, total N contents decreased, compared with native savanna. The availability of N under legume-based pastures and legume-based pasture/crop rotations was higher than under native savanna and continuous cropping systems.

*Keywords:* Brazilian savannas, *Cerrados*, land use, mineralization, nitrogen, nitrogen availability, nitrogen management index, Oxisol, potassium permanganate nitrogen

## Introduction

Available nitrogen (N) can be defined as N found in the rhizosphere and in chemical forms that can be readily absorbed by roots (Scarsbrook 1965). The most important forms of N for plant uptake are ammonium and nitrate (Tisdale et al. 1993). To efficiently use fertilizer N, the amount of N that becomes available through mineralization must be predicted, hence the development of various nitrogen availability indices (Keeney 1982). Recommended nitrogen availability indices are ammonium production under anaerobic incubation in the laboratory, and ammonium released after autoclaving or boiling in dilute calcium chloride solution (Appel and Mengel 1990; Houba et al. 1995; Keeney 1982).

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Another promising and relatively easily measured chemical index for N availability is the amount of N released through oxidation and extraction by permanganate acid (Stanford and Smith 1978). Nitrogen released on oxidation and extraction of soil organic matter (SOM) with permanganate acid was correlated with potential N mineralization (aerobic incubation; Stanford and Smith 1978), and N uptake by wheat (Hussain et al. 1984) and maize (Thicke et al. 1993).

Recently, oxidation of soil organic carbon (SOC) with potassium permanganate was used to separate SOC into (1) a labile fraction that was strongly influenced by land use, and (2) a stable fraction that was less influenced (Lefroy et al. 1993; Loginow et al. 1987). Blair et al. (1995) used the lability of SOC, obtained from the susceptibility of SOC to oxidation with potassium permanganate, to calculate a carbon management index (CMI) for agricultural systems. The CMI is more sensitive to land-use changes than are total SOC contents.

Nitrogen released on oxidation and extraction with potassium permanganate probably represents labile N, whereas the fraction that remains unaffected can be thought of as the "more stable N". Following the calculations of Blair et al. (1995) for the CMI, a nitrogen management index (NMI) can be calculated.

This study tested whether the NMI is a useful parameter to monitor differences in N availability caused by differences in land use in the Brazilian savannas, also known as the *Cerrados.* A legume-based pasture, continuous cropped fields, pasture/crop rotations, and native savanna were compared with respect to inorganic N; potentially mineralizable N, as estimated by anaerobic incubation in the laboratory; and labile and stable N fractions, as separated by oxidation and extraction with potassium permanganate. The correlation of labile N, stable N, total N, and the NMI with potentially mineralizable N was also studied.

## Materials and Methods

### *Site description*

The research site and its characteristics are described in Chapter 6, pages 65-66, together with the land-use systems studied. The fertilization regimes, soil sampling methods, and the techniques for determining exchangeable cations are described in Chapter 10, pages 124-125. Total C and total N, before and after extraction, were measured with an Elementar Vario EL CHNS analyzer. Some selected chemical properties of the land-use systems studied are listed in Table 1.

### *Extraction of nitrogen fractions*

To extract N fractions, the same extraction method for PEOC and total SOC was used, as described in Chapter 10, page 125. Nitrogen in the untreated soil is called total N ($N_t$), and N remaining after extraction with potassium permanganate is called stable N ($N_s$). Nitrogen released on oxidation with potassium permanganate was calculated by the difference between $N_t$ and $N_s$, and is called permanganate-extractable N (PEN). Potentially mineralizable nitrogen ($N_{pot}$) was measured as described on page 125 in Chapter 10. Inorganic nitrogen ($N_i$) in the 0-40 cm layer was estimated as the sum of ammonium and nitrate extracted with KCl (1 *M* soil to water at 1:10) from field-fresh soil samples taken on 16 January 1996. Ammonium and nitrate were analyzed, using steam distillation (Keeney and Nelson 1982).

Table 1. Selected chemical properties of topsoils (0-10 cm) under different land-use systems studied on an Oxisol in the Brazilian savannas. (Soil samples taken in January 1996.)

| Land use[a] | pH ($H_2O$) | C (g/kg) | N (g/kg) | C/N ratio | Exchangeable cations ($\text{cmol}_c$/kg soil) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Mg | Ca | K | Al |
| P F2 | 5.6 | 29.6 | 1.7 | 17.1 | 0.45 | 1.26 | 0.05 | 0.02 |
| C F1 | 5.1 | 25.0 | 1.5 | 16.7 | 0.08 | 0.46 | 0.03 | 0.21 |
| C F2 | 5.4 | 23.1 | 1.5 | 15.4 | 0.17 | 0.95 | 0.04 | 0.08 |
| PC F1 | 5.4 | 25.2 | 1.6 | 16.1 | 0.10 | 0.68 | 0.04 | 0.19 |
| PC F2 | 5.6 | 27.4 | 1.6 | 16.8 | 0.21 | 1.45 | 0.04 | 0.03 |
| Native savanna | 4.8 | 25.0 | 1.5 | 16.4 | 0.01 | 0.04 | 0.05 | 0.37 |

a. P F2 = continuous legume-based pasture with conventional applications of fertilizer;
C F1 = continuous cropping system with a rotation of soybean and maize and low rates of fertilizer applications;
C F2 = continuous cropping system with a rotation of soybean and maize and conventional rates of fertilizer applications;
PC F1 = legume-based pasture/crop rotations with low rates of fertilizer applications;
PC F2 = legume-based pasture/crop rotations with conventional rates of fertilizer applications.

### *Statistical analyses*

The effects of land use and time of sampling on $N_t$, $N_s$, PEN, and $N_{pot}$ were studied, using analysis of variance for a randomized complete block design, with time of sampling and land use as the factors that explained variability (Little and Hill 1978). Per sampling date, the averaged values over the four subplots per land-use system were used (three sampling dates and six land-use systems, *df* = 18 for the whole experiment). If the analysis gave a significant effect of time of sampling on N fractions, additional tests were done to separate sampling times (Duncan's multiple range test; Little and Hill 1978). Differences between sampling dates could also occur because of spatial variability rather than because of a "real" effect of time. We assumed that spatial variability becomes negligible with a large number of samples, which is why we discuss the temporal dynamics of soil quality for the whole experiment and not for the individual land-use systems.

The land-use systems were divided in four subplots, but were not replicated in the strict meaning of the word. No additional statistical tests were therefore possible for studying the effect of land use on soil quality. To make comparisons between land-use systems possible, 95% confidence limits (Little and Hill 1978) were calculated for every land-use system, using the subplot samples for all sampling dates (4 subplots x 3 sampling dates = 12 measurements). In addition, because several different pastures, rotations, and cropped fields were studied, we could make some general conclusions about the effects of pastures and crops on soil quality.

Correlation coefficients of N fractions with $N_{pot}$ were calculated, using the average values per land-use system per sampling date (6 land-use systems, 3 sampling dates; n = 18, 16 degrees of freedom; Little and Hill 1978).

## Results and Discussion

### *Effect of land use on N fractions*

Five years of land use had a significant ($P < 0.10$) effect on $N_t$ contents in the topsoils of the land-use systems studied. The treatments P F2 and PC F1 had higher, PC F2 and C F1 comparable, and C F2 lower $N_t$, compared with native savanna (Table 2). It is remarkable that the addition of 150 kg/ha fertilizer N in 5 years on C F2 could not prevent the decrease in $N_t$, although soybeans (N-fixing) played an important role in the rotation. In 1991, 1992, and 1994, soybeans were planted and, in 1993 and 1995, maize. Stable N values decreased in the order P F2 > C F1 > native savanna > PC F1 > PC F2 > C F2 (Table 2). No significant effect of land use on $N_s$ and PEN could be seen. Permanganate-extractable N was higher in P F2, PC F1, and PC F2 than in C F1 and C F2. Native savanna had an intermediate value, indicating that continuous cropping depleted the PEN fraction and that the legume-based pastures enriched the soil in PEN. The increase in labile N was also shown by higher $N_{pot}$ under P F2, PC F1, and PC F2, compared with native savanna, C F1, and C F2 (Table 2).

Inorganic nitrogen contents under all cropping systems were relatively high on 16 January 1996: C F1 had 13, C F2 had 16, PC F1 had 65, and PC F2 had 27 kg/ha of $N_i$ in the 0-40 cm layer. In terms of productivity, in this experiment, between 50 and 100 kg/ha N was taken up annually (Büll 1993), indicating that nitrogen was abundant and probably did not limit crop yield.

Results for the P F2 and PC F2 treatments, legume-based pastures that received similar treatment before PC F2 was plowed in May 1995, showed P F2 with higher and PC F2 with lower $N_s$, compared with native savanna (Table 2). In December 1994, when the PC rotations were still in the pasture phase, differences between all the pastures were also reflected in the aboveground biomass: 4662 kg/ha for P F2, with 9.3% legumes; 4031 kg/ha for PC F2, with 5.0% legumes; and 3884 kg/ha for PC F1, with 63% legumes. These data reflect a variability in pasture quality in our experiment, which limits the possibility of drawing general conclusions on the effect of legume-based pastures on N fractions. However, it seems safe to conclude that a well-established legume-based pasture leads to an increase in, especially, PEN and $N_{pot}$, but may lead to higher $N_s$ levels as well.

### Effect of time of sampling on N fractions

Soil density changed with time and, to eliminate this influence, averaged densities were used. Differences in density between land-use systems were small and differences in N content

Table 2. Effects of land use on total N ($N_t$), permanganate-extractable N (PEN), stable N ($N_s$), and potentially mineralizable N ($N_{pot}$). Soil samples were taken from an Oxisol of the Brazilian savannas.[a] All N fractions are measured in kilos per hectare.

| Land use[b] | $N_t$ | $N_s$ | PEN | $N_{pot}$ |
|---|---|---|---|---|
| P F2 | 1673 ± 159 | 974 ± 57 | 699 ± 64 | 24 ± 3 |
| C F1 | 1518 ± 107 | 949 ± 55 | 569 ± 38 | 20 ± 2 |
| C F2 | 1450 ± 149 | 856 ± 41 | 594 ± 49 | 19 ± 2 |
| PC F1 | 1604 ± 85 | 934 ± 25 | 670 ± 41 | 26 ± 2 |
| PC F2 | 1537 ± 108 | 873 ± 33 | 664 ± 36 | 25 ± 2 |
| Native savanna | 1567 ± 99 | 941 ± 53 | 626 ± 38 | 21 ± 1 |

a. Confidence limits (95%).
b. See Table 1 for explanation of codes used.

discussed earlier were due to differences in N content per gram of soil rather than differences in soil density. Time of sampling had significant effects ($P < 0.05$) on all N fractions investigated except $N_s$ (Table 3). The decrease of $N_t$ that occurs under all land-use systems between September and October was probably caused by the mineralization flush that usually follows when dry soils are rewetted (Birch 1958; Orchard and Cook 1983; Sørensen 1974; Van Gestel et al. 1993). Sánchez (1976) stated that, in tropical regions, 23-121 kg/ha N could be mineralized in the first few weeks after the first rainfall. On the average, in this study, 164 kg/ha N was mineralized and lost from the 0-10 layer through leaching or denitrification. At this time, maize had not yet been planted, so the soil was bare and plant uptake played a role only on native savanna and P F2. The treatment PC F1 showed the lowest (67 kg/ha) and PC F2 the highest (and an extremely high) decrease (374 kg/ha).

The existence of an easily mineralizable pool at the end of the dry period is indicated by a high average $N_{pot}$ value in September. Averaged over all land-use systems, over 80% of the decrease in $N_t$ from September to October was attributable to the decrease in the PEN fraction, indicating that this fraction is more susceptible to biological oxidation than $N_s$. The significant increase of $N_t$ and PEN from October to March indicates an incorporation of surplus fertilizer N in organic fractions. Strangely, $N_{pot}$ does not increase significantly.

Table 3. The effect of time of sampling on total N ($N_t$), permanganate-extractable N (PEN), stable N ($N_s$), and potentially mineralizable N ($N_{pot}$). Soil samples were taken from an Oxisol in the Brazilian savannas.[a] All N fractions are measured in kilos per hectare.

| Sampling date | $N_t$ | $N_s$ | PEN | $N_{pot}$ |
|---|---|---|---|---|
| September 1995 | 1605 a | 912 ns | 693 a | 27 a |
| October 1995 | 1442 b | 883 ns | 559 b | 20 b |
| March 1996 | 1627 a | 968 ns | 659 a | 21 b |
| Average | 1558 | 921 | 637 | 23 |

a. Values in the same column with the same letter are not significantly different (Duncan's multiple range test, $P < 0.05$); ns = not significant.

## Nitrogen fractions as indicators for potentially mineralizable N

The PEN is positively and highly significantly correlated with $N_{pot}$ ($r = 0.73$, $P < 0.01$), whereas $N_t$ ($r = 0.54$, $P < 0.05$) and $N_s$ ($r = 0.10$) show a lower or no correlation with $N_{pot}$ (Figure 1). This confirms that PEN may be used as an index for $N_{pot}$ in Oxisols in the Brazilian savannas. Similar results for other soils (Hussain et al. 1984; Stanford and Smith 1978; Thicke et al. 1993) indicate that the PEN fraction is a suitable indicator for N availability in a wide range of soil types.

## Nitrogen management index as an indicator for potentially mineralizable N

The NMIs of P F2, PC F1, PC F2, C F1, and C F2 were calculated in a manner similar to the CMI (Blair et al. 1995), using native savanna as reference (equations 1 to 4).

Nitrogen pool index (NPI) $= N_{t\ sample} * N_{t\ cerrados}^{-1}$ [1]

Lability of N (LN) $= N_{labile} * N_s^{-1}$ [2]

Lability index (LI) $= LN_{sample} * LN_{cerrados}^{-1}$ [3]

Nitrogen management index (NMI) $= NPI * LI * 100$ [4]

Native savanna, used as reference, always has a value of 100. Values below 100 indicate a degrading system

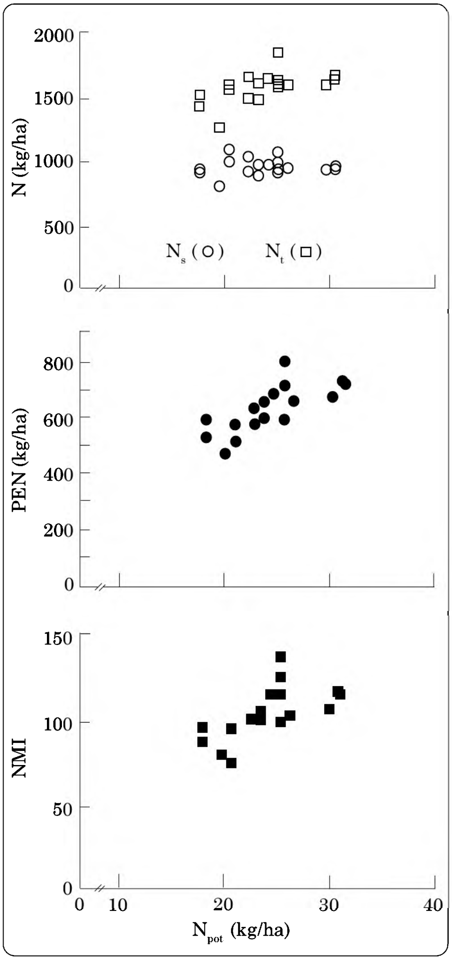

Figure 1. Scatter plot showing correlations of potentially mineralizable N ($N_{pot}$), as measured in the laboratory, with total N ($N_t$), permanganate-extractable N (PEN), and stable N ($N_s$) fractions and the nitrogen management index (NMI). Soil samples were taken from an Oxisol of the Brazilian savannas.

with respect to N, and values above 100 indicate improving systems. The NMI of the land-use systems studied decreased in the order P F2 (115) > PC F2 (112) > PC F1 (110) > native savanna (100) > C F2 (96) > C F1 (88).

The NMI correlates better with $N_{pot}$ than with $N_t$ and $N_s$, but not as well as with PEN ($r = 0.68$, $P < 0.01$, Figure 1). A high (>100) NMI does not necessarily mean a higher $N_t$ or PEN (e.g., compare $N_t$, PEN, and NMI for PC F2 with $N_t$, PEN, and NMI for native savanna), compared with native savanna, but instead a higher lability (LN, eq. 2) than for native savanna. The use of the NMI leads to a loss of information about the total amount of N in a system. Furthermore, it might be difficult to find an undisturbed natural system that can be used as a reference. This complicates the use of the NMI as a single parameter for nitrogen in land-use system evaluation studies. By contrast, total nitrogen and labile nitrogen extracted with potassium permanganate represent a simple and rapid way of evaluating the soil's N status.

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# CHAPTER 12

# Characterizing Labile and Stable Nitrogen

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## Abstract

The permanganate oxidation procedure is easily performed and may help monitor large areas for their soil organic matter (SOM) quality and nitrogen (N) availability. Knowledge of the chemical characteristics of fractions that are lost or remain after oxidation will help explain results obtained by this method. We found that amino acid N contributed 22.7% to the permanganate-extractable N fraction (PEN) and amino sugar N 9.1%, but the remaining 68.2% of the PEN was of "unknown" N. Stable N had lower amounts of amino acid N (15.5%) and amino sugar N (6.2%). Permanganate-extractable N and stable N may be spatially separated, that is, PEN is found outside microaggregates, whereas stable N is inside, where it is protected from permanganate extraction and probably also from microbial breakdown. Together with physically protected N, the stable N fraction also contained an important amount of chemically recalcitrant, not-extractable, "unknown" N with a chemical composition that is hypothesized to be different from that of the permanganate-extractable "unknown" N.

*Keywords:* Land use, mineralization, nitrogen, nitrogen availability, Oxisols

## Introduction

Nitrogen released after oxidation with permanganate has been correlated with potential nitrogen (N) mineralization (Stanford and Smith 1978; Westerhof et al. 1998) and N uptake by weeds (Hussain et al. 1984) and maize (Thicke et al. 1993). Furthermore, permanganate-extractable soil organic carbon (SOC) was more influenced by land use and seasonal mineralization-immobilization processes than were total and stable, not-extractable, SOC fractions (Blair et al. 1995; Lefroy et al. 1993; Loginow et al. 1987; Westerhof et al. 1998). The permanganate oxidation procedure is easily performed and may help monitor large areas for their SOM quality and N availability.

Chemical extractions of available N usually try to mimic the action of biological enzymes in the soil but not much is known about the source and nature of the N compounds that are released this way (Juma and Paul 1984).

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Chemical characterization of easily mineralizable N led to the conclusion that this fraction consists predominantly of amino acid N and amino sugar N (Hayashi and Harada 1969; Mengel 1996; Van Gestel et al. 1993). It was also shown that fertilizer N was rapidly immobilized (within 7 days) into microbial biomass when glucose was added and that this newly formed "active" SOM was enriched in amino acid N, compared with native humus (Kelley and Stevenson 1985).

However, only 15%-25% of the net N mineralization during a 12-week incubation was derived from soil biomass (Juma and Paul 1984) and only a small proportion of N extracted by permanganate originated from soil biomass (Juma and Paul 1984; Kelley and Stevenson 1985). Neither long-term cropping nor the addition of organic amendments to the soil greatly affected the relative distribution of the various forms of N, although Stevenson (1982) showed that the proportion of amino acid N decreased with cultivation. Thus, amino sugar N and amino acid N can be regarded as among the most biologically labile N fractions.

Because permanganate extracts that fraction of soil N that is susceptible to biological mineralization (Stanford and Smith 1978), the PEN may contain a considerable amount of amino sugar N and amino acid N. Knowledge of the chemical characteristics of the fraction that is lost on oxidation will help explain results obtained by this method.

This study chemically characterizes N fractions, separated by extraction with permanganate, from soil samples taken from different land-use systems on an Oxisol in the Brazilian savannas.

## Materials and Methods

The research site and soil sampling are described in Chapter 6, pages 65-66, and Chapter 10, pages 124-125. For each composite sample, four replicates (visible roots sorted out by hand) were treated with permanganate (333 m*M*; Blair et al. 1995, as modified by Westerhof et al. 1998). Then, four untreated replicates per treatment and all treated soil samples were finely ground and analyzed for total N with an Elementar Vario EL element analyzer. Nitrogen in the samples was recalculated to kg/ha in the 0-10 cm soil layer. Nitrogen in the untreated samples was called total N and N still present after oxidation with permanganate was called stable N. The PEN was lost in the extraction and its amount calculated as the difference between total and stable N. Standard deviations of measurements for total and stable N were 5%.

Half a gram each of untreated and treated samples was finely ground and put in small, air-tight, hydrolysis flasks. We then added 1.5 mL of 6 *N* HCl. Hydrolysis of nitrogenous constituents was done at 105 °C for 12 h, and $NH_3$-N, amino acid N, and amino sugar N were determined in the hydrolysate, using steam distillation (Stevenson 1982). Standard deviations of a complete measurement (n = 4), including permanganate extraction, acid hydrolyses, and N fractionation, were 8% ($NH_3$-N), 27% (amino sugar N), and 13% (amino N) for total and stable N. The unknown N fraction was calculated as the difference between total N as determined by dry combustion and the sum of the identified fractions. Although Stevenson (1982) made a distinction between unknown acid-hydrolyzable N and acid-insoluble N, we did not, because neither acid-soluble N nor acid-insoluble N was characterized chemically. The amount of N in a fraction was recalculated to kg/ha in the 0-10 cm soil layer, and PEN in a fraction was calculated as the difference between total and stable N in the same fraction. Because we analyzed one composite sample per land-use system, we do not detail the effect of land use on N chemistry, but focus on the chemical differences between total, stable, and PEN.

## Results and Discussion

About 40% of total N was identified as amino sugar N, amino acid N, and $NH_3$-N (Table 1). Usually, 30%-50% of total N can be accounted for in known substances (Kelley and Stevenson 1985). Normal ranges in soils are 30%-45% amino acid N, 5%-10% amino sugar N, and 20%-35% $NH_3$-N (Stevenson 1982), indicating our values to be low with respect to $NH_3$-N and amino acid N.

Part of the "unknown" N is thought to be a structural component of humic substances and another part as the result of condensation reactions during acid hydrolysis (Stevenson 1982). Schulten et al. (1997) recently showed, through analytical pyrolysis of the structure of "unknown" soil nitrogen, that heterocyclic N compounds are major components. However, "unknown" N has been shown to be biodegradable (Ivarson and Schnitzer 1979, cited in Schulten et al. 1997) and is of practical relevance for soil fertility (Schulten and Leinweber 1996, cited in Schulten et al. 1997). Thirty percent of the fertilizer N that was immobilized in the microbial biomass after adding glucose was, within 7 days, found in the "unknown" N fraction. This shows that the "unknown" N contributes to part of the "unknown" soil N (Kelley and Stevenson 1985).

The value of 13.8% $NH_3$-N for total N might be surprising, because Oxisols do not have the 2:1 layer clays that can fix ammonium, and mineral N extracted by KCl (1 *M*) accounted for less than 2% of total N. Interestingly, no $NH_3$-N was lost by extraction with permanganate (Table 1). Possibly the $NH_3$-N was occluded in microaggregates (<2 mm) and therefore protected against the action of permanganate or extraction by KCl. Acid hydrolysis at low pH (<1) dissolved all Al and Fe oxides, thus liberating the occluded $NH_3$-N. This effect may have been reinforced by grounding the soil before submitting it to acid hydrolysis. Furthermore, an unknown part of the $NH_3$-N can arise from the breakdown of amino sugars and amino acids during hydrolysis (Kelley and Stevenson 1985).

When averaged over all land-use systems, stable N and PEN accounted for 57% and 43% of total N,

Table 1. Chemical characterization of total, stable, not-extractable (i.e., "unknown" ) N, and permanganate-extractable N (PEN) in the topsoils (0-10 cm) of an Oxisol in the Brazilian savannas. Values refer to kg/ha of N type.

| N fraction | N in fraction | Amino acid N | Amino sugar N | $NH_3$-N | "Unknown" N |
|---|---|---|---|---|---|
| Total N | 1612 | 304 | 121 | 222 | 965 |
| % | *100* | *18.8* | *7.5* | *13.8* | *59.9* |
| Stable N | 917 | 142 | 56 | 241 | 478 |
| % | *100* | *15.5* | *6.2* | *26.3* | *52.0* |
| PEN | 695 | 162 | 65 | –19 | 468 |
| % | *100* | *23.3* | *9.4* | — | *67.3* |

respectively. On absolute terms, "unknown" N was evenly distributed over stable N and PEN. Stable N accounted for all $NH_3$-N and PEN had slightly more amino sugar N and amino acid N than did stable N.

Permanganate-extractable N consisted of about 22.7% amino acid N and about 9.1% amino sugar N (Table 1), which means that PEN was enriched in these N fractions, compared with total N and stable N. The high amount of "unknown" N in the PEN fraction does not give much hope for chemical characterization. However, the high share of amino sugar N and amino acid N in the PEN fraction indicates that chemical oxidation by permanganate probably attacks the same chemical substances as biological oxidation by microbes.

By contrast, stable N did not contribute significantly to decomposition (Westerhof et al. 1998). Interestingly, over 20% of the stable N (198 kg/ha in the 0-10 cm soil layer) consists of amino sugar N and amino acid N that appear to be unavailable to both biomass and permanganate.

When treated with permanganate, the surface of soil particles became dark. When those aggregates that were not disrupted by permanganate treatment were crushed and examined under a microscope, their insides were seen not to have changed color. Grounding the soils before oxidation with permanganate decreased the stable N fraction by 10%, which shows that part of the stable N was physically protected inside aggregates. These results partly support the hypothesis that "soil architecture is the dominant control over microbial-mediated decomposition processes in terrestrial ecosystems" (Van Veen and Kuikman 1990). The "unknown" N in the stable N fraction resisted extraction with permanganate and may be chemically different from the permanganate-extractable "unknown" N. These chemically recalcitrant N compounds may also resist microbial decomposition.

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# CHAPTER 13

# Phosphorus Fractions under Different Land-Use Systems in Oxisols of the Brazilian *Cerrados*

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## Abstract

We examined whole-soil samples and particle-size fractions to study the distribution of different phosphorus (P) fractions after land-use change from native savanna to crops, pasture, and reforestation on clayey and loamy Oxisols of the Brazilian savannas. Phosphorus was extracted sequentially, according to a modified Hedley procedure, into inorganic and organic P (NaOH-extractable $P_i$ and $P_o$, respectively), and recalcitrant P ($P_{HCl}$ and $P_{res}$). Under natural conditions of strong P deficiency, over 60% of NaOH-extractable P was organic, reflecting the high contribution of $P_o$ to plant nutrition. Fertilization elevated inorganic P forms but had only small effects on $P_o$. The increase of inorganic P forms from fertilizer P was greatest in the $P_i$ and lowest in the $P_{res}$ fractions. After fertilization, the reforested sites maintained high NaOH-extractable P through efficient recycling, whereas at the crop and pasture sites, P tended to accumulate in recalcitrant forms. Possibly, the adsorption of P to oxyhydroxides was reduced at the more acid reforested sites by complexation of Fe and Al oxides with organic acids. The ratio of NaOH-extractable $P_i$ to $P_o$ appeared to effectively reflect the P status of the land-use systems, and P deficiency increased in ascending order from native savanna > pasture > reforestation > crop, independently of soil type.

The particle-size separates reflected P transformations along a biological and mineralogical gradient, which is discussed with respect to origin and distribution of natural and fertilizer P forms. That is, (1) P in particle-size separates was enriched in the clay and depleted in the sand fractions such that 70%-87% of total P was bound in the clay; (2) residual P increased relatively at the expense of HCl-extractable P with decreasing particle-size, indicating a continuously stronger adsorption to oxyhydroxides; (3) the proportions of organic P were generally lowest in the 20-50-µm fraction because P in particulate organic matter was already depleted and transformed into microbially mediated $P_o$, which was enriched in the clay and silt fractions; (4) fertilizer P accumulated in the 20-50-µm fraction and was subsequently transferred to the silt and clay fractions but remained largely in inorganic form.

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*Keywords:* Brazilian savannas, *Cerrados*, land-use change, organic phosphorus, Oxisols, particle-size separation, sequential phosphorus fractionation

## Introduction

Phosphorus (P) deficiency is well known as a major agronomic constraint in the highly weathered soils of the Brazilian savannas, also known as the *Cerrados* (Goedert 1983; Leal and Velloso 1973a; Lopes 1984). This deficiency is caused mainly by strong phosphate sorption to Al and Fe oxyhydroxides (Fontes and Weed 1996; Mesquita Filho and Torrent 1993). Agricultural practices that allow a reasonable economic return are not possible under these conditions without applications of high rates of P fertilizers. Intensive research during the past 2 decades has improved the effectiveness of P amendments (Sousa and Lobato 1988) and thus assisted in the agronomic development of the *Cerrados* (Villachica et al. 1990). However, little is still known on how land-use change affects P cycling in soils of this region.

Hedley et al. (1982) developed a sequential P-extraction procedure that allows one to follow transformations of biologically, as well as geochemically, bound P of different levels of plant availability. This has led to the development of conceptual models of P cycling in soils (Cross and Schlesinger 1995). In low-fertility systems, both plants and microorganisms actively compete for orthophosphate, found at meager levels in soil solution (Tate 1984). This leads to a dynamic, internal P cycling in which biologically mediated P mineralization and immobilization occur simultaneously so that only small net changes between bioavailable organic and inorganic P ($P_o$ and $P_i$, respectively) are detected (Stewart and Tiessen 1987). Hence, plants seem to satisfy their part of their P requirements from organic P forms (Beck and Sánchez 1994; Bowman and Cole 1978; Thien and Myers 1992; Tiessen et al. 1984). With increasing fertilization, competition with microorganisms for orthophosphate in the equilibrium solution diminishes, slowing down the internal P cycling and leading to proportionately lower $P_o$ levels. The ratio of bioavailable $P_i$ to $P_o$ can, therefore, be used as to indicate the P status of a given soil (Beck and Sánchez 1994).

In Oxisols of the *Cerrados*, adsorption to Fe and Al oxyhydroxides is accentuated and further diminishes P availability. Bioavailability of these secondary Al and Fe phosphates is considered low because of specific adsorption caused by ligand exchange (Goldberg and Sposito 1985). However, good residual fertilizer effects (Sousa and Lobato 1988; Warren 1994) and a preliminary application of the Hedley fractionation to *Cerrados* soils (Lilienfein et al. 1996) indicated that the so-called recalcitrant fractions may be more bioavailable than expected. These findings corroborate conclusions drawn by Tiessen et al. (1994) and Oberson et al. (1995).

The application of the Hedley fractionation to particle-size separates can give further insight into the dynamic transformation of differently available P fractions, because P pools can be studied along a gradient from coarse to fine particles. This gradient is related to decomposition and humification of organic matter (Christensen 1992). Along a toposequence of weakly developed Entisols and Inceptisols of semiarid Northeast Brazil, Agbenin and Tiessen (1995) showed that both organic and recalcitrant P forms increased with decreasing particle-size at the expense of primary Ca phosphates. In highly weathered soils, where Ca-apatites are rare or absent, interactions of bioavailable fractions with secondary Fe and Al oxides should become more apparent.

In this study, we applied a simplified Hedley fractionation to whole-soil samples and to particle-size separates of differently managed clayey and loamy Oxisols in the Brazilian savannas. Our main objectives were to (1) follow transformations of bioavailable and recalcitrant P in highly weathered tropical Oxisols after land-use change from native savanna to crop, pasture, and tree plantations; and (2) discuss the implications of these differences for sustainable land use in the region.

## Materials and Methods

### *Study area and site history*

The study area has already been described in Chapter 4, pages 38-39, with an overview of the management histories of all the sites given in that chapter's Table 1. A summary of selected physical and chemical properties of the topsoil under different management systems is also given in Tables 1 and 2 of Chapter 5, pages 54-55.

### *Soil sampling and pretreatment*

Soil sampling was done as described in Chapter 8, page 91.

### *Particle-size fractionation*

Particle-size fractionation was carried out as described in Chapter 8, pages 91-92, and the results listed in that chapter's Table 1, page 93.

### *Sequential phosphorus fractionation*

A simplified sequential P fractionation, based on Hedley et al. (1982) and Tiessen and Moir (1993), was done (Figure 1). We shook samples of soil, each measuring 500-1000 mg, end-over-end in 30 mL of 0.1 *M* NaOH for 16 h. The samples were then centrifuged, and the supernatants kept refrigerated in PE bottles until

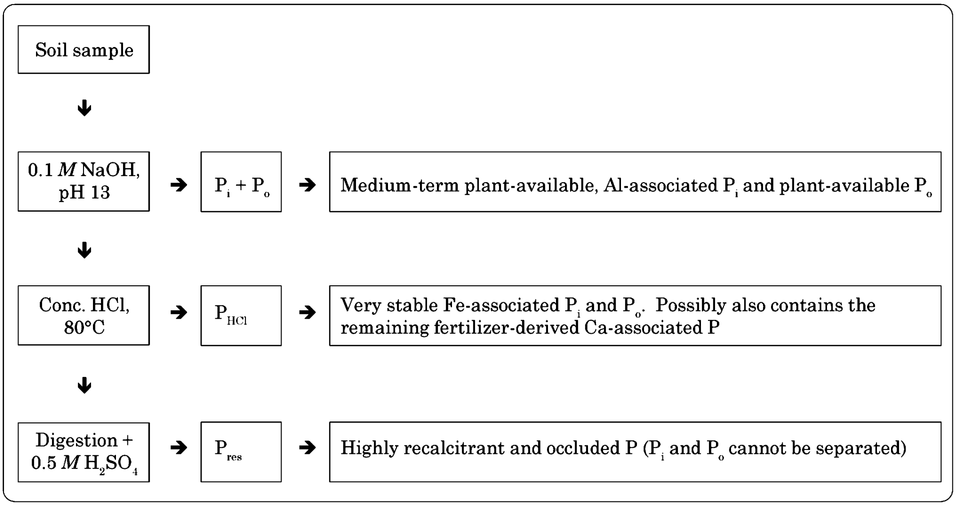

Figure 1. The simplified sequential P fractionation used to study the distribution of P fractions after changes of land use on Oxisols of the Brazilian savannas.

determination of NaOH-extractable P (note that $P_i$ and $P_o$ in the text refers to the NaOH-extractable, bioavailable P, or plant-available P). We then washed the residue with deionized water, added 10 mL of concentrated HCl, and left it to react for 10 min after the mixture reached a temperature of 80 °C. Then, another 5 mL of concentrated HCl were added and the whole gently stirred for 1 h.

The resulting samples were centrifuged, washed with deionized water twice, and the combined supernatants stored for measurement ($P_{HCl}$). The residues were dried and weighed again for accurate reference before digestion at 560 °C. After digestion, 50 mL of 0.5 $M$ $H_2SO_4$, were added, and the residues shaken end-over-end for 16 h. Subsequently, they were centrifuged, and the supernatants stored for analysis ($P_{res}$).

The resin, bicarbonate, and dilute HCl-extractable fractions were omitted in this study, because:

1. Resin-P was assumed to be too low to be determined in these highly weathered, well-drained soils;

2. Bicarbonate-P correlates only moderately with plant nutrition because plants seem to have access to more strongly adsorbed P forms under low-fertility conditions (Beck and Sánchez 1994); and

3. Dilute HCl-extractable P is very low or absent in highly weathered soils because mainly Ca phosphates are extracted, which are uncommon in acid soils (Agbenin and Tiessen 1995).

Neither was separation between organic and inorganic P extractable in concentrated HCl undertaken, because Lilienfein et al. (1996) showed that this fraction contained only inorganic P in the soils under study. Phosphorus in the residual fraction is taken as entirely inorganic (Tiessen and Moir 1993).

### Analytical methods

Total P in the NaOH, HCl, and $H_2SO_4$ fractions was measured with ICP-AES (GBC Integra XMP). Inorganic P ($P_i$) in the NaOH extracts was determined colorimetrically, according to Murphy and Riley (1962). Analytical precision of both methods was better than 10%. The amount of organic P ($P_o$) in the NaOH extracts was calculated as the difference between the amounts of total and inorganic P.

### Statistical analysis

Statistical analyses were done with Statistica software (Statsoft). Homogeneity of P fractions between the three plots per treatment was verified with MANOVA, using Tukey's HSD test ($P < 0.05$). Management effects were explained by the mean ±95% confidence interval ($n = 3$).

## Results and Discussion

### Phosphorus fractions in whole soil

Phosphorus contents in the clayey soils were three to four times as high as in the loamy soils (Table 1). The difference between the soils was visible in all P fractions, but was most apparent for $P_{res}$. In the clayey soils, the most recalcitrant fraction contained, on the average, 37% of total P. Loamy soils had only 16% (significant at $P < 0.001$, Tukey's HSD test). These results confirm those of Tiessen et al. (1984), who, after an extensive study comprising eight soil orders, found a significant positive correlation between clay content and the proportion of residual P. The proportions of all other P fractions ($P_o$, $P_i$, and $P_{HCl}$) were significantly higher

Table 1. Phosphorus contents (±95% confidence intervals; n = 3) in various fractions after sequential extraction, total P, and the $P_i/P_o$ ratio in differently managed clayey and loamy Oxisols of the savannas of central Brazil. Proportions of total phosphorus contents are given in parentheses.

| Oxisol Treatment | Bioavailable P (mg/kg) | | Recalcitrant P (mg/kg) | | Total P (mg/kg) | Bioavailable $P_i/P_o$ ratio |
|---|---|---|---|---|---|---|
| | $P_o$ | $P_i$ | $P_{HCl}$ | $P_{res}$ | | |
| Very fine Anionic Acrustox | | | | | | |
| Native savanna | 83 ± 1 (22) | 43 ± 1 (12) | 99 ± 2 (27) | 146 ± 8 (39) | 371 ± 8 | 0.5 |
| Crop | 96 ± 3 (17) | 132 ± 7 (23) | 158 ± 11 (27) | 191 ± 5 (33) | 577 ± 20 | 1.4 |
| Pasture | 88 ± 3 (19) | 58 ± 5 (12) | 151 ± 24 (32) | 178 ± 15 (37) | 475 ± 44 | 0.7 |
| Pine | 102 ± 8 (24) | 69 ± 2 (16) | 89 ± 7 (21) | 159 ± 6 (38) | 419 ± 22 | 0.7 |
| Coarse-loamy Typic Haplustox | | | | | | |
| Native savanna | 39 ± 2 (34) | 15 ± 2 (13) | 41 ± 1 (35) | 21 ± 1 (18) | 116 ± 1 | 0.4 |
| Crop | 41 ± 6 (22) | 70 ± 10 (37) | 49 ± 2 (26) | 27 ± 3 (14) | 187 ± 8 | 1.7 |
| Pasture | 38 ± 2 (35) | 19 ± 3 (18) | 29 ± 1 (27) | 22 ± 1 (20) | 108 ± 2 | 0.5 |
| Eucalyptus | 50 ± 3 (35) | 33 ± 2 (23) | 39 ± 3 (28) | 19 ± 2 (13) | 141 ± 6 | 0.7 |

in the loamy soils than in the clayey soils at $P < 0.001$, Tukey's HSD test (n = 24). If the NaOH-extractable fraction is assumed to be plant available for the medium term (as proposed by Beck and Sánchez [1994], Tiessen et al. [1984], and Wagar et al. [1986]), then that P is more "labile" in the loamy soil. For simplicity, NaOH-extractable P is referred to as "bioavailable P" in this study.

Within each soil type, management effects on $P_i$ decreased with increasing recalcitrance of the fraction. Effects were even smaller on a proportional basis, indicating that the P fractions were in a physicochemically controlled equilibrium where all fractions were affected according to their recalcitrance. Similar results were reported by Oberson et al. (1995).

Because both adsorption and desorption from variable charge surfaces are determined by electrolyte concentration, pH, temperature, and time of contact (Barrow 1983; Leal and Velloso 1973a, 1973b), P distribution from fertilizer in different land-use systems depends on the amount of P applied, year of application, and addition of lime. The source of fertilizer P could also be of significance (Ball-Coelho 1993). In contrast, $P_o$ was only slightly affected by management, indicating that microbial processes of P mineralization and immobilization may continue independently of adsorption/desorption processes or the amount of fertilizers added. Hence, under conditions of high P availability, only the competition for P in the soil solution was reduced.

Because $P_i$ was mainly affected by management, the ratio of bioavailable $P_i$ to $P_o$ ($P_i/P_o$ ratio) can be used to compare the P status of soils of different texture and/or under different management. The results confirm those of Beck and Sánchez (1994) that $P_o$ would make an important contribution to plant nutrition under low-fertility conditions. According to the $P_i/P_o$ ratio, P deficiency increased in the order crop << pine/eucalyptus ≤ pasture < native savanna, independently of soil type. The ratios were comparable with those calculated for savanna and grassland soils of a Colombian Oxisol (Guggenberger et al. 1996; Oberson et al. 1995), and for a regularly fertilized Brazilian Ultisol cropped with sugarcane (Ball-Coelho et al. 1993). Such ratios may also be useful for comparing the P status of highly weathered soils under different temperature and precipitation regimes.

Compared with the respective native savanna control, at both forest sites, only bioavailable $P_i$ and $P_o$ were enriched beyond the 95% confidence intervals, whereas at the crop sites and on the clayey substrate under pasture, accumulation was restricted largely to the inorganic fractions. Yet, while regular fertilization at the crop sites maintained available $P_i$ high, P increments on the clayey soil under pasture were strongly related to the recalcitrant fractions. However, under pasture on the loamy soil, only $P_{HCl}$ was reduced; the other fractions were comparable with those of the native savanna.

Apparently, both pine and eucalyptus effectively recycle fertilizer P applied at establishment, whereas at the crop sites only regular fertilization maintains bioavailable P forms at high levels. If regular fertilization ends because of a change in land use, the cropped sites may develop a P distribution similar to that under the pastures. In the clayey substrate, recalcitrant P could remain strongly adsorbed to Al and Fe oxyhydroxides, while bioavailable P is progressively depleted. In the loamy substrate, the increase of recalcitrant P under crop might be completely reversible, considering that the changes under pasture were small. However, because P additions on the loamy pasture were far below the amounts recommended for permanent grassland (Couto et al. 1988), and some P was probably exported with the rice harvest, no predictions on future developments are attempted.

## *Phosphorus fractions in particle-size separates*

The sum of total P in the particle-size separates was similar to total P in the whole soil (Table 2). Between 70% and 87% of total P were associated with the clay fraction, the proportions being, on the average, 10% higher in the clayey than the loamy soil. Proportions were also higher in the silt fraction, whereas in the two sand fractions together, yields of total P corresponded to only 1%-5% in the clayey soils, compared with 15%-25% in the loamy soils. However, such a strong enrichment in the clay as reported here is typical of soils under tropical to subtropical conditions and advanced weathering only because, in other soils, the proportion of P associated with clay is much lower (Agbenin and Tiessen 1995; Sumann 1997; Tiessen et al. 1983).

Figure 2 shows that the differently available P forms in the particle-size separates have a complex distribution, which depends on soil type and land use. In the clayey soil, the clay and silt fractions were very similar under native savanna, reflecting the clayey nature of silt-sized microaggregates. The proportion of bioavailable P was about 30% of total P in all particle-size fractions, and 60% was in organic forms. Compared with clay and silt, total P concentrations were strongly reduced in the 20-50-µm fraction and they were even lower in the 50-2000-µm fraction. In the 20-50-µm fraction, the $P_i/P_o$ ratio was elevated. This is probably related to microbial degradation of P in the particulate organic matter (POM) and its subsequent accumulation in the clay and silt fractions. Sand-associated $P_o$ is therefore considered predominantly plant-derived, while clay- and

Table 2. Yields of total phosphorus in particle-size separates of differently managed clayey and loamy Oxisols of the savannas in central Brazil. Percentage of sum of separates (Σ) in parentheses.

| Oxisol Treatment | P (mg/kg soil) in particle-size separates (μm) | | | | | P in whole soil (mg/kg soil) |
|---|---|---|---|---|---|---|
| | <2 (clay) | 2-20 (silt) | 20-50 (fine sand) | 50-2000 (medium to coarse sand) | Σ | |
| Very fine Anionic Acrustox | | | | | | |
| Native savanna | 334 (87) | 42 (11) | 2 (1) | 8 (2) | 386 | 371 |
| Crop | 447 (80) | 82 (15) | 17 (3) | 12 (2) | 558 | 577 |
| Pasture | 395 (83) | 60 (13) | 11 (2) | 12 (3) | 478 | 465 |
| Pine | 349 (79) | 83 (19) | 2 (0) | 5 (1) | 439 | 419 |
| Coarse-loamy Typic Haplustox | | | | | | |
| Native savanna | 85 (69) | 7 (6) | 3 (2) | 28 (23) | 123 | 116 |
| Crop | 155 (75) | 17 (8) | 7 (3) | 27 (13) | 206 | 187 |
| Pasture | 95 (76) | 11 (9) | 3 (2) | 16 (13) | 125 | 115 |
| Eucalyptus | 107 (70) | 15 (10) | 5 (2) | 25 (16) | 152 | 141 |

silt-associated $P_o$ is taken as microbially mediated.

With land-use change in the clayey soil, the proportion of bioavailable P increased in the clay fraction of all management systems but decreased in the silt and sand fractions of the cropped and pasture sites. Land-use change to pine increased the proportion of bioavailable P in all particle-size fractions. This indicates that P in the clay fraction might be less recalcitrant than could be expected from results on soil organic matter dynamics (Neufeldt 1998). The higher proportion of bioavailable P, explained by effective P recycling under pine, might be related to the lower pH, compared with the native savanna. Chelation of Fe and Al oxyhydroxides with organic acids of low molecular weight and competition for anion adsorption sites on the clay minerals by organic anions may explain the greater P availability under acid conditions (Lee et al. 1990; López-Hernández et al. 1986; Young and Bache 1985).

Land-use change to crop and pasture in the clayey Oxisol led to a strong accumulation of $P_{HCl}$ in the 2-20 and 20-50-μm fractions. This enrichment was also visible in the 50-2000-μm fraction to some extent. Tiessen et al. (1983) reported a similar accumulation of recalcitrant P in the coarse silt fraction of cultivated Mollisols. One explanation may be that granular fertilizer P accumulated in these size separates. Being in equilibrium with more or less bioavailable forms, the fertilizer subsequently elevated the contents not only of bioavailable P but also of $P_{res}$ in the 2-20 and 20-50-μm fractions. Some of the dissolved fertilizer P also accumulated in the clay fraction in a bioavailable form, mainly as $P_i$, but did not affect $P_{res}$ or $P_{HCl}$. Possibly clay-associated P is more accessible to microorganisms than P in the 2-20 and 20-50-μm fractions. Greater microbial accessibility of P associated with clay, and hence a higher turnover rate, could also be indicated by the decrease of the $P_i/P_o$ ratio.

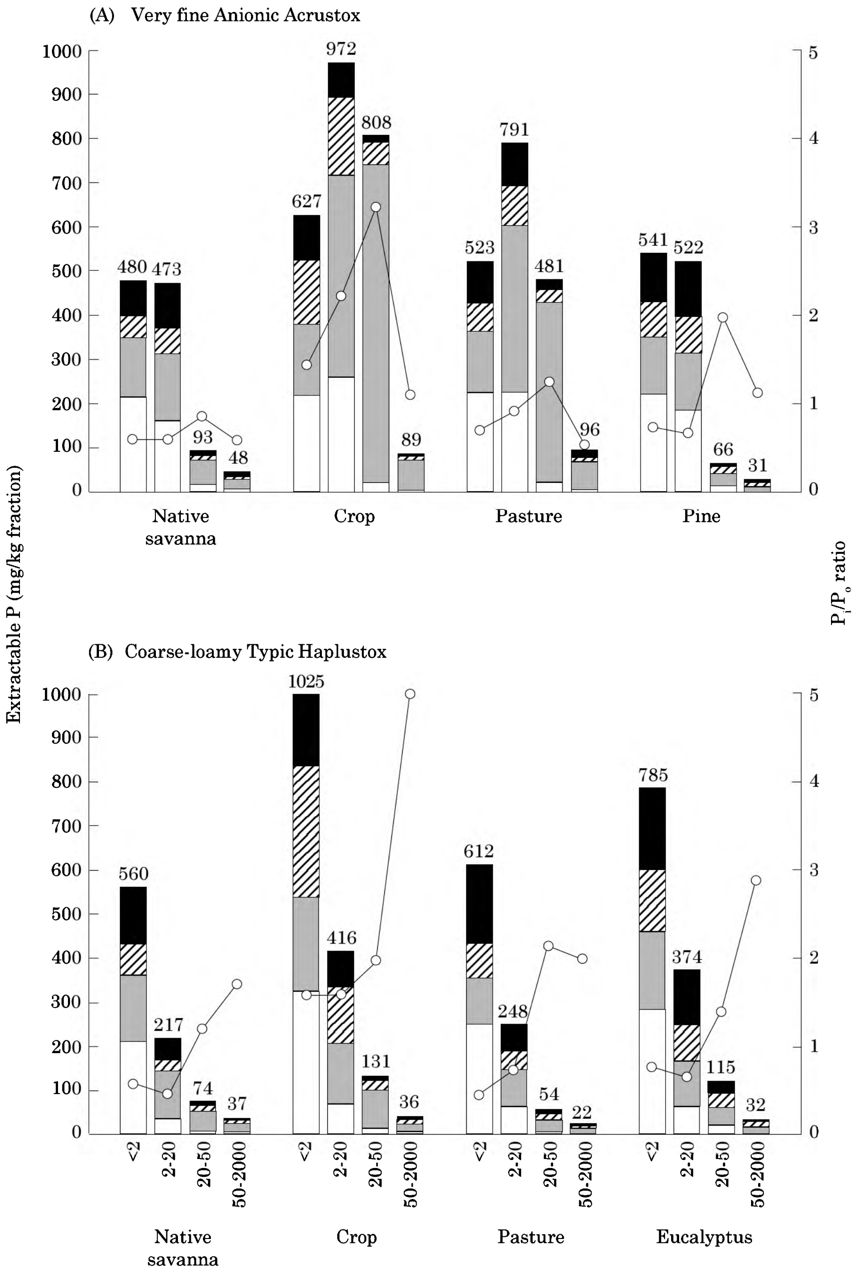

Figure 2. Phosphorus fractions in particle-size separates and the $P_i/P_o$ ratio (○) in differently managed clayey (A) and loamy (B) Oxisols of the Brazilian savannas. (■ = NaOH-$P_o$; ▨ = NaOH-$P_i$; ■ = $P_{HCl}$; □ = residual P.)

In the loamy soil, the P distribution was similar under natural and modified conditions with an overall P enrichment in the order native savanna ≤ pasture < eucalyptus < crop, which affected all but the 50-2000-µm fraction. Independently of land use, P contents increased progressively with decreasing particle size. Concurrently, the proportion of $P_{HCl}$ decreased at the expense of $P_{res}$, indicating that recalcitrance increased from the sand to the clay. In contrast to the clayey soils, the proportion of bioavailable P generally increased at the expense of $P_{HCl}$ in all particle-size fractions with land-use change. Hence, P became more labile than P under native savanna. This could be related to the lower contents of oxyhydroxides in the loamy soils. The increase of bioavailable P after land-use change was marginally highest under eucalyptus, followed by the cropped site, and pasture. At the cropped site, bioavailable P was kept high through regular fertilization, but, at the eucalyptus site, effective recycling at a lower pH is suggested, similar to the dynamics under pine. At the pasture site, the proportion of bioavailable P was only slightly elevated, compared with the native savanna. Whether this is still related to the added fertilizer or is within the margin of error is not known.

In the loamy soils, the increasing $P_i/P_o$ ratio in the silt fraction reflects a shift in the source of bioavailable P, such that $P_o$ was increasingly derived from POM. Inorganic P in the sand fractions was possibly related to Fe and Al oxide coatings on quartz grains because no P-containing primary minerals persisted with prolonged weathering. The reason why the $P_i/P_o$ ratio in the clayey substrate did not show a continuous increase is attributed to the low amount of sand and, hence, the small contribution of $P_i$ in oxide coatings.

The higher proportion of $P_{HCl}$ in the 20-50-µm fraction of the loamy soil under crop may reflect fertilizer P, as with the clayey soils. However, because the fertilizer source was more soluble than that given to the clayey soils, most of the fertilizer may already be dissolved. In contrast, in the clay and silt fractions, fertilizer P accumulated mostly as $P_i$ and was in equilibrium with the more recalcitrant forms of P and with $P_o$.

To critically evaluate these results is difficult, because the few studies in which different P pools were analyzed in particle-size fractions were either restricted to young soils (Agbenin and Tiessen 1995; Tiessen et al. 1983) or did not analyze comparable P fractions (Day et al. 1987; Sinaj et al. 1997), or examined only some particle-size separates (Sumann 1997). Nonetheless, in most studies, total P increased with decreasing particle size, in a manner similar to that of the P distribution in loamy soils, which highlights the significance of the clay fraction as a P sink. The relative contribution of bioavailable P and residual P increased continuously from sand to clay at the expense of primary Ca-apatites (Agbenin and Tiessen 1995; Tiessen et al. 1983). Likewise, in the soils under study, the proportion of $P_{res}$ increased from sand to clay at the cost of $P_{HCl}$, whereas the contribution of bioavailable P was more influenced by land use and not by mineralogy. In contrast to the highly weathered soils studied, in young soils, P contents not only increase toward the clay fraction but are also enriched in the sand fraction as a function of P-containing primary minerals associated with the sand fraction (Agbenin and Tiessen 1995). In younger soils, Ca-apatites undergo a gradual transformation into secondary Fe and Al phosphates during pedogenesis. Under the given conditions of advanced weathering (where primary phosphates have already been transformed into secondary phosphates), however, decreasing proportions of $P_{HCl}$, at the expense of $P_{res}$, might reflect stronger adsorption in the clay fraction due to greater particle surface area.

## Conclusions

The Hedley fractionation method is appropriate for studying P transformations in Oxisols of varying texture and under different management systems. Our use of it verified the general concepts of P dynamics in highly weathered soils. In general, P is more labile in soils with lower clay contents but, independently of substrate, the proportion of bioavailable P increases after fertilization. In high-fertility systems, mainly labile $P_i$ is enriched, while bioavailable $P_o$ is unaffected by land use because biological immobilization and mineralization continue. Hence, the ratio of bioavailable $P_i$ to $P_o$ is a sensitive indicator of the P status of a given land-use system in highly weathered tropical soils.

Recalcitrant P forms accumulate according to the amount and frequency of P applications and the contents of oxyhydroxides in the soil. Reforestation seems to efficiently recycle added fertilizer without losing it to recalcitrant forms, while in pasture and crop sites, P tends to accumulate in forms unavailable to plants.

The analysis of P fractions in particle-size separates helps identify major forms of P in physically defined pools and along a biological and mineralogical gradient that is related to both organic decomposition and pedogenesis. That is:

1. Phosphorus is nearly completely associated with the clay fraction because primary P sources in the sand and silt fractions do not contribute any more,
2. Proportions of residual P increase with decreasing particle size because of stronger adsorption,
3. Organic P is transformed from primarily plant-derived into microbially mediated forms, and
4. Fertilizer P is enriched in the coarse silt and fine sand fractions and the dissolution products can be found in smaller particle-size fractions.

## Acknowledgments

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# CHAPTER 14

# Phosphorus Pools in Bulk Soil and Aggregates of Differently Textured Oxisols under Different Land-Use Systems in the Brazilian *Cerrados*

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*Miguel A. Ayarza***, and *Wolfgang Zech**

## Abstract

This study assessed the influence of land use (continuous cropping, CC; tree plantations, F; pasture, PG; and native savanna, NS) on P concentrations and partitioning in bulk soil and two aggregate size fractions of two Oxisols, one loamy and one clayey. The quantity and quality of physically protected P within aggregates were also determined. Total P in bulk soil and macroaggregates (0.25-2 mm and 2-8 mm) was partitioned into inorganic and organic P fractions ($P_i$ and $P_o$, respectively) after sequential extraction, using $NaHCO_3$ (Olsen), NaOH, HCl, and $H_2SO_4$ (residual). Additionally, P binding was examined with $^{31}P$ nuclear magnetic resonance spectroscopy. Total P concentrations were 70-170 mg/kg in the loamy and 300-450 mg/kg in the clayey soil. The largest P fraction was the NaOH-soluble P (33%-55% of total P concentration). The proportion of easily extractable P was higher in the loamy than in the clayey soil. Because of fertilization, CC and F had higher total and, particularly, higher easily available P concentrations than NS and PG. In the loamy soil, $P_i$ and, in the clayey soil, both $P_i$ and $P_o$, were higher in CC and F than in NS and PG. In the loamy soil, P concentrations in macroaggregates (>2 mm) were higher than in bulk soil. Higher monoester P proportions within the large macroaggregates in unplowed systems indicated older intra-aggregate soil organic matter than at the aggregate surfaces. In the plowed system, the monoester/diester ratio was not different between bulk soil and aggregate fractions, indicating faster aggregate turnover.

*Keywords:* Brazilian savannas, *Cerrados*, land-use change, Oxisols, phosphorus fractions, soil phosphorus

## Introduction

Phosphorus deficiency and high P fixation are major limitations for intensive cropping of the Oxisols found in the savannas (or *Cerrados*) of central Brazil (Goedert 1983). Organic P ($P_o$) is an important source of plant nutrition in highly weathered soils (Beck and Sánchez 1994; Cross and Schlesinger 1995). The $P_o$ fraction is dominated by orthophosphate monoester, which is less easily hydrolyzable and thus less plant-available than the orthophosphate diester fraction (Condron et al. 1990; Forster and Zech 1993). Cultivation

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without fertilization results in P loss, especially of $P_o$ (Beck and Sánchez 1994; Condron et al. 1990). Easily hydrolyzable orthophosphate diesters disappear completely (Condron et al. 1990). Phosphorus fertilization compensates for losses of $P_o$ and increases the percentage of inorganic P ($P_i$) forms. The enrichment is most apparent for the more easily extractable P forms (Beck and Sánchez 1994; Rubaek and Sibbesen 1995). Recalcitrant P fractions are not usually influenced by P fertilization (Beck and Sánchez 1994).

Soil organic matter and thus organically bound P can be protected against microbial attack by adsorption onto clay particles (Greenland 1965; Van Gestel et al. 1991) or by incorporation within soil aggregates (Beare et al. 1994; Gregorich et al. 1989; Gupta and Germida 1988). Cultivation of virgin soils results in aggregate disruption and in enhanced mineralization of protected organic matter (OM). Better aeration and nutrient supply by fertilization also contributes to faster mineralization of soil organic matter (Dalal and Mayer 1986).

The sequential P extraction procedure, developed by Hedley et al. (1982), allows partition of soil P according to availability for plants. $^{31}P$ nuclear magnetic resonance spectroscopy (NMR) is a comparatively simple and direct method for characterizing different forms of P (Condron et al. 1985). Compounds of varying resistance to microbial decomposition can be distinguished with this method (Tate and Newman 1982). Data on the P partitioning in Oxisols are limited to a few studies (Cross and Schlesinger 1995; Friesen et al. 1997). No data are available on the characteristics of physically protected $P_o$.

The objectives of this study are to:

1. Evaluate the effect of land use on P concentrations and partitioning in bulk soil and macroaggregates (>0.25 mm),
2. Establish whether physically protected $P_o$ exists within soil macroaggregates, and
3. Assess the quality of physically protected $P_o$ within soil macroaggregates.

## Materials and Methods

### *Study area and sample pretreatment*

The study was carried out on two Oxisols—one coarse-loamy and one clayey—for each of four different land-use systems in the region of Uberlândia, State of Minas Gerais, Brazil. The sites were those used in Lilienfein et al.'s study (1998). The management systems were:

1. Continuous cropping (CC), involving an annual disking to a depth of 20 cm, soybean/maize rotation for 9 years, and fertilization with P at 75-80 kg/ha per year.
2. Pure-grass pasture (PG) of *Brachiaria decumbens* Stapf that was 12 years old and which had received a total fertilization of P at about 130 kg/ha.
3. Tree plantations (F). The plantation on the loamy soil was 13 years old, comprising *Eucalyptus citriodora* Hook (EU). The amount and type of establishment fertilization is unknown. The plantation on the clayey soil was 20 years old, comprising pine (*Pinus caribaea*),

which was fertilized with 10 g of superphosphate per plant when established.

4. Native savanna (NS) as reference.

Conventional methods to characterize the soil properties of the different land-use systems and the results are given in Lilienfein et al. (1998). The loamy soil is a coarse-loamy, isohyperthermic, Typic Haplustox and the clayey soil is a very fine, isohyperthermic, Anionic Acrustox (Soil Survey Staff 1992).

Three 10-$m^2$ subplots per system were chosen at random for soil sampling. From each subplot, a composite sample (0-12 cm), consisting of eight subsamples, was taken at the beginning of the rainy season in October 1995. An Uhland auger was used, which allowed the soil to be sampled without destroying aggregates. Field-fresh soil samples were sieved to 8 mm to homogenize the soil and then air-dried (40 °C).

## *Aggregate fractionation*

Aggregate fractionation was carried out with a Yoder sieving apparatus (eight subsamples of 100 g each, sieving time 30 min, 21 oscillations per minute, amplitude 3 cm). Before sieving the soil, it was left to rewet by capillary action for 5 min on a sieve placed in a beaker containing water, the level of which rested just in contact with the soil. Two fractions of macroaggregates were separated: large (2-8 mm, LMA) and small (0.25-2 mm, SMA). The aggregate fractions were then air-dried (40 °C) and the LMAs broken and sieved to <2 mm to homogenize the soil. Sand concentration (>250 µm) of the aggregate fractions was determined by sieving after chemical dispersion with 0.1 *M* NaOH.

## *Soil extractions and chemical analyses*

The modified Hedley fractionation (Tiessen and Moir 1993) was used to sequentially partition soil P into several organic and inorganic P fractions. The fractionation scheme and characterization of the obtained fractions are given in Figure 1. The original procedure was shortened by removing two fractions: the resin $P_i$ and dilute HCl-$P_i$. Resin-$P_i$ corresponds to water-soluble P, which is not usually detected in these well-drained soils, poor in P. Dilute HCl extracts primarily Ca-associated P (Ca-P). This is common in young, less weathered soils (e.g., Entisols and Inceptisols) and is rare or absent in highly weathered soils (Agbenin and Tiessen 1995) such as the Oxisols. In addition, bicarb-P (shaken for 16 h), used by Tiessen and Moir (1993), was replaced by Olsen-P (shaken for 0.5 h, Page et al. 1982), because the latter can be compared with literature data on plant-available P (Bowman and Cole 1978). To determine total P in the extracts, an aliquot of the extracts was digested with $K_2S_2O_8$ in $H_2SO_4$ at >150 °C to oxidize OM (Bowman 1989). Total P was also determined by the digestion method of Saunders and Williams (1955), as modified by Walker and Adams (1958) ($P_{SW}$), corresponding to the last step of the Hedley fractionation (Figure 1).

Inorganic P of the P fractions was measured colorimetrically (molybdenum blue method, Page et al. 1982) with a PERKIN-ELMER 550 SE UVIVIS spectrophotometer. Total P was also measured with inductively coupled plasma-atomic emission spectroscopy (ICP-AES; GBC Integra XMP). Results of the different methods agreed well. Organic P was calculated as the difference between P and $P_i$.

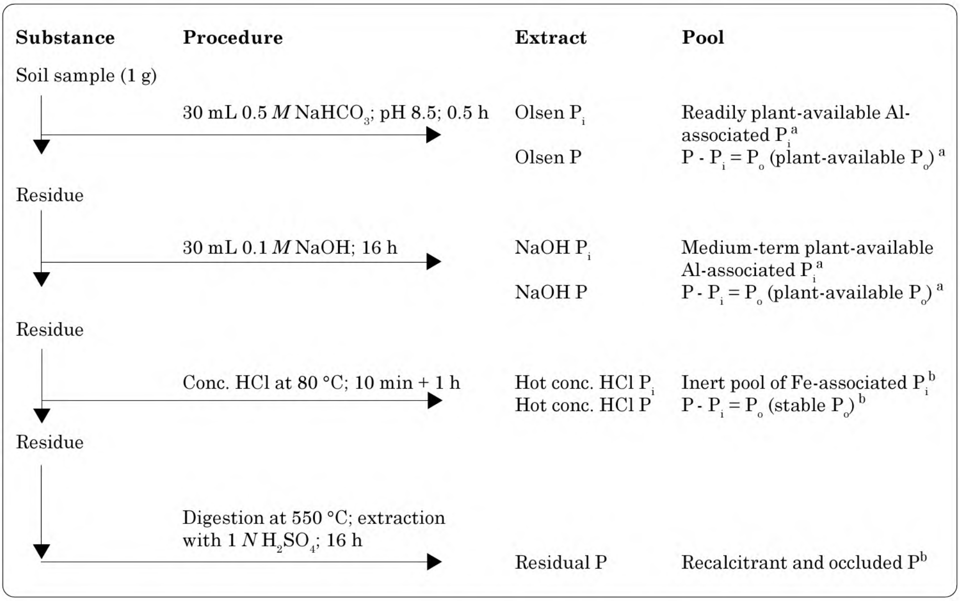

Figure 1. Fractionation scheme for phosphorus and characterization of the obtained P fractions. Soil samples were from two Oxisols of the Brazilian savannas.

SOURCES: a. Hedley et al. (1982).
b. Agbenin and Tiessen (1995).

### *$^{31}$P nuclear magnetic resonance spectroscopy*

The binding of P was examined with a $^{31}$P nuclear magnetic resonance spectroscopy ($^{31}$P NMR) for bulk soil and macroaggregates (>2 mm) of the four land-use systems. A sample of 50 g of air-dried soil from each fraction was shaken for 16 h in 500 mL 0.1 *M* NaOH. The suspensions were centrifuged and dialyzed until the conductivity was below 1 µS. For the dialysis, NaF was added to give a NaF concentration of 0.05 *N* NaF. Sodium fluoride impedes the creation of insoluble organic Fe complexes and Fe is removed from the solution during dialysis. After the dialysis, the solutions were freeze-dried. An aliquot of the freeze-dried material was redissolved in 0.1 *M* NaOH and analyzed for P with ICP-AES.

For NMR, 150 mg of the freeze-dried material was dissolved in 3 cm$^3$ 0.5 *M* NaOH in 10-mm NMR tubes. A Bruker AVANCE DRX500 spectrometer, operating at a frequency of 202 MHz was used to give non-$^1$H-coupled spectra after collecting 1600 scans. Additional recording conditions were temperature = 20 °C; pulse angle = 90°; pulse delay = 0.2 s; and acquisition time = 0.1 s. Peaks were assigned as described at Condron et al. (1990) and integrated electronically.

### *Statistical analyses*

Main and interactive affect means were tested by using Tukey's honestly significant difference (HSD) mean separation test at $P < 0.05$ (Hartung and Elpelt 1989). Variance analyses were performed with Statistica software for Windows 5.1.

# Results and Discussion

## *Distribution of water-stable aggregates*

Large differences were found between the aggregate size distributions of the two textural groups (Table 1). The clayey soil tends to have higher LMA concentrations under NS, PG, and CC than does the loamy one, which is significant for PG only. In both the loamy and clayey soils, LMA concentrations are significantly lower, and those of SMA are significantly higher under CC than under NS. This is probably related to plowing. LMA and SMA concentrations under PG and F are not significantly different from those under NS in the loamy soil, but they are in the clayey soil.

## *Phosphorus fractions in bulk soil*

***Loamy soil.*** The total P concentration is similar under NS and PG but greater under EU and CC because of fertilization (Table 2). As the crops use only a small part of the fertilizer P and leaching is negligible because of the high P-fixation capacity of Oxisols (Goedert 1983), P accumulates in the soil (Wagar et al. 1986). Although PG was fertilized when established, no significant difference was found in total P concentrations between PG and NS.

The highest P concentrations were extracted with NaOH. Generally, P concentrations decrease in the order NaOH-P > HCl-P > residual-P > Olsen-P (Figure 2). The residual-P concentration is not significantly different between the systems, suggesting that this P fraction is hardly affected by land use. While significant differences in HCl-P occurred only between NS and PG, under EU and CC, the plant-available Olsen-P and NaOH-P are significantly greater than under NS. Increasing concentrations of the more easily extractable P were also found by many other authors (e.g., Beck and Sánchez 1994; Rubaek and Sibbesen 1995). As in our study, fertilization had no significant effect on residual-P in bulk soil (Beck and Sánchez 1994).

***Clayey soil.*** Total P is about three times higher in the clayey than in the loamy soil (Figure 2). Plant-available P (Olsen-P and NaOH-P) is only about two times higher, resulting in a lower percentage of these fractions of the total P concentration. The higher P concentrations of the clayey Oxisol under NS are to be expected because no P was introduced into either system.

Table 1. Amounts (g/kg) of small and large macroaggregates (SMA, 0.25-2 mm; and LMA, 2-8 mm, respectively) in the loamy and clayey Oxisols of the savannas of central Brazil.[a]

| Land-use system | Loamy soil | | Clayey soil[b] | |
|---|---|---|---|---|
| | LMA | SMA | LMA | SMA |
| Native savanna | 270 a | 640 ab | 310 b | 620 c |
| Pure-grass pasture | 210 a | 680 b | 430 a* | 520 b* |
| Tree plantations | 240 a | 590 a | 140 c* | 770 a* |
| Continuous cropping | 60 b | 780 c | 210 c* | 720 a |

a. Values in the same column followed by the same letter are not significantly different ($P < 0.05$), according to Tukey's HSD mean separation test.

b. Values followed by an * in the clayey soil are significantly different from corresponding values in the loamy soil ($P < 0.05$), according to Tukey's HSD mean separation test.

Phosphorus fractions (mg P/kg soil) of the loamy Oxisol in bulk soil, and large and small macroaggregates (LMA, 2-8 mm; SMA, 0.25-2 mm, respect
savannas of central Brazil.[a]

| system[b] action | Olsen |  | NaOH |  | HCl $P_i$[c] | Residual P[d] | $\Sigma P_i$ | $\Sigma P_o$ | $P_{Hedley}$ | $P_{SW}$ |
|---|---|---|---|---|---|---|---|---|---|---|
|  | $P_i$ | $P_o$ | $P_i$ | $P_o$ |  |  |  |  |  |  |
| ulk | 2.5 Aa | 3.3 Aa | 14 Aa | 24 Aa | 36 Ab | 15 Aa | 67 Aa | 27 Aa | 95 Aa | 55 Aa |
| MA | 3.2 Aa | 3.9 Aa | 16 Aa | 36 Aa | 42 Ab | 14 Aa | 75 Aab | 40 Aa | 115 Aa | 71 Ba |
| MA | 3.2 Aa | 3.4 Aa | 13 Aa | 29 Aa | 38 Ab | 13 Aa | 67 Aab | 33 Aa | 100 Aa | 55 A |
| ulk | 3.2 Aa | 2.1 Aa | 15 Aa | 29 Aa | 27 Aa | 14 Aa | 59 Aa | 31 Aa | 90 Aa | 53 A |
| MA | 3.6 Aa | 2.6 Aa | 18 Aa | 33 Aa | 29 Aa | 18 Aa | 69 Aa | 35 Aa | 104 Aa | 63 A |
| MA | 3.4 Aa | 1.6 Aa | 16 Aa | 26 Aa | 28 Aa | 14 Aab | 62 Aa | 28 Aa | 89 Aa | 57 A |
| ulk | 5.6 Aa | 5.1 Aa | 27 Ab | 33 Aa | 34 Aab | 12 Aa | 75 Aa | 38 Aa | 113 Aa | 70 A |
| MA | 8.0 Ab | 5.0 Aa | 36 Ab | 36 Aa | 37 Aab | 16 Aa | 97 Ab | 41 Aab | 138 Aa | 89 B |
| MA | 7.6 Ab | 2.4 Aa | 29 Ab | 32 Aa | 35 Aab | 14 Aab | 86 Ab | 34 Aa | 120 Aa | 73 A |
| ulk | 15.0 Ab | 3.1 ABa | 53 Ac | 40 ABa | 43 Ab | 16 Aa | 127 Ab | 44 ABa | 170 Ab | 101 A |
| MA | 17.0 Ac | 5.5 Aa | 77 Bc | 54 Ab | 85 Bc | 28 Bc | 207 Bc | 60 Ab | 267 Bb | 140 B |
| MA | 14.0 Ac | 2.0 Ba | 58 Ac | 28 Ba | 41 Ab | 21 Ab | 134 Ac | 30 Ba | 163 Ab | 104 A |

followed by the same uppercase letter between aggregate size classes within one land-use system are not significantly different ($P < 0.05$), accordin
HSD mean separation test.
followed by the same lowercase letter between land-use systems within one aggregate size class are not significantly different ($P < 0.05$), according
HSD mean separation test.
ative savanna; PG = improved pure-grass pasture; EU = tree plantation of *Eucalyptus citriodora* Hook; CC = continuous cropping.
ted $P_o$ in the HCl extract (i.e., HCl-P minus HCl-$P_i$) equals zero.
al-P is assumed to be completely inorganic, because it is not possible to distinguish between $P_i$ and $P_o$ in this fraction.

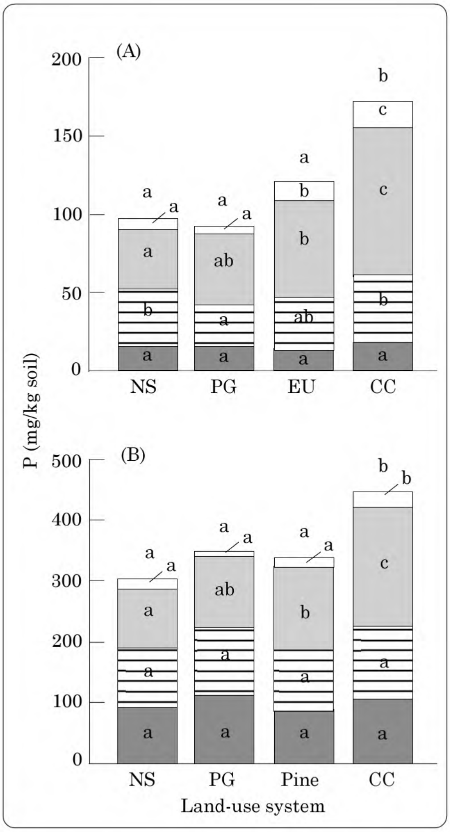

Figure 2. Partitioning of total P in bulk-soil samples of loamy (A) and clayey (B) Oxisols of the Brazilian savannas (note different scales). NS = native savanna; PG = improved pure-grass pasture; EU = tree plantation of *Eucalyptus citriodora* Hook; Pine = tree plantation of *Pinus caribaea*; CC = continuous cropping. Values within one fraction followed by the same letter are not significantly different at $P < 0.05$, according to Tukey's HSD mean separation test. (□ = Olsen-P; ▒ = NaOH-P; ▤ = $P_{HCl}$; ■ = residual P.)

Our finding of smaller percentages of plant-available P in the clayey soil than in the loamy soil agrees with findings of other authors (O'Halloran et al. 1987). Because Fe concentration in the clayey soil is higher than in the loamy soil, the fixation of fertilizer P may be more efficient. This hypothesis is supported by Cox (1994), who reported decreasing proportions of extractable fertilizer P as clay concentrations increase after fertilization in different soil types, including Brazilian Oxisols. The loamy soil's higher pH, when under the same land use, may also promote a higher proportion of plant-available P (i.e., loamy: NS = 4.7; clayey: NS = 4.6; PG = 5.4, 5.3; F = 5.0, 4.5; CC = 5.9, 5.6). As pH increases, the mineralization rate and solubility of Al-P and Fe-P also increases (Stewart and Tiessen 1987).

The sum of all fractions of the sequential extraction ($P_{Hedley}$) is about twice the concentration extracted by a simple digestion method ($P_{SW}$) (Tables 2 and 3). The digestion method may not include all the P fractions extracted by the sequential extraction. Probably, the hot HCl extract includes P fractions (especially Fe-P) that cannot be extracted by the simple digestion method. In addition, the efficiency of a multistep extraction method is generally higher than that of a one-step extraction method.

### ***$P_i/P_o$ ratios in bulk soil***

***Loamy soil.*** Inorganic P concentrations are significantly higher under CC and also higher, but not significantly, under EU than under NS and PG (Table 2). Organic P concentrations do not differ between the four systems. Fertilization of EU and CC seemed to have increased inorganic soil P concentrations only. This finding agrees with those of Tiessen et al. (1983). Thus, the $P_i/P_o$ ratios under EU and CC are higher than those under NS (Figure 3).

***Clayey soil.*** The concentrations of both organic and inorganic P forms under pine and CC are higher than under NS and PG (Table 3). However, the differences are significant for $P_i$ in all fractions for CC and, for pine, in the NaOH fraction only. Differences in osphorus fractions (mg P/kg soil) of clayey Oxisol of the Brazilian savannas in bulk soil, and large and small macroaggregates (LMA, 2-8 mm, and 35-2 mm, respectively).[a]

| stem[b] Fraction | Olsen $P_i$ | Olsen $P_o$ | NaOH $P_i$ | NaOH $P_o$ | HCl $P_i$ | HCl $P_o$[c] | Residual $P^d$ | $\Sigma P_i$ | $\Sigma P_o$ | $P_{Hedley}$[e] |
|---|---|---|---|---|---|---|---|---|---|---|
| Bulk | 4.3 Aa | 6.2 Aa | 33 A | 66 Aa | 100 Aa | n.d. | 93 Aa | 230 Aa | 73 Aa | 303 Aa |
| LMA | 4.7 Aa | 5.2 Aa | 33 Aa | 70 Aa | 100 Aa | n.d. | 92 Aa | 229 Aa | 75 Aa | 305 Aa |
| SMA | 4.4 Aa | 5.4 Aa | 34 Aa | 70 Aa | 87 Aa | n.d. | 107 Aa | 232 Aa | 75 Aa | 307 Aa |
| Bulk | 4.6 Aa | 4.4 Aa | 33 Aa | 82 Aab | 117 Aa | n.d. | 108 Aa | 263 Aa | 86 Aab | 349 Aa |
| LMA | 4.4 Aa | 4.6 Aa | 30 Aa | 90 Aab | 115 Aa | n.d. | 95 Aa | 245 Aa | 94 Aa | 339 Aa |
| SMA | 3.4 Aa | 5.3 Aa | 32 Aa | 76 Aab | 101 Aa | n.d. | 93 Aa | 229 Aa | 81 Aa | 310 Aa |
| Bulk | 5.8 Aa | 6.2 Aab | 49 Aa | 90 Ab | 97 Aa | n.d. | 88 Aa | 240 Aa | 97 Ab | 337 Aa |
| LMA | 4.5 Aa | 6.8 Aa | 49 Aa | 77 Aa | 111 Aa | n.d. | 101 Aa | 265 Aa | 84 Aa | 349 Aa |
| SMA | 5.3 Aa | 5.1 Aa | 55 Aa | 75 Aab | 104 Aa | n.d. | 91 Aa | 255 Aa | 80 Aa | 336 Aa |
| Bulk | 14.0 Ab | 8.6 Ab | 95 Ab | 100 Ab | 94 Aa | 33 A | 106 Aa | 278 Aa | 142 Aa | 444 Ab |
| LMA | 13.0 Ab | 7.6 Aa | 92 Ab | 98 Ab | 88 Aa | 39 A | 101 Aa | 294 Aa | 144 Ab | 438 Ab |
| SMA | 13.0 Ab | 7.2 Aa | 90 Ab | 95 Ab | 98 Aa | 34 A | 99 Aa | 300 Aa | 137 Ab | 437 Ab |

lowed by the same uppercase letter between aggregate size classes within one land-use system are not significantly different ($P < 0.05$), according
n separation test.
lowed by the same lowercase letter between land-use systems within one aggregate size class are not significantly different ($P < 0.05$), according to
n separation test.
ve savanna; PG = improved pure-grass pasture; Pine = tree plantation of *Pinus caribaea*; CC = continuous cropping.
determined; that is, calculated $P_o$ in the HCl extract (HCl-P minus HCl-$P_i$) equals zero.
P is assumed to be completely inorganic because distinguishing between $P_i$ and $P_o$ in this fraction is not possible.
tracted by Hedley's sequential extraction method ($P_{Hedley}$) and Saunders and Williams's simple digestion method ($P_{SW}$).

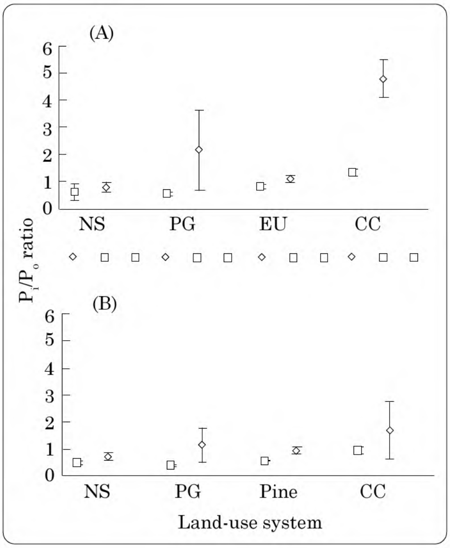

Figure 3. $P_i/P_o$ ratios and standard deviations of the Olsen and NaOH extracts of P from loamy (A) and clayey (B) Oxisols (n = 3) in the Brazilian savannas. NS = native savanna; PG = improved pure-grass pasture; EU = tree plantation of *Eucalyptus citriodora* Hook; Pine = tree plantation of *Pinus caribaea*; CC = continuous cropping. (◇ = Olsen-P; □ = NaOH-P.)

$P_i/P_o$ ratios are small, with perhaps a slightly higher $P_i/P_o$ ratio for CC than for the other systems (Figure 3). This suggests that, in the clayey soil, inorganic fertilizer increases $P_o$, but this is still a debatable issue in the literature. Tiessen et al. (1983) found that P fertilization increases Pi fractions but not the organic ones. In contrast, Stewart and Tiessen (1987) found that $P_i$ fertilization results in higher organically bound P concentrations. They concluded that the transformation of Pi into organic binding depends mainly on biological activity. Inorganic P fertilization may result in an accumulation of $P_o$ only when adequate C and N supplies are available. The accumulation of $P_i$ only may therefore be interpreted as an indicator of low biological activity.

The microbial biomass is higher in the clayey than in the loamy soil (TE Renz 1997, personal communication), probably because of higher $CEC_e$ and nutrient contents in the clayey soils (Lilienfein et al. 1998). O'Halloran et al. (1987) also reported that higher clay concentrations result in higher fertility, improved moisture status, better plant growth, and higher microbial activity. This may explain why fertilizer P is partly transformed into $P_o$ in the clayey, but not in the loamy soil. Thus, according to Stewart and Tiessen (1987), EU and CC on loamy soils seem to be rapidly degrading systems, whereas, on clayey soils, land-use systems seem more stable.

## Phosphorus in aggregate fractions

***Loamy soil.*** $P_{Hedley}$ concentrations in the LMAs are higher than in the bulk soil under all systems (Table 2). The differences are significant under CC only. Under NS, 60% of the difference in P concentrations between LMAs and bulk soil is $P_o$, whereas under CC, 83% is $P_i$. Plowing destroys aggregates, which are reformed subsequently. The high supply of inorganic fertilizer P in CC results in incorporation mainly of $P_i$ into the newly formed large macroaggregates. As plant roots mainly grow between aggregates (Materechera et al. 1994), the P of aggregate surfaces and of soil material between aggregates is depleted preferentially by plant uptake, whereas intra-aggregate P is relatively inaccessible. This may explain the higher P concentrations within large macroaggregates, compared with bulk soil. The difference may also be explained by dilution in bulk soil by sand-sized mineral grains, which are not incorporated into aggregates and which contain neither OM nor P. Identifying the correct single-grain concentrations of the macroaggregate fractions is not possible because of incomplete dispersion of the pseudosand aggregates. Nevertheless, we estimated the sand-sized, single-grain concentration by sieving after NaOH dispersion and found that the results remained almost unchanged. Thus, all data refer to uncorrected values.

***Clayey soil.*** In contrast to the loamy Oxisol, P concentrations of the two aggregate size classes do not differ from bulk soil and thus are not differentially affected by land use.

### $^{31}$P nuclear magnetic resonance spectroscopy

Phosphorus concentrations in the NaOH extract for the NMR measurements ($P_{NMR}$) are smaller than those measured in the NaOH extract of the Hedley fractionation. This is because P is lost during dialysis, during which the extracts must be cleaned to properly identify peaks. In particular, most of the orthophosphate and pyrophosphate ions and lower molecular-weight $P_o$ species are lost, whereas the higher molecular-weight $P_o$ species remain in solution. Probably $NaHCO_3$-soluble $P_o$ and $P_i$ forms extracted by the Hedley et al. (1982) procedure (Olsen-$P_i$ and Olsen-$P_o$) were not detected by $^{31}$P NMR spectroscopy of dialyzed NaOH extracts because the smaller molecules extracted by NaOH pass through the membrane during dialysis and are lost. Large organic molecules and the ions bound to these molecules (e.g., by metal bridges) remain in the sample. Thus, the more-labile forms are lost at a larger degree than the more-recalcitrant ones. Dialysis of the extracts for the loamy Oxisol under NS, pasture, and EU led to a loss of about 50% of total NaOH-P. For loamy soil under CC and clayey soils, about 70%-80% was lost. Distribution of P species is presented in Table 4.

In the loamy soil, P concentrations are higher in the dialyzed NaOH extract than in the clayey soil, averaging 1530 mg/kg for the loamy soil and 1140 mg/kg for the clayey soil, even though the $P_{SW}$ and the sum of the Hedley fractions were lower in the loamy soil. Isolating humic and fulvic acid extracts from soils containing higher amounts of clay is usually more difficult. Edwards and Bremner (1967) account this fact to the close binding of clay particles and OM to microaggregates.

The most apparent differences with respect to the distribution of P forms are recorded between the loamy and the clayey bulk soils. In the loamy soil, the dominant P forms are orthophosphate monoesters (δ 5.0-5.3 ppm) and orthophosphate diesters (δ 0-0.3 ppm). In the clayey soil, the concentrations of orthophosphate diesters are similar to that of the loamy soil, whereas those of the orthophosphate monoesters are higher. This results in different ratios of orthophosphate monoesters to orthophosphate diesters (Table 4).

The higher monoester-to-diester ratio of the clayey soil implies that P is less plant-available. The higher microbial activity in the clayey soils may result in faster transformation of the fertilizer P into a stable monoester form. This agrees with higher $P_o$ concentrations in the fertilized clayey soils than under NS.

The proportion of orthophosphate (δ 6.5 ppm) and pyrophosphate (δ -4.4 ppm) is only about 10%-15% of $P_{NMR}$ for both soils, due to the high loss of $P_i$ during dialysis. In the loamy soil under CC, the proportion of $P_i$ is higher (25% of $P_{NMR}$), because of the high concentration of $P_i$ in the NaOH extract of the loamy soil under CC, presumably due to fertilization.

The large macroaggregates show a slight enrichment of orthophosphate

Table 4. Partitioning of phosphorus compounds by $^{31}P$ nuclear magnetic resonance spectroscopy, using soil samples from two Oxisols of the Brazilian savannas.

| Land-use system[a] | Fraction | Ortho-phosphate | Monoester-P | Diester-P | Pyro-phosphate | Monoester/diester | $P_{NMR}$ (mg/kg) |
|---|---|---|---|---|---|---|---|
| | | Chemical shift range (δ ppm) | | | | | |
| | | 6.5 | 5.0-5.3 | 0-0.3 | -4.4 | | |
| | | Signal intensity (% of total intensity) | | | | | |
| Loamy Oxisol | | | | | | | |
| NS | Bulk | 5 | 40 | 39 | 6 | 1.0 | 19 |
| | LMA | 10 | 48 | 20 | 4 | 2.4 | 21 |
| PG | Bulk | 8 | 41 | 31 | 6 | 1.3 | 18 |
| | LMA | 18 | 46 | 13 | 5 | 3.5 | 26 |
| EU | Bulk | 5 | 38 | 40 | 5 | 0.9 | 43 |
| | LMA | 11 | 45 | 21 | 3 | 2.2 | 37 |
| CC | Bulk | 15 | 39 | 17 | 15 | 2.33 | 24 |
| | LMA | 9 | 38 | 24 | 15 | 1.6 | 24 |
| Clayey Oxisol | | | | | | | |
| NS | Bulk | 8 | 61 | 11 | 3 | 5.4 | 23 |
| | LMA | – | – | – | – | – | 38 |
| PG | Bulk | 8 | 65 | 4 | 4 | 14.6 | 54 |
| | LMA | 6 | 60 | 7 | 5 | 8.2 | 32 |
| Pine | Bulk | 10 | 57 | 12 | 4 | 4.6 | 33 |
| | LMA | 9 | 59 | 14 | 4 | 4.3 | 55 |
| CC | Bulk | 7 | 52 | 10 | 8 | 5.0 | 44 |
| | LMA | 8 | 53 | 12 | 9 | 4.3 | 41 |

a. NS = native savanna; PG = pure-grass pasture; EU = tree plantation of *Eucalyptus citriodora* Hook; Pine = tree plantation of *Pinus caribaea*; CC = continuous cropping; LMA = large macroaggregate of soil.

monoesters and a depletion of orthophosphate diesters, compared with the bulk soils of NS, PG, and CC on the loamy soils. This results in higher ratios of orthophosphate monoesters to orthophosphate diesters. According to Smeck (1985), nucleic acids and phospholipids, which belong to the orthophosphate diester fraction (Zech et al. 1985), are easily hydrolyzed, whereas inositols, which belong to the orthophosphate monoester fraction (Zech et al. 1985), are less easily hydrolyzed and tend to accumulate in soil. The bulk soil contains more fresh plant material than is present within the aggregates as plant roots mainly grow in the interaggregate pores (Materechera et al. 1994). Thus, the microbial transformation of soil $P_o$ is less advanced in bulk soil than in the large macroaggregate fraction. Under CC, no differences between the soil fractions are visible. The OM within the macroaggregates under plowed systems is younger than that under unplowed systems, because the aggregates of plowed systems have a more frequent turnover (Beare et al. 1994).

In the clayey soils, no differences were found between bulk soil and aggregate fractions.

## Conclusions

Land use influences the total P concentrations under F and CC, but not under PG. Fertilizer-P accumulates in labile and medium-labile forms. In loamy soil, $P_i$ concentrations are higher under intervened systems than under NS and fertilization compensates for the loss of $P_o$. In the clayey soil, P fertilization results in an accumulation of inorganic and organic fractions due to a higher microbial activity.

The percentage of the plant-available total P is smaller in the clayey than in the loamy soil.

Large macroaggregates of the loamy soil contain physically protected $P_o$, whereas in the clayey soil, P concentrations in macroaggregates are not different from those of the bulk soil. The physically protected $P_o$ accumulates as stable orthophosphate monoesters in the loamy soil, because orthophosphate diesters are more easily hydrolyzed.

According to Stewart and Tiessen (1987), the accumulation of fertilizer P in only the $P_i$ fractions indicates rapidly degrading systems. This was the case of the loamy soil we studied. The increase of $P_i$ and $P_o$ fractions after P fertilization of the clayey soil indicates a more stable system with higher microbial activity.

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## Chapter 15

# Acid Monophosphatase: An Indicator of Phosphorus Mineralization or of Microbial Activity? A Case Study from the Brazilian *Cerrados*

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## Abstract

Plant production in the Brazilian savannas, also known as the *Cerrados*, is limited mainly by low P availability. In tropical soils, rich in sesquioxides, P supply of plants depends heavily on the transformation of organic P by phosphatase enzymes into $HPO_4^{2-}$ and $H_2PO_4^-$. We examined two Oxisols—one clayey and one loamy—under different land uses for their potential acid monophosphatase activity (PAMA) and potential microbial activity. We measured dimethyl sulfoxide reduction, pH, total C and N, and NaOH-extractable organic and inorganic P. For all parameters other than pH, values were about twice as high in the clayey as in the loamy soil. Land use was found to strongly affect phosphatase activity, which was reduced by both cropping and reforestation. In the clayey soil, pastures seemed to have a positive effect on phosphatase activity. A change of continuous cropping to pasture resulted in a rapid recovery of phosphatase activity, microbial activity, and C and N levels. However, it retained the high inorganic P ($P_i$) levels found in fertilized crops. A comparison of phosphatase activity with microbial activity, total C and N, and P fractions showed that phosphatase was strongly related to microbial activity in the soil and therefore depended much more on soil organic matter than on soil P levels. We also found that, although PAMA is useful for indicating a soil's P mineralization capacity, it does not indicate actual P mineralization rates. However, when combined with findings for microbial activity and $P_i$, it indicates the level of microbially available P, a lack of which probably implies strong competition between plants and microorganisms for this element.

*Keywords:* Brazilian savannas, *Cerrados*, land management, microbial activity, Oxisols, phosphatase activity, phosphorus

## Introduction

Agricultural production on soils in the Brazilian savannas, also known as the *Cerrados*, is usually limited by low available P levels (Klink et al. 1993). Plants take up this element mainly as inorganic orthophosphate but, in highly weathered tropical soils, organic P ($P_o$) compounds may be dominant (Stewart and Tiessen 1987; Tiessen et al. 1992).

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To convert $P_o$ compounds into plant-available inorganic P ($P_i$), phosphatase enzymes may be of particular importance for plant nutrition in the tropics. Harrison (1982) showed a significant positive relationship between potential phosphatase activity and P mineralization rates. According to Tate (1984), these mineralization rates are more important for P availability to plants than $P_o$ values as such. Speir and Cowling (1991) therefore suggested the use of soil phosphatase as an index of plant productivity in P-limited low-fertility pastures, where most plant P can be assumed to be derived from soil organic matter.

Only potential phosphatase activity can be measured. It correlates positively with the clay fraction (Dick and Tabatabai 1993) and the organic C content of the soil (e.g., Kulinska et al. 1982). Moderately labile P also influences phosphatase activity (Speir and Ross 1978). Cropping strongly affects phosphatase and other enzymatic activities (Dick 1994).

Soil P varies in its stability and plant availability, which can be quantified by sequential P-fractionation procedures (e.g., Hedley et al. 1982). The $NaHCO_3$-extractable fraction comprises labile P. This fraction is probably closely linked to plant nutrition and microbial activity (Cross and Schlesinger 1995). In the tropics, however, the organic $NaHCO_3$-$P_o$ pool rapidly replenishes and differs little between various sites. The more resistant NaOH-extractable $P_o$ fraction seems to reflect better the overall changes in P levels (Beck and Sánchez 1994; Tiessen et al. 1992), and can thus provide more information on differences in P availability for phosphatases than can $NaHCO_3$-$P_o$ (Oberson et al. 1998).

This paper examines the effects of different land-use practices such as pastures, crops, and reforestation on acid monophosphatase activity in Oxisols of the Brazilian savannas and assesses the controlling factors of this activity in these soils. We also tested the suitability of using phosphatase as an indicator of the soil's P status and its P mineralization capacity.

## Materials and Methods

### *Study area and land-use systems*

The study area is located in the Uberlândia region in the State of Minas Gerais, Brazil, at 19°S and 48°W, and between 900 and 950 m above sea level. Mesozoic and Tertiary sediments dominate the weakly undulating landscape.

Following Köppen's system (1936), the climate is classified as Aw. Average humidity is about 70% and annual precipitation averages 1650 mm, with more than 75% occurring between November and March. A marked dry season occurs from June to September. Average monthly temperatures range from 18 °C in July to 23 °C in October.

Two soils were included in the study. The first one was classified as a very fine, allitic, isohyperthermic, Anionic Acrustox. Its clay, silt, and sand contents were 68%, 7%, and 25%, respectively. The second soil was a coarse-loamy, mixed, isohyperthermic, Typic Haplustox with 18% clay and 82% sand (Neufeldt 1998).

On the clayey soil, three types of land-use systems had been established and managed by commercial farmers: reforestation, no-tillage cropping and tilled cropping—both with maize —and pastures. Pastures included a degraded pasture, an improved grass pasture, an improved grass/legume pasture, and a pasture after crop. The last pasture was recently established on a field that had been under maize/ soybean rotation. On the loamy soil, a conventionally tilled crop and a degraded pasture were studied. More information about management and fertilization is given in Table 1. Native savanna was used as control for each of the two soils.

### Soil sampling

Samples were taken in February 1996 during the rainy season along three transects, about 100 m long, for each treatment. On each transect, eight subsamples were taken from the topsoil (0-10 cm) with an Edelman auger and pooled. Samples were air-dried and sieved through a <2-mm mesh. Visible roots were removed.

### Chemical analyses

Total C and N were measured with a C/N analyzer (Elementar Vario EL), using ground soil samples.

Moderately available P was extracted with 30 mL 0.1 *N* NaOH from 1 g of soil according to Tiessen and Moir (1993). The total amount of P (i.e., NaOH-$P_t$) was determined with an ICP-AES (GBC Integra XMP). Inorganic P (NaOH-$P_i$) in the extracts was analyzed, using the method based on Murphy and Riley (1962) and $P_o$ (NaOH-$P_o$) was calculated by difference.

Three field replicates were analyzed and, in the laboratory, duplicate (for P) or triplicate analyses (for other parameters) were performed on each sample.

### Analysis of phosphatase and microbial activity

Before analyzing phosphatase activity and microbial biomass, soil samples were preincubated. The preincubation was to (1) revitalize microbes, (2) create comparable humidity conditions, thus excluding water content as a factor influencing microbial activity, and (3) ensure the microbial origin of phosphatase activities analyzed. According to Ladd (1978), preincubation of soil after air-drying favors microbially produced enzymes over those derived from plant or animal residues. Root removal was also necessary, to reduce the contribution of plant-borne phosphatase activity, which is almost entirely confined to root tissue, with very little occurring extracellularly (Dick et al. 1983; Nakas et al. 1987).

One week before phosphatase and microbial activity were analyzed, 10 g of air-dried soil samples were rewetted to about 70% their water-holding capacity. They were then incubated at 30 °C in 40-mL glass vials, which were closed by cotton balls and placed in an incubator adjusted to 100% relative humidity.

Acid monophosphatase activity was determined according to Tabatabai and Bremner's method (1969), as described in Alef et al. (1995), except that the phosphatase substrate concentration in the final incubation solution was 20 m*M*. Preliminary experiments had shown this concentration to be necessary to ensure a zero-order enzymatic reaction with the given soils.

Potential microbial activity was assessed with the dimethyl sulfoxide (DMSO) reduction method (Alef and Kleiner 1989), as modified by Sklorz and Binert (1994). Temporal linearity of DMSO reduction over 24 h was verified, and critical toxicity levels of DMSO assessed. Finally, 950 µL of distilled water were added to each sample of 1 g of preincubated soil placed in 20-mL headspace vials that were closed with teflon-covered rubber septums. We added, with a syringe, nagement and fertilization of the land-use systems studied on two Oxisols in the Brazilian savannas.

| ystem | Year of establishment | Plants and management | Fertilization |
|---|---|---|---|
| ery fine Anionic Acrustox | | | |
| on | 1975 | *Pinus caribaea* ssp. *caribaea* planted in a 3 x 3 m spacing | 20 g monocalcium phosphate per seedling at planting |
| no tillage | 1985 | Maize/soybean rotation | N-P-K at 120-110-90 kg in 1995/96 |
| | Since 1994 | No tillage | |
| illage | 1985 | Maize/soybean rotation | N-P-K at 120-110-90 kg in 1995/96 |
| asture | 1986 | *Brachiaria decumbens* | 616 kg calcitic lime; 1 t gypsum; 300 kg/ha of partially acidu phosphate (equivalent to 78 kg of $P_2O_5$) at establishment |
| pasture | 1992 | *B. decumbens*, planted on part of the degraded pasture | 1 t lime; 90 $P_2O_5$, 32 $K_2O$, and 12 N kg/ha at establishment |
| ne pasture | 1992 | *B. decumbens* and *Stylosanthes* sp. planted on part of the degraded pasture | 1 t lime, 90 $P_2O_5$, 32 $K_2O$, and 12 N kg/ha at establishment |
| er crop | 1992 | *Panicum maximum* cv. Vencedor, planted on part of the now no-tillage crop field | No fertilization at establishment |
| oarse-loamy Typic Haplustox | | | |
| illage | 1985 | Maize/soybean rotation | N-P-K at 110-100-100 kg in 1995/96 |
| asture | 1986 | *B. decumbens* | Unknown amounts of rock phosphate and lime at establishm |

50 μL of a solution containing DMSO and about 100 μL/L deuterated dimethyl sulfide (DMS) as an internal standard. The resulting 5% DMSO was nontoxic, but ensured a zero-order reaction with the substrate in abundance. The possibility of abiotic DMSO reduction was checked with controls, using 1 *N* NaOH to stop microbial activity (Grandel 1994).

The incubation was performed with a rotating water bath at a temperature of 30 °C. After 6 h, the reaction was stopped by injecting 100 μL of 2 *N* NaOH into each sample. The evolved and deuterated DMS in the vial headspace was determined the same day with a GC-MS (Hewlett Packard HP 5890 Series II, MSD HP 5970 B).

Again three field replicates were analyzed. All measurements were performed in triplicate.

## Results

### *Chemical parameters*

The $pH_{H_2O}$ value ranged from 4.7 under reforestation to about 6 in the clayey soils under pastures and conventional tillage (Table 2). For all treatments, the amounts of C, N, and P in the clayey soil were about twice those in the loamy soil. Generally, pastures showed the highest C concentrations in both soils. Nitrogen exhibited the same trends. Reforestation resulted in the highest C/N values in the topsoil.

In the clayey treatments, NaOH-$P_o$ ranged from 67 to 88 μg/g soil (Table 2). The lowest values were measured under native savanna and the highest were found in the grass/legume pasture and pasture-after-crop. No measurable differences were found within the loamy soil systems. Variations in NaOH-$P_i$ were far more accentuated than those in NaOH-$P_o$, with values ranging from 29 to 119 μg/g soil in the clayey soil and 11 to 54 μg/g in the loamy soil (Table 2). In both soils, NaOH-$P_i$ amounts were about 3 to 4 times as high under arable use than under native savanna and the pastures (except the pasture-after-crop). Under the no-tillage system, values were clearly higher than under conventional tillage.

### *Phosphatase and microbial activity*

Acid monophosphatase activity was consistently lower in the loamy than in the clayey soil (Table 3). In the case of the clayey soil, the pastures showed by far the highest levels of phosphatase activity, followed by the pasture-after-crop and native savanna. Phosphatase activity was lowest in the soils under crops and reforestation. Under the no-tillage system, the acid monophosphatase was about 20% higher than under conventional tillage. In the loamy soil, however, pasture and native savanna did not differ in phosphatase activity. Again the crop field showed the lowest levels of activity.

The DMSO reduction showed the same pattern as the acid monophosphatase activity (Table 3). This observation was confirmed by the close correlation between both sets of soil biological parameters (Figure 1). An exception was for the loamy soil where microbial activity under crop and pasture was clearly lower than under native savanna.

## Discussion

### *Phosphatase activity and soil texture*

Enzymes can be protected from degradation by clay minerals, which bind proteins (Dick and Tabatabai 1993). According to Sarkar et al. (1989), enzymes stabilized by clay pH, total C and N, C/N ratio, and NaOH-extractable P of two Oxisols under different land-use systems (mean ± SD) in the Brazilian savannas.

| ment | $pH_{H_2O}$ | C (mg/g soil) | N (mg/g soil) | C/N ratio | NaOH-$P_i$ (µg/g soil) | NaOH-$P_o$ (µg/g soil) |
|---|---|---|---|---|---|---|
| soil: very fine Anionic Acrustox | | | | | | |
| ve savanna | 4.9 | 22.7 ± 1.2 | 1.41 ± 0.05 | 16.1 | 29± 2 | 67 ± 3 |
| st | 4.7 | 20.8 ± 0.6 | 1.12 ± 0.04 | 18.6 | 47± 1 | 77 ± 2 |
| with no tillage | 5.4 | 22.2 ± 0.8 | 1.43 ± 0.05 | 15.5 | 119± 25 | 80 ± 12 |
| with tillage | 6.0 | 20.1 ± 0.5 | 1.29 ± 0.04 | 15.6 | 77± 6 | 70 ± 2 |
| aded pasture | 5.8 | 25.4 ± 0.7 | 1.55 ± 0.05 | 16.4 | 30± 2 | 82 ± 3 |
| -grass pasture | 5.6 | 24.3 ± 1.9 | 1.48 ± 0.09 | 16.5 | 32± 1 | 78 ± 2 |
| s/legume pasture | 5.7 | 25.3 ± 2.0 | 1.56 ± 0.17 | 16.3 | 34± 7 | 88 ± 4 |
| ure after crop | 6.0 | 24.6 ± 1.0 | 1.59 ± 0.10 | 15.5 | 89± 29 | 86 ± 6 |
| ge clayey soil[a] | 5.4 | 23.4 | 1.5 | 16.0 | 50 | 76 |
| soil: coarse-loamy Typic Haplustox | | | | | | |
| ve savanna | 5.2 | 8.9 ± 0.4 | 0.70 ± 0.05 | 12.6 | 11± 2 | 38 ± 3 |
| | 5.4 | 8.0 ± 0.6 | 0.61 ± 0.05 | 13.1 | 54± 12 | 38 ± 4 |
| aded pasture | 5.4 | 9.9 ± 0.2 | 0.70 ± 0.01 | 14.1 | 15± 1 | 41 ± 6 |
| ge loamy soil | 5.3 | 8.9 | 0.7 | 13.3 | 27 | 39 |

sure comparability with the average of the loamy soil treatments, only native savanna, no-tillage cropping, and the degraded pasture were taken ir
nt for this value.

Table 3. Acid monophosphatase activity and dimethyl sulfoxide (DMSO) reduction rates under different land-use systems studied (mean ± SD) in two Oxisols of the Brazilian savannas.

| Oxisol<br>Treatment | Phosphatase activity [nitrophenol at μg/(g soil*h)] | DMSO reduction [DMS at μg/(g soil*h)][a] |
|---|---|---|
| Clayey soil: very fine Anionic Acrustox | | |
| Native savanna | 549 ± 26 | 0.68 ± 0.10 |
| Forestation | 406 ± 19 | 0.49 ± 0.01 |
| Crop with no tillage | 464 ± 15 | 0.48 ± 0.04 |
| Crop with tillage | 385 ± 29 | 0.45 ± 0.05 |
| Degraded pasture | 893 ± 120 | 0.97 ± 0.12 |
| Pure-grass pasture | 892 ± 72 | 0.94 ± 0.06 |
| Grass/legume pasture | 947 ± 80 | 1.09 ± 0.23 |
| Pasture after crop | 647 ± 63 | 0.64 ± 0.03 |
| Þ Average clayey soil[b] | 635 | 0.71 |
| Loamy soil: coarse-loamy Typic Haplustox | | |
| Native savanna | 343 ± 32 | 0.56 ± 0.08 |
| Crop with no tillage | 245 ± 17 | 0.27 ± 0.04 |
| Degraded pasture | 338 ± 40 | 0.35 ± 0.06 |
| Þ Average loamy soil | 309 | 0.39 |

a. DMS = dimethyl sulfide.

b. To ensure comparability with the average of the loamy soil treatments, only native savanna, no-tillage crop, and the degraded pasture were taken into account for this value.

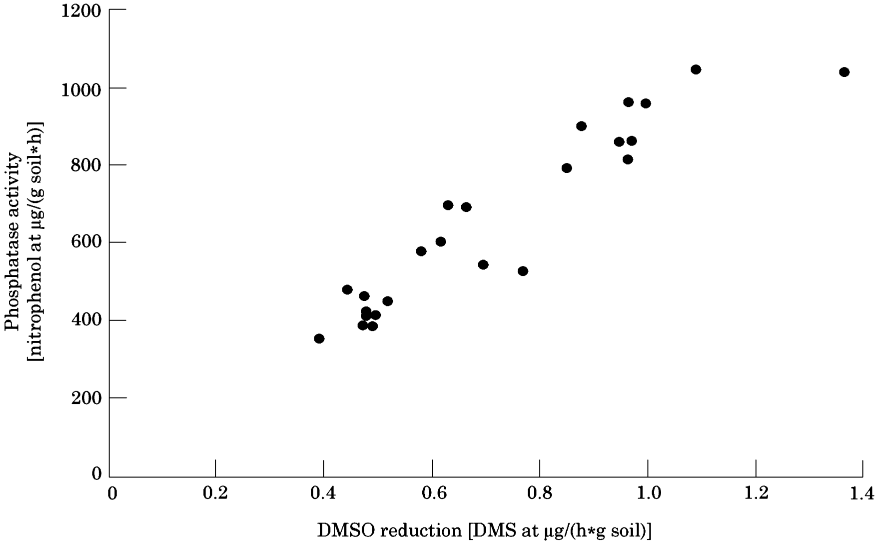

Figure 1. Correlation of dimethyl sulfoxide (DMSO) reduction and phosphatase activity in the clayey Oxisols of the Brazilian savannas (treatments: n = 24). Spearman's Rho is 0.92. (DMS = dimethyl sulfide.)

still retain most of their activity. Therefore, in clayey soils, bacteria-derived phosphatase, stabilized by clay minerals, seems to be of major importance, whereas in sandy soils, plant- or fungi-derived phosphatases linked to organic matter (OM) may dominate (Feller et al. 1994). Because our study concentrated on microbe-borne phosphatases, this stabilization may be one reason for the relatively high values of phosphatase activity in the clayey treatments, compared with the loamy ones.

### *Phosphatase activity and soil management systems*

Soil phosphatase activity values found in the Uberlândia soils under different land-use systems are, overall, similar to the results of other studies, for example,

- Nahas et al. (1994), who measured very low acid phosphatase values under *Pinus*, compared with native tropical forest and several pastures.
- Feller et al. (1994) and Gupta and Germida (1988) found phosphatase activity to be lower under cultivation, and Deng and Tabatabai (1996) confirmed that it is higher in the topsoil of no-tillage cropping systems than in tilled systems.
- Oberson et al. (1998), after analyzing two pasture soils and a native savanna soil in Colombia, found higher acid monophosphatase activity in clayey soils under pastures than under native savanna. However, they also found clear differences between an improved grass and a grass/legume pasture, in contrast to our study, where the three pastures analyzed were indistinguishable.

According to Kulinska et al. (1982), such differences in phosphatase activity may have resulted from the quality and quantity of litter material added to the soil. For the *Cerrados*, they found acid monophosphatase to be four times higher under native trees (known as *Cerradão*) than under fallow.

### *Consequences of crop/pasture rotation on soil fertility parameters*

Crop/pasture rotation, or “ley farming”, is often considered a promising alternative to either pure cropping or pure cattle ranching (Spain et al. 1996). The results presented here support this view (Figure 2): just 3 years after conversion from crop to pasture, phosphatase activity under the pasture-after-crop was clearly higher than that under maize in a nearby field, and microbial activity much higher than under native savanna. For phosphatase, these results confirm those of Feller et al. (1994). Levels of C and N were similar to those of the established pastures. These results suggest evidence of biological and chemical recovery in the soil. Evidently, cropping and the additional use of fertilizer ensure consistently high $P_i$ levels in a soil. Subsequent use as a pasture, combined with higher rhizodeposition and thus increased OM input, stimulates microbial activity.

### *Phosphomonoesterase in relation to soil chemistry and microbiology*

Acid monophosphatase usually correlates negatively with pH (Dick 1984) but, occasionally, the relationship is positive (Nahas et al. 1994). In this study, soil pH had no clear influence on the activities measured (Table 4), probably because of the narrow range in pH values and the high variability of other factors in the soils (*cf* Feller et al. 1994).

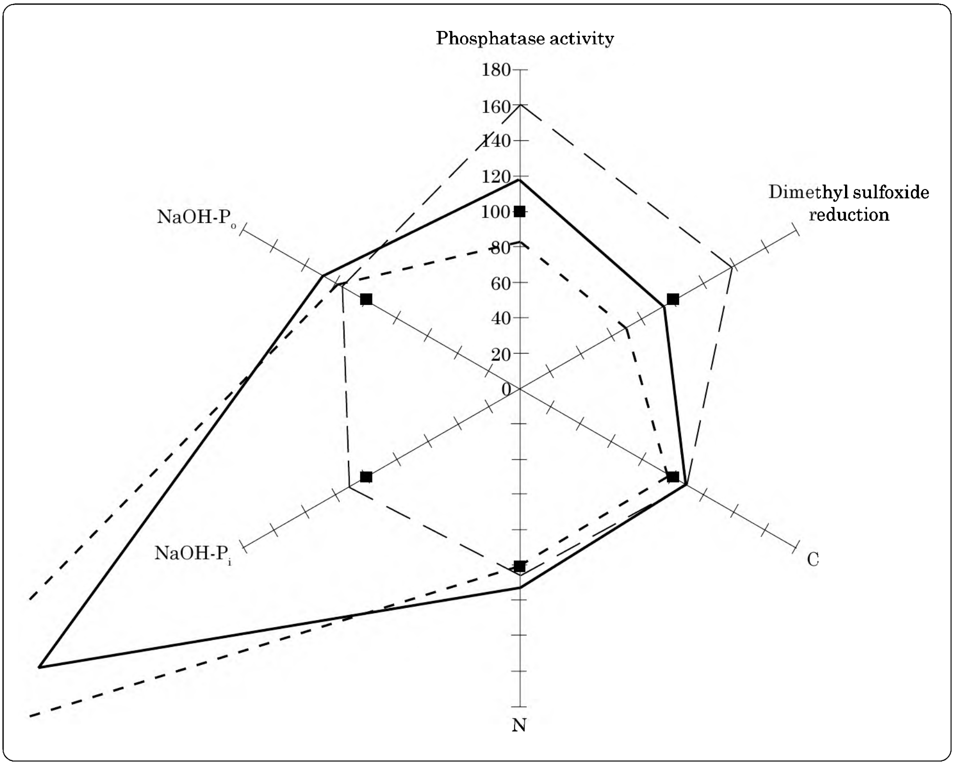

Figure 2. Star plot comparing, for soil microbial and chemical parameters, cropping with no tillage (– – –), pure-grass pasture (—— ——), and pasture-after-crop (——) grown on a clayey soil under native savanna (■), Brazil. Values are set 100% for native savanna.

Sharpley (1985) and Speir and Ross (1978) found potential phosphatase activity to be positively related to $P_o$. In the clayey soil, however, phosphatase activity was less correlated with $P_o$ than with C and N (Table 4). Thus, presumably, $P_o$, which forms the substrate for phosphatases, is not the major parameter responsible for the synthesis of these enzymes.

The significant negative correlation between phosphatase activity and NaOH-$P_i$ indicates that phosphatase activity was product-inhibited to some extent (Table 4). However, such a conclusion might be misleading, because a similar correlation exists between DMSO reduction and NaOH-$P_i$ values. This reduction does not involve any P compounds and thus should not be inhibited by $P_i$. In addition, in the laboratory studies, product inhibition of phosphatases was found only at $P_i$ concentrations that were well above even those found in cultivated fields (Juma and Tabatabai 1988; Speir and Ross 1978). According to Baligar et al. (1988), at low levels of available P, added $P_i$ may, at first, even stimulate phosphatase activity.

Phosphatase activity was significantly correlated with organic C (Table 4), a result obtained by most other studies on soil enzymes (Deng and Tabatabai 1996; Dick 1984; Dick et al. 1988; Frankenberger and Dick 1983; Kulinska 1982). Feller et al. (1994) showed a much closer relationship between phosphatase activity and soil organic carbon than

Table 4. Correlations found between phosphatase, microbial activity (as expressed by DMSO reduction[a]), and chemical parameters under different land-use systems on a clayey Oxisol in the Brazilian savannas (Spearman's Rho). Marked values are significant at $P < 0.05$ (*), < 0.01 (**), < 0.001 (***), and < 0.0001 (****) for n = 24.

| | Phosphatase | DMSO reduction |
|---|---|---|
| Phosphatase | | 0.92**** |
| DMSO reduction[a] | 0.92**** | |
| C | 0.89**** | 0.82**** |
| N | 0.80**** | 0.68*** |
| $P_i$ | –0.52** | –0.63** |
| $P_o$ | 0.52** | 0.31 |
| $pH_{H_2O}$ | 0.28 | 0.15 |

a. DMSO reduction = dimethyl sulfoxide reduction.

between phosphatase activity and P. An explanation for the direct influence of organic C on soil enzymes may be the latter's preferential binding to humo-protein complexes (Harrison 1983). This would also explain the high correlations found with soil N.

But the obvious relationship between phosphatase activity and C could also be explained indirectly. The good correlation of phosphatase with DMSO reduction (Figure 1) clearly shows that phosphatase activity in the soils analyzed was closely related to microbial activity, which, in turn, was highly influenced by C, the major element limiting microbial growth (Smith and Paul 1990; Zak et al. 1990). This close relationship of acid monophosphatase activity and microbial activity is remarkable, because acid monophosphatase enzymes present in soil are generally considered to be the result of numerous generations of microbes, which means that they cannot be associated exclusively to living tissue (Dick and Tabatabai 1993). Despite the presumably high accumulation of these enzymes in soil (Speir and Ross 1978), here they seemed to be in equilibrium with potentially active soil microbes. This also explains their high sensitivity to land-use changes. Finally, microbial activity is mainly determined by the availability of organic substrates, which depends on parameters such as root density and the quantity and quality of litter.

With OM availability being of greater importance for phosphatase activity than soil P, the measurement of phosphatase activity in a given soil cannot serve to assess actual P mineralization rates; instead, it indicates only potential P mineralization capacities. However, microbial growth stimulating phosphatase activity is also important for P mineralization. In many cases, what limits the rate of $P_o$ mineralization may be the initial microbial breakdown of organic compounds and not the hydrolytic cleavage of ester bonds catalyzed by phosphatases (Speir and Ross 1978).

The observation that microbial excretion of phosphatase enzymes depended strongly on microbial activity and the availability of OM and, at best, only weakly on NaOH-$P_i$ suggests that demand for microbial $P_i$ surpassed supply in all land-use systems. Competition between microorganisms and plants for $P_i$ can therefore be assumed, although P is not regarded as a major growth-limiting element for the given microorganisms; no positive correlation was found between microbial activity and NaOH-$P_i$.

An open question is the availability of $P_o$. If it were high, actual $P_o$ mineralization by phosphatases could counterbalance the lack of $P_i$. Only in such a case could soil phosphatase be possibly used as an index of plant productivity for low fertility soils, as was proposed by Speir and Cowling

(1991). However, $P_o$ values found in a sequential P fractionation (Lilienfein 1996) suggest a somewhat low availability in the Brazilian Oxisols compared with soils studied in other regions (e.g., Oberson et al. 1993).

## Conclusions

Potential acid monophosphatase activity in the Brazilian savannas was found to be much higher in the clayey than in the loamy soil analyzed. It responded, within a few years, to land-use changes. In the soils under cultivation and under *Pinus caribaea*, phosphatase activity was significantly lower than under native savanna. In contrast, the highest levels of activity were found under pastures in the clayey soil.

Phosphatase activity in the soil that had formerly been under cultivation and is now under pasture was significantly higher than under continuous cropping, indicating the high sensitivity of this enzymatic parameter. Data showed that pasture/crop rotation could form an interesting alternative to classical systems: when fertilized regularly, cropping encourages an accumulation of $P_i$, whereas the pasture component stimulates microbial activity and the buildup of OM.

Correlations of potential acid monophosphatase activity with soil microbial activity and with soil C were significantly higher than with moderately labile P fractions. Potential phosphatase activity could not therefore serve as a measure of actual P mineralization rates in the given systems. However, it indicates a soil's potential to mineralize available phosphomonoesters.

Based on the assumption that phosphatase belongs to the group of induced, rather than constitutive, enzymes, the lack of a strongly negative correlation between phosphatase and NaOH-$P_i$ indicates a lack of available $P_i$ for microbes. This implies the existence of a certain degree of competition between plants and microbes for $P_i$, although P did not seem to be a major limit to microbial growth. In the soils studied, where available $P_o$ is assumed to be low, the possibility of using potential phosphatase activity as an index for plant growth has to be questioned.

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## CHAPTER 16

# Microbial Biomass, Microbial Activity, and Carbon Pools under Different Land-Use Systems in the Brazilian *Cerrados*

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## Abstract

In the Brazilian savannas, or *Cerrados*, the rapid advance in agriculture and cattle ranching is affecting soils through, for example, accelerated erosion and depletion of soil organic matter (SOM). Changes in soil microbial biomass are good indicators of changes in SOM. We therefore assessed the effects of agricultural and pastoral use of a clayey Oxisol in the *Cerrados* on soil microbial biomass, and evaluated the usefulness of this parameter in studying SOM dynamics in savanna ecosystems. Surface soil horizons under a pine forest and different crop and pasture treatments were compared with the control soil under native savanna. Soil microbial carbon ($C_{mic}$), potential microbial activity, pH, organic C, water-extractable organic carbon (WEOC), and total N were assessed for the different systems. Compared with native savanna, crop cultivation and reforestation depleted $C_{mic}$. The $C_{mic}$/C quotients indicated that C might continue to decline in these two systems. Changing from conventional to no tillage appears to slow down the depletion of topsoil $C_{mic}$, C, and other parameters measured. Pasture establishment in native savanna did not clearly change $C_{mic}$, but stimulated microbial activity. The ratio of microbial activity to $C_{mic}$ was higher under pastures than under the other systems. Soil microbial carbon was shown to be closely related to the soil carbon cycle. Water-extractable organic carbon, possibly the most important source of C for microbes, consists of root exudates and litter degradation products. Root density, together with organic matter (OM) input and soil cover, was therefore assumed to be a major factor controlling the amount of $C_{mic}$. Microbial growth was hypothesized to be C-limited in the crop systems and possibly N-limited in the pastures. The results indicate that the $C_{mic}$/C ratio can be used as an indicator of OM dynamics in highly weathered tropical soils.

*Keywords:* Brazilian savannas, carbon pools, *Cerrados*, land management, Oxisols, soil microbial biomass, water-extractable organic carbon

## Introduction

Soil microbial biomass is both an important, easily accessible, pool of plant nutrients and a nutrient sink (Dick 1992; Gregorich et al. 1994;

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Smith and Paul 1990). Because it is rapidly affected by cultivation (McGill et al. 1986; Zak et al. 1990), it may serve to indicate changes in soil organic matter (SOM) long before they can be detected in the whole soil (Carter 1986; Carter and Rennie 1982).

Few microbes are active at any given time (McGill et al. 1986). Active microbes are certainly more important for nutrient cycling than dormant ones, and might also form part of the microbial fraction in soil that is not physically protected (Hassink 1994). Dimethyl sulfoxide (DMSO) reduction (Alef and Kleiner 1989) is a sensitive and rapid method for evaluating potential microbial activity, considering the lack of a method to determine actual activity (Sparling and Searle 1993).

Water-extractable organic carbon (WEOC) is the organic substrate that is immediately accessible to soil microorganisms (McGill et al. 1986). According to Zsolnay (1996), its main sources are surface and subsurface litter, including decaying roots and exudation products.

The quotient of microbial carbon to total organic carbon, $C_{mic}/C$, is used to relate soil microbial biomass to the dynamics of organic carbon. Anderson and Domsch (1989) and Sparling (1992) assume that increasing $C_{mic}$ values after land-use changes indicate future increase of organic C as well, and vice versa.

The Brazilian savannas, also known as the *Cerrados*, extends for almost 2 million km$^2$. Within this region, agriculture, particularly cattle ranching, has expanded enormously over the last 40 years. The area planted to pastures tripled between 1970 and 1985 (Alho et al. 1995). Sensitive indicators for changes in SOM caused by different land-use systems are needed for better management of these marginal soils. Potentially valuable indicators include soil microbial parameters.

We wanted to assess the direct and indirect effects of agriculture and pastoral use on the microbial biomass of *Cerrados* soils. Priority was given to the questions of (1) whether soil microbial biomass could serve as an indicator of sustainable land use with regard to SOM, and (2) whether this parameter is correlated with potential microbial activity and soil C pools.

## Materials and Methods

### *Study area and land-use systems*

The study area and its climate are described in Chapter 15, page 174. A clayey soil, classified as a very fine, allitic, isohyperthermic, Anionic Acrustox, was used for the study. Clay, silt, and sand contents in the surface horizons (0-10 cm) were 68%, 7%, and 25%, respectively (Neufeldt et al. 1998). Seven land-use systems, six of which were established and managed by commercial farmers, were analyzed:

Pine reforestation;

Two continuous cropping systems with maize and either no tillage (CCN) or conventional tillage (CCT);

Three pasture systems: degraded, improved pure-grass, and improved grass-legume (see "Clayey soil" in Table 1, Chapter 15, page 176, for data on management and fertilization); and

Native savanna, carrying the original vegetation that had been dominant before cultivation. It was used as reference.

Because the systems were located at no more than 2000 m from each other, we assumed identical edaphic and climatic conditions.

### *Soil sampling and storage*

Samples were taken three times: in September 1995, at the end of the dry season; in December 1995, and February, 1996 during the rainy season. For each system, sampling took place along three transects of about 100 m long. On each transect, eight subsamples were taken from the 0-10 cm topsoil by means of an Edelman auger and pooled. To measure microbial biomass, samples were stored at field moisture and at about 4 °C. For all other analyses, subsamples were air-dried and sieved through a 2-mm mesh. Visible roots were picked out from either sample type.

### *Chemical analyses*

Total C and N were measured with a C/N analyzer (Elementar Vario EL), using ground soil samples. Water-extractable organic carbon was extracted, using deionized water at room temperature (20 °C) and a soil-to-water ratio of 1:2.5. Extraction was done in an end-over-end shaker at about 60 rpm for 1 h. After centrifuging, the extracts were filtered through a membrane (0.45 µm, Gelman Supor). Carbon in the extracts was determined, using a Shimadzu Total Organic Carbon Analyzer TOC 5050. Three samples per field were analyzed. In the laboratory, measurements were performed in triplicate.

### *Soil microbiological analyses*

One week before analysis for $C_{mic}$, all the samples were passed through a 2-mm sieve, and visible roots were removed. The samples were then preincubated at a temperature of 30 °C (water content was about 70% of water-holding capacity) (Kirchmann and Eklund 1994). Because moisture is the most important factor for seasonal microbial biomass variability, incubation reduces the influence of short-term soil moisture dynamics on the measurements (Cattelan and Vidor 1990; McGill et al. 1986). Incubation also diminishes the effects of soil structure on microbial biomass and the influence of living roots that still remain in the sample after soil preparation (Sparling et al. 1985).

Soil microbial carbon was determined by a fumigation extraction procedure, developed by Vance et al. (1987), in which fumigation time was 24 h and extraction on a horizontal shaker at about 150 rpm took 1 h. Carbon was then determined by dichromate oxidation. To calculate $C_{mic}$ values, a quotient $k_{EC}$ was needed to describe the proportion of $C_{mic}$ actually mineralized and extracted, and was set at 0.38 for all systems (Joergensen 1996).

Potential microbial activity was assessed as described in Chapter 15, pages 175 and 177.

## Results

### *Chemical parameters*

Soil chemical data presented below refer to the samples taken in February 1996 (see “Clayey soil” in Table 2, Chapter 15, page 178):

1. The $pH_{H_2O}$ ranged from 4.7 under pine to around 6 under pastures and CCT.

2. Carbon contents showed relatively few differences and ranged from 2.0% to 2.6%. They were highest under pastures and lowest under CCT and pine.

3. For WEOC, a clear distinction between two different groups could be made: WEOC values under native savanna and pasture fields were nearly twice as high as those under pine and the two cropping systems.

4. Nitrogen contents ranged from 0.11% to 0.16%, and presented a similar picture to C, with small differences between treatments. The exception was pine, with a comparatively low N content, and thus the highest C/N ratio.

### *Soil microbial carbon and microbial activity*

With regard to $C_{mic}$, the systems could be divided into two groups as for WEOC, with the native savanna and pastures on the one hand, showing higher values, and the crops and forest on the other (Table 1). These results were consistent over the three sampling dates. For the native savanna, $C_{mic}$ remained constant over that time. Values of the pastures fluctuated more. Thus, they could not be ranked with regard to $C_{mic}$, although levels under the grass/legume pasture were always higher than those under the degraded pasture. Values for CCN were highest at the end of the dry season, decreasing and remaining unchanged during the rainy season. For the forest, $C_{mic}$ was about 20% lower in the samples from February 1996 than in those taken before. The CCT was sampled only in February 1996 and showed $C_{mic}$ values that were slightly lower than CCN.

Potential microbial activity was lowest in the forest and crop systems (Table 1). Activity values for the pastures were higher than those of the native savanna, but they showed no clear differences between each other.

## Discussion

### *Contents and temporal variations of soil microbial carbon*

With about 2% to 3% of C, $C_{mic}$ contents measured in this study were similar to those found in soils of other regions of the world (Table 2; Jenkinson and Ladd 1981). As we observed low temporal variations in microbial biomass, we discuss only the last sampling date. The slight decline in $C_{mic}$ over time for most treatments may be explained by preincubation effects rather than by factors in the actual field situation. At the end of the dry season, easily mineralizable material could have been more abundant than during the later rainy season. It might have offered a substrate for rapid

Table 1. Soil microbial carbon and microbial activity in the dry seasons and according to land-use systems on a clayey Oxisol of the Brazilian savannas (mean ± SD).

| Land-use system | Soil microbial carbon (μg/g soil) | | | DMSO[a] reduction (μg/g soil per hour) |
|---|---|---|---|---|
| | Sept 1995 | Dec 1995 | Feb 1996 | Feb 1996 |
| Native savanna | 743 ± 30 | 728 ± 17 | 718 ± 89 | 0.68 ± 0.10 |
| Forest | 600 ± 83 | 560 ± 47 | 455 ± 49 | 0.49 ± 0.01 |
| Crop with no tillage | 578 ± 54 | 491 ± 32 | 465 ± 13 | 0.48 ± 0.04 |
| Crop with tillage | n.m.[b] | n.m.[b] | 428 ± 22 | 0.45 ± 0.05 |
| Degraded pasture | 769 ± 20 | 697 ± 25 | 684 ± 56 | 0.97 ± 0.12 |
| Grass pasture | 686 ± 44 | 764 ± 13 | 751 ± 27 | 0.94 ± 0.06 |
| Grass/legume pasture | 838 ± 40 | 860 ± 33 | 730 ± 44 | 1.09 ± 0.23 |

a. DMSO = dimethyl sulfoxide.
b. n.m. = not measured.

Table 2. Relationships between soil microbial carbon ($C_{mic}$), water-extractable organic carbon (WEOC), and other parameters analyzed in soil samples from a clayey Oxisol of the Brazilian savannas.

| Land-use system | $C_{mic}$/C (%) | WEOC/C (%) | WEOC/$C_{mic}$ (%) | N/$C_{mic}$ (mg/mg) | DMSO-red./$C_{mic}$ (µg DMS per hour per mg $C_{mic}$)[a] |
|---|---|---|---|---|---|
| Native savanna | 3.2 | 0.46 | 14 | 2.0 | 1.0 |
| Forest | 2.2 | 0.31 | 14 | 2.5 | 1.1 |
| Crop with no tillage | 2.1 | 0.26 | 13 | 3.1 | 1.0 |
| Crop with tillage | 2.1 | 0.25 | 12 | 3.0 | 1.1 |
| Degraded pasture | 2.7 | 0.46 | 17 | 2.3 | 1.4 |
| Grass pasture | 3.1 | 0.44 | 14 | 2.0 | 1.3 |
| Grass/legume pasture | 2.9 | 0.47 | 16 | 2.1 | 1.5 |

a. DMSO-red. = reduction of dimethyl sulfoxide; DMS = dimethyl sulfide.

microbial growth when optimal moisture conditions were created artificially.

### *Soil microbial carbon and land management*

Contents of $C_{mic}$ found in the different land-use systems generally correspond well to the results of other studies. The comparably low values of $C_{mic}$ under pine coincide with Sparling's results (1992) from a comparison of microbial biomass under such a forest with that under different pastures and crops on allophanic soils in New Zealand. The trees extended most of their roots in the humus layer, presumably because of a better nutrient supply there. Because microbes encounter the best living conditions in the rhizosphere (Smith and Paul 1990), they should accumulate in this humus layer rather than in the mineral soil. This assumption is supported by Kolk (1994), who measured high $C_{mic}$ values of about 2000 µg/g dry material in a Oa horizon under a German pine forest.

For both cropping systems, a clear decrease in soil microbial biomass was observed, compared with native savanna (Figure 1). This agrees with a study by Kirchmann and Eklund (1994) in which they compared savanna woodland with an adjacent field cropped with maize and groundnuts in Zimbabwe. They found significantly lower $C_{mic}$ values in the topsoil of the cropping system. They explained this as a result of reduced ground cover and lower inputs of organic matter (OM). Cattelan and Vidor (1990), working in southern Brazil, also used the argument of differences in ground cover to explain that microbial biomass was lower under cultivation than under native grasslands.

Moreover, such differences in ground cover may explain why the no-tillage system tended to have a slightly higher microbial activity than the tilled one (Figure 1). However, because the no-tillage system was established only in 1994, the observation may be speculative, even though other authors working in temperate regions reported similar findings (Carter 1986; Carter and Rennie 1982; Elsner and Blume 1993; Franzluebbers and Arshad 1996). When analyses of different soil depths were compared, gains of microbial biomass in the upper layers of a no-tillage system were often

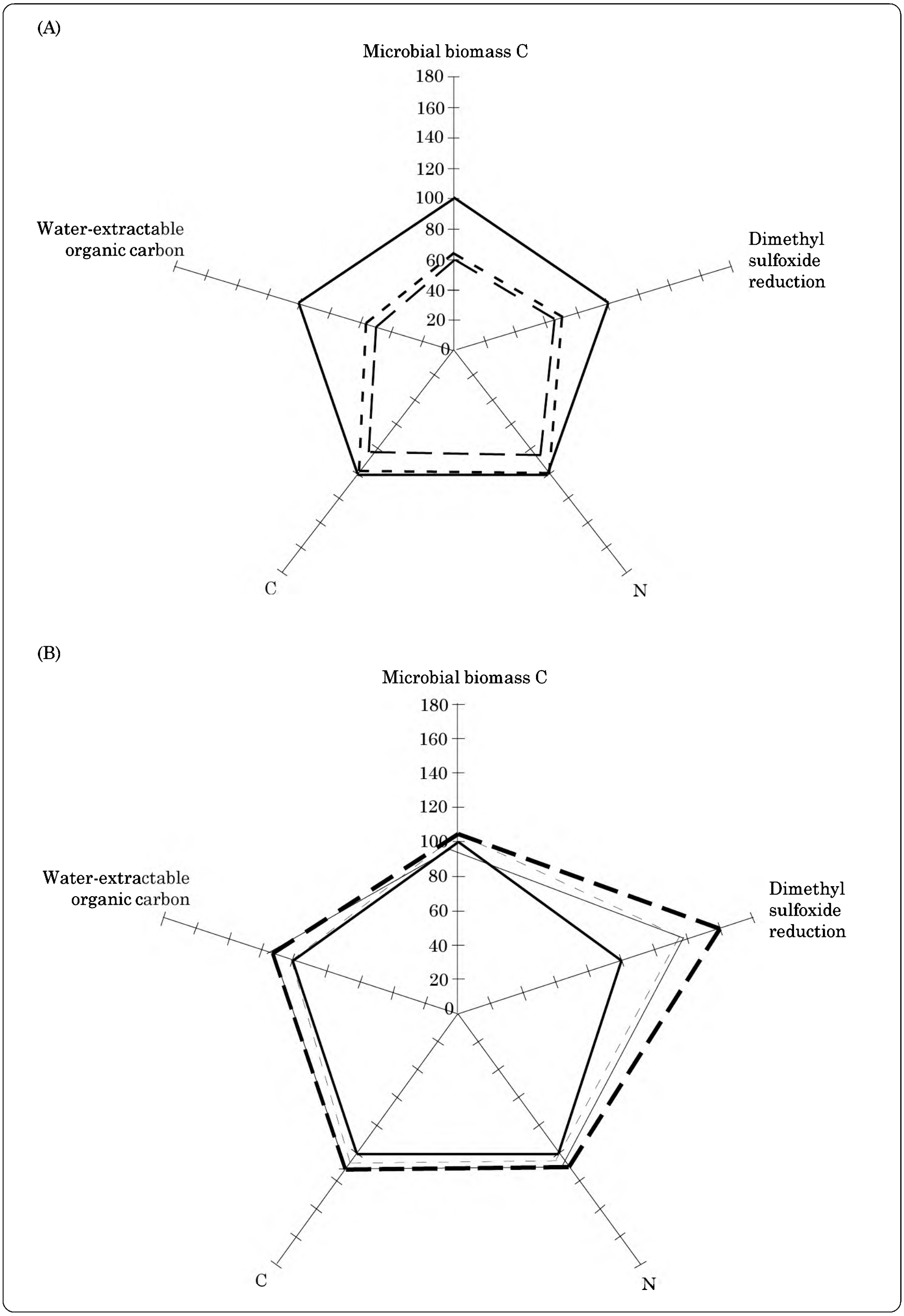

Figure 1. Star plots comparing cropping systems (A) and pastures (B) with native savanna for soil microbial and chemical parameters. Values are set at 100% for the savanna. Soil samples were taken from a clayey Oxisol of the Brazilian savannas. (——— = native savanna; – – – – – – = cropping with no tillage; — — — = cropping with tillage; ——— = degraded pasture; – – – – – – = pure-grass pasture; ▬ ▬ ▬ = grass/legume pasture.)

found to be balanced over time by respective losses in the subsoil (Carter and Rennie 1982).

The high $C_{mic}$ values found in the pastures, compared with the cropping systems, agree with results obtained in several other studies (Beck 1984; Carter 1986; Cattelan and Vidor 1990; Sparling 1992). All authors explained $C_{mic}$ accumulation in pastures as being caused by high root densities and OM inputs. The assumption that root distribution could have been an important parameter in the given systems has been confirmed by MA Ayarza and L Vilela (unpublished data), who found higher root densities under native savanna and pastures than under cropping systems and forest.

Although differences were clearly visible between the three pastures with regard to aboveground biomass, variations in both $C_{mic}$ and C were limited. This contrasts with Sparling's findings (1992) when he compared an unfertilized with a fertilized pasture on a clayey loam. He found about 20% higher microbial biomass and C values in the top 5 cm of soil under the improved treatment. However, these systems had been established 35 years previously and the improved pasture had been fertilized and resown regularly.

## *Soil microbial carbon and microbial activity*

Potential soil microbial activity was closely correlated with $C_{mic}$ (Table 3). The ratio of the two parameters, expressed as DMS/$C_{mic}$, could be used to indicate the conditions that microbes meet under different treatments. Respective ratios of the pastures were well above those of the other treatments and native savanna (Table 2). This indicates that microbes in the pastures have been the most active, possibly because of an abundance of fine roots that is typical of such systems (Follett and Schimel 1989).

## *Soil microbial carbon and other soil carbon pools*

The main parameters assumed above to explain $C_{mic}$ in different management systems were soil cover, organic inputs, and roots. The key link between those parameters and $C_{mic}$ seems to be WEOC. A product of surface and subsurface litter decay and root exudates, it probably forms the principal source of microbe-available C (McGill et al. 1986; Zsolnay 1996). The high correlation between WEOC and $C_{mic}$ that we obtained in our study confirms this assumption (Table 3). The fact that WEOC made up only 10% to 20% of $C_{mic}$ (Table 2) shows that either it had an extremely high turnover rate (McGill et al. 1986; Zak et al. 1990) or that a high proportion of bacteria and fungi was dormant (Smith and Paul 1990). Based on the assumption of WEOC as the main source of C, the quotient of WEOC to $C_{mic}$ could be used as an indicator in how far microbes were C-limited. It

Table 3. Correlations between $C_{mic}$, soil microbial activity as measured by DMSO[a] reduction, and chemical parameters (Spearman's Rho). Marked values are significant at $P < 0.01$ (**), < 0.001 (***), < 0.0001 (****) for n = 21.

| | $C_{mic}$ | DMSO reduction |
|---|---|---|
| $C_{mic}$ | | 0.82**** |
| DMSO reduction | 0.82**** | |
| C | 0.79**** | 0.84**** |
| N | 0.71*** | 0.76**** |
| WEOC[b] | 0.83**** | 0.92**** |
| $pH_{H_2O}$ | 0.07 | 0.19 |

a. DMSO = dimethyl sulfoxide.
b. WEOC = water-extractable organic carbon.

was lower in the cropping systems than in most of the pastures (Table 2). Thus C-limitation may have been of greater importance for the cropping systems with their reduced litter input. Schimel (1986) also found that microbes were C-limited in agriculturally used fields, whereas N-limitation was dominant in pastures. For the given soil data, such a N-limitation is indicated by the N/$C_{mic}$ ratios being lower in the pastures than in the crop systems (Table 2). However, measurements of microbe-available labile N would be needed to verify this assumption.

The close link of $C_{mic}$ to the C cycle in soil is confirmed by the close correlation of $C_{mic}$ with C (Table 3), thus agreeing with the results of other studies. In a long-term field experiment, correlation coefficients above 0.9 have been found for $C_{mic}$ and C on agriculturally used plots (Houot and Chaussod 1995). Zak et al. (1990) examined a succession on an old field and found an $R^2$ of 0.87.

The $C_{mic}$/C quotients found for the different systems correspond well with those obtained by Anderson and Domsch (1989), Sparling (1992), and Srivastava and Singh (1988). With their $C_{mic}$/C quotients being about one-third lower than that of native savanna, neither the cropping systems nor the pine forest can be considered as sustainable with regard to soil organic carbon, which is predicted to possibly decline even further. In contrast, the pastures may have reached stability in soil organic carbon levels. Similar conclusions have been drawn by Sparling (1992) who found an obvious decline in the $C_{mic}$/C ratio with continuous cropping over time, which he explained by the decreased OM input, compared with permanent pasture.

# Conclusions

Land management was shown to strongly influence soil microbiology. Microbial carbon declined under both cultivation and pine. For the topsoil of the CCN system, cultivation effects seemed to have been slightly less negative than for the CCT system. The establishment of pastures had no obvious effect on microbial biomass and even stimulated microbial activity. Thus, the ratio of microbial activity to microbial carbon was higher under pastures than under native savanna.

According to data, which showed a clear relationship between WEOC and $C_{mic}$, WEOC is possibly the most important C source for microbes. It consists mainly of root exudates and litter degradation products. Apart from soil physical parameters, which were not in the scope of this study, root density, OM input, and soil cover were therefore assumed to be major parameters causing land use to have an impact on $C_{mic}$. However, the microbes of all systems may not have been C-limited to the same extent. The WEOC/$C_{mic}$ ratios indicated that C-limitation was most pronounced in the cropped fields. As N/$C_{mic}$ ratios show, microbes under pastures may even have been N-limited.

Differing OM inputs in the systems were reflected by the C contents which, however, varied much less between the systems than did $C_{mic}$. Water-extractable organic carbon and, consequently, microbial biomass reacted much more rapidly to changes in land use than total C. Data thus indicate that the $C_{mic}$/C ratio can be put forward as a fairly useful indicator of sustainability with regard to soil organic carbon development for highly weathered tropical soils. According to this ratio, the pastures were sustainable, whereas the cropping systems and pine forest were not.

In summary, results showed that findings obtained in other regions of the world can also be applied to the soils of the Brazilian *Cerrados*. Further research still needs to be carried out, especially with regard to the function of WEOC as a key link between $C_{mic}$ and land management and the possible differences in soil microbiology between varying pasture systems.

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# CHAPTER 17

# Organic Matter in Termite Mounds of the Brazilian *Cerrados*

*Wolfgang Zech, Wulf Amelung,* and *Henry Neufeldt**

## Abstract

This study assessed differences between soil organic matter (SOM) in termite mounds and that of surrounding clayey and loamy Oxisols in the Brazilian savannas, also known as the *Cerrados*. Samples were fractionated into clay (<2 μm), silt (2-50 μm), and sand (50-250 μm), and the fractions' SOM was characterized according to C, N, lignin, and carbohydrates. In the mounds, soil organic carbon (SOC) is enriched by a factor of 3.5 and 11.5 in the clayey and loamy Oxisols, respectively. Especially in the sand fraction, the SOC accumulated as particulate SOM. However, in all size fractions, we found higher lignin contents, lower ratios of acids to aldehydes of lignin-derived phenols, and lower ratios of microbial to plant-derived monosugars than in the fractions of the surrounding soil. These findings suggest that the SOM of the mounds is less decomposed.

*Keywords:* Brazilian savannas, carbohydrates, *Cerrados*, lignin, Oxisols, soil organic matter, termites

## Introduction

Termites probably contribute to soil fertility by replenishing organic compounds in the soil (Varma et al. 1994). The termites consume litter, excrete most of the organic material, which accumulates in the mounds until the colonies die, when the mounds usually become reincorporated into the soil, and thus contribute to the selective allocation of soil nutrients (Martius 1994; Salick et al. 1983).

Sugars inside the termite gut are either digested by cellulase produced by the termite itself or consumed by a symbiotic community of hemicellulose-degrading microorganisms (Schäfer et al. 1996; Varma et al. 1994). Although the role of this gut microflora in lignin turnover is still controversial (Cookson 1992; Varma et al. 1994), the overall effect is the alteration of organic matter as it passes through the gut. The composition of soil organic matter (SOM) in termite mounds is therefore different to that of the surrounding soil (Arshad et al. 1988). Little is known, however, about the decomposition of saccharides and lignin in termite mounds under field conditions.

Particle-size fractionation is useful for identifying SOM pools at various degrees of decomposition (Christensen 1992). We therefore compared the lignin and carbohydrate signatures in

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particle-size fractions obtained from two termite mounds and surrounding topsoils.

## Materials and Methods

### *Samples*

Samples were collected from the tops of termite mounds and surrounding topsoils at two sites on native savanna near Uberlândia, Brazil. The mounds belonged to termites of the *Armitermes* genus in a clayey Oxisol (very fine, isohyperthermic, Anionic Acrustox) and the *Dihoplotermes* genus in a loamy Oxisol (coarse-loamy, isohyperthermic, Typic Haplustox).

### *Particle-size fractionation*

Bulk samples, dry-sieved to remove >2-mm particles, were treated ultrasonically at 1500 J/mL with a probe type sonicator (Heat Systems, model W 185 F) in a soil-to-water ratio of 1:10. Aggregates that resisted this intense treatment were pressed mechanically through a 50-µm sieve. After separating the remaining 50-2000-µm sand fraction, the clay fraction (<2 µm) was separated from silt (2-50 µm) by centrifuging. Samples of all fractions were dried at 40 °C (Christensen 1992) and ground for chemical analysis.

### *Soil analysis*

Subsamples of the fine-earth and clay-size fractions were analyzed for total C, N, and S with a C/N/H/S-analyzer (Elementar). Because the samples did not contain lime, the total C determined was organic in nature.

The amount and degree of oxidative lignin decomposition were estimated from lignin parameters, using a modified alkaline CuO oxidation procedure at 170 °C for 2 h (Hedges and Ertel 1982). Sugars were determined according to Amelung et al. (1996), after hydrolysis with 4 *M* trifluoroacetic acid at 105 °C for 4 h.

After size fractionation, the average recovery, relative to the concentrations of the bulk-soil samples, was 119% for lignin-derived phenols and 105% for neutral sugars, suggesting that no significant losses of lignin or sugars occurred during ultrasonic treatment and size fractionation. Because the recovery rate of hexoses and pentoses averaged 103%, we conclude that microbial transformation of SOM because of sample rewetting and drying did not occur.

## Results and Discussion

### *Particle-size distribution*

The yields of sand, silt, and clay were similar for both mound and clayey topsoils, suggesting that the activity of *Armitermes* sp. does not affect soil texture at this site. The mounds inhabited by *Dihoplotermes* sp., however, showed higher silt and lower sand contents than the surrounding soil, whereas the yields of clay fractions were similar.

### *Soil organic carbon and N*

The termite mounds contain 90.2 g/kg organic C in the clayey and 109 g/kg in the loamy Oxisols, compared with 26.1 and 9.5 g/kg C in the respective surrounding topsoils. Nitrogen was enriched by a factor of 3 and a factor of 7 in the mounds of clayey and loamy Oxisols, respectively. Obviously, termite mounds provide an important sink for SOM in savanna ecosystems.

Although, in this study, the accumulation of organic matter in the mounds of both loamy and clayey Oxisols was not restricted to a particular size fraction, it was most pronounced for the SOC concentrations of particulate organic matter (POM) in the sand fractions. In the mounds inhabited by *Armitermes* sp., POM concentrations in the sand exceeded those of the surrounding soil by a factor of 10; in the mounds of *Dihoplotermes* sp., by a factor as high as 70.

For all samples, the SOC concentrations in silt exceeded those in clay. The concentration of POM of the sand fractions was lower than that of the clay fractions, except for the mounds of *Armitermes* sp. in the clayey Oxisol, where POM was 149, compared with 41 g/kg sand in loamy soil under native savanna. Obviously, most of the organic matter stored in the mounds of *Armitermes* sp. is particulate in nature, which may be attributed to *Armitermes* feeding on intact wood (K Kitayama 1996, personal communication).

## *Lignin signature*

Alkaline CuO oxidation releases phenols from reactive sites of the lignin macromolecule. Consequently, the sum of vanillyl, syringyl, and cinnamyl phenolic CuO oxidation products (VSC) gives a directly proportional, relative measure of the total lignin, that is, the VSC-lignin. Absolute lignin contents cannot be determined, because the contribution of VSC-lignin to total lignin is unknown. The mass ratio of acid-to-aldehyde for vanillyl and syringyl units $[(Ac/Al)_{V,S}]$ is used to determine the degree of oxidative decomposition of lignin within a sample. In contrast, selective losses of syringyl units during lignin degradation are reflected by the mass ratio of syringyl to vanillyl units (S/V) (Ertel and Hedges 1984).

The highest concentration of VSC-lignin is found in the POM in sand fractions. With decreasing particle size, the amount of lignin-derived phenols (in g/kg SOC) decrease, that is, from sand > silt > clay. Increasing ratios of phenolic acids-to-aldehydes with decreasing particle size confirm Guggenberger et al.'s findings (1994) that the finer the particle size of this fraction, the more altered is that fraction's SOM.

In the mounds, VSC concentrations are significantly higher (90 g/kg soil in fine-textured and 51 g/kg soil in coarse-textured mounds of *Armitermes* sp. and *Dihoplotermes* sp., respectively) than in the corresponding, surrounding topsoil (14 and 21 g/kg SOC). This can be attributed to the preferential accumulation of POM rich in VSC. Because the trend is sustained for the finer particle-size fractions, such as clay (Figure 1), we conclude that termite activity in the Brazilian savannas enriches the soil with plant-derived structures such as lignin.

## *Carbohydrate signature*

Individual ratios of sugar monomers can be used to estimate the relative contribution of microbially derived

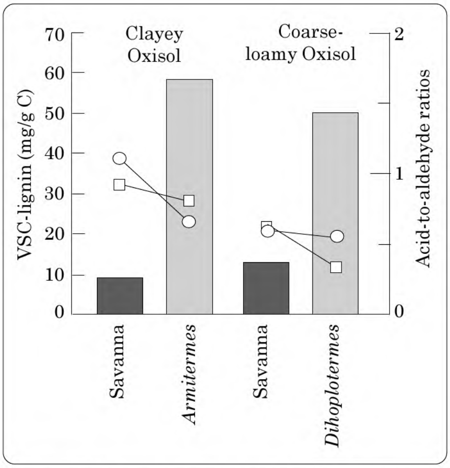

Figure 1. Lignin signature in the clay fraction of termite mounds (☐) and topsoils of the surrounding savanna (■). Samples were taken from two Oxisols (one clayey and one coarse-loamy) of the Brazilian savannas. ○ = $(Ac/Al)_V$; ☐ = $(Ac/Al)_S$; see text for explanation of these ratios.

saccharides to the soil's sugar composition. Microorganisms synthesize little, if any, pentose, and xylose and arabinose are important components in plant cells. Different ratios of galactose + mannose (gal+man) to arabinose + xylose (ara+xyl) would therefore indicate levels of microbial contribution to the sugar spectrum (Oades 1984). In addition, Murayama (1984) attributes increasing ratios of fucose + rhamnose (also synthesized by microorganisms; fuc+rham) to (ara+xyl) to the preferential, microbial production of deoxysugars.

In both Oxisols, the highest concentration of neutral sugars occurred in the clay fraction of the surrounding topsoils at a rate of about 200 g of carbohydrates per kilo of SOC in clay. In the termite mounds, the highest sugar concentrations were found in POM of the sand separates (170-190 g of saccharides per kilo of SOC in POM), whereas those of the clay fractions were substantially lower (<150 g of saccharides per kg of SOC; Figure 2). This suggests that the turnover of saccharides in the mounds differs from that in the surrounding Oxisol.

Increasing ratios of hexoses to pentoses with decreasing particle size confirmed other authors' findings that microbially derived compounds contribute more to the SOM of finer fractions than than they do to coarser fractions (Christensen 1992; Guggenberger et al. 1994). In the native savanna, the (glu+man)/(ara+xyl) and (fuc+rham)/(ara+xyl) ratios of all fractions exceeded those of the corresponding fractions obtained from the mounds by a factor between 1.3 (clay fraction, clayey Oxisol, Figure 2) and 5.4 (silt fraction, clayey Oxisol). This result agrees with findings of the lignin analyses: that SOM, especially that which has been little altered by microbes, accumulates in the termite mounds, despite an effective saccharide degradation in the termite gut (Varma et al. 1994).

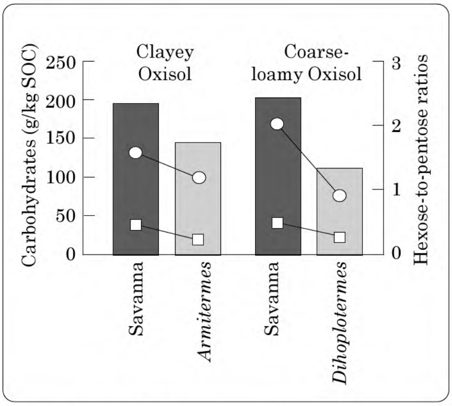

Figure 2. Carbohydrate signature in the clay fraction of termite mounds (☐) and topsoils of the surrounding savanna (■). Samples were taken from two Oxisols (one clayey and one coarse-loamy) of the Brazilian savannas. ○ = (gal+man)/(ara+xyl); □ = (fuc+rham)/(ara+xyl); see text for explanation of these ratios.

# Conclusions

In the Brazilian savannas, termite mounds inhabited by *Armitermes* sp. and *Dihoplotermes* sp. have higher SOM contents than the surrounding Oxisols. In all size separates of the termite mounds, SOM is less decomposed than that in the surrounding soil, as indicated by higher lignin contents, lower ratios of acids-to-aldehydes of the vanillyl and syringyl structural units of lignin, and lower ratios of microbially to plant-derived monosugars. The termites in this region therefore selectively choose fresh and partly decomposed organic matter for their mounds, which then form an important, temporary sink of carbon and nitrogen for this tropical ecosystem.

## Acknowledgments

We are most grateful to Prof. Emeritus Dr. Kiniti Kitayama for identifying the termite genera.

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## CHAPTER 18

# Pesticides in Soil, Sediment, and Water Samples from a Small Microbasin in the Brazilian *Cerrados*

*Volker Laabs, Wulf Amelung,* and *Wolfgang Zech**

## Abstract

The expansion of intensive agriculture in the tropics is leading to increasing concern about environmental pollution from pesticides in these regions. This study was conducted in the Brazilian savannas, also known as the *Cerrados*, near Uberlândia, to determine the magnitude of biocide concentrations in the small catchment of the Pantaninho stream and its reservoirs. Samples of soils, surface and well water, and sediments were collected on 10-12 December 1995, and analyzed for 15 herbicides and insecticides. In all surface-water samples, atrazine was detected at concentrations of 0.05-0.13 µg/L. The sampled well water (used for drinking) on farms did not contain detectable residues of biocides. Sediments, taken from the stream's banks, were contaminated at two sampling locations with either λ-cyhalothrin (at 4.0 µg/kg) or simazine (at 3.2 µg/kg). Soil samples from maize fields usually showed higher concentrations of simazine, atrazine, and chlorpyrifos (ranging from 80 to 180 µg/kg at 18 to 35 days after application) than did those from soybean fields. Fluazifop-butyl, monocrotophos, and λ-cyhalothrin were found 0-8 days after application at concentrations between 5 and 25 µg/kg. Carry-over residues of metolachlor, atrazine, simazine, cyanazine, and trifluralin were also detected at concentrations of around 2-15 µg/kg, indicating that pesticides can accumulate in tropical soils. Sampling at depth in a maize field proved that simazine and atrazine, although mainly restricted to the top 10-cm layer (40-120 µg/kg), are highly mobile, as was triazine, which was continuously detected at the maximum sampling depth (70 cm) in concentrations of 2-4 µg/kg. Although, when compared with temperate regions, these concentration levels of biocides were medium to low, they showed a potential for accumulation and leaching, which, over the long term, may lead to pollution of water resources.

*Keywords:* Brazilian savannas, *Cerrados*, environmental pollution, Oxisols, pesticides, water

## Introduction

Pesticide use is increasing worldwide, especially in tropical regions, where agriculture is still expanding. Although pesticide applications have become an integral part of agriculture in the Brazilian savannas (also known as the *Cerrados*), few studies have been conducted on the behavior of these

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substances in this environment. A sustainable development of the *Cerrados* means, among other things, that pesticides do not accumulate in significant quantities in soils nor contaminate water resources, whether surface or underground, or for drinking purposes.

In temperate regions, many studies have been conducted to evaluate the threat that pesticide applications pose for the environment. As growing numbers of biocides were detected in surface and underground waters of Europe (van den Berg and van den Linden 1994) and the United States of America (Ritter 1990), research concentrated on identifying and quantifying the input processes to the water bodies. Because of their high mobility and persistence, several compounds, such as atrazine, were consequently restricted in their use (Hanson et al. 1997) or banned from further application (Heintz and Reinhardt 1993). But many drinking water resources had already been polluted and annual costs for purification (e.g., in Germany, 250 million Deutsche marks per year) are high. Even though biocides are known to degrade much more rapidly in tropical environments, some studies indicate that certain pesticides persist in tropical soils for relatively long periods (Ferreira et al. 1988; Machado-Neto and Victória-Filho 1995). Research on the behavior of biocides in tropical environments is therefore needed to ascertain if pesticide application will lead to contaminated water and soil resources.

In this study, biocide concentrations in an agricultural microbasin of the *Cerrados* are measured in soil, sediments, and surface and underground water to give a first approximation of the magnitude of biocide levels in this ecosystem.

## Materials and Methods

### *Study site and sampling strategy*

The study was conducted in the microbasin of the Pantaninho stream, which is located about 10 km west of Iraí de Minas, central Brazil. The surface area of this catchment is about 20 km$^2$, with medium to low slopes toward the stream's banks. Sampling sites are shown in Figure 1.

Agriculture in this area is dominated by soybean and maize production, which comprises about 80% of the planted area. Besides conventionally tilled and no-tillage fields, many plots are pivot-irrigated.

To assess the environmental impact of pesticide use, farm soils, the surface waters and sediments of the Pantaninho stream, and underground water from farmers' wells were sampled and analyzed for biocides. Sampling was done during 10-12 December 1995, when most of the major herbicides and insecticides (fluazifop-butyl, haloxyfop-methyl, trifluralin, monocrotophos, and $\lambda$-cyhalothrin) for soybeans are applied and about 3 weeks after the last application of the major herbicides and insecticides (atrazine, cyanazine, and simazine; chlorpyrifos and metolachlor) for maize.

The catchment of the Pantaninho stream within the study area (Figure 1) was sampled from the source (at W1 in Figure 1) down to the last reservoir (W5) before its junction with the next stream. The sediment samples were taken along the stream's banks at the same locations as the surface-water samples, except at the stream's source, where no sediment sample could be collected because of swamp, with its intensive growth of algae and water plants. An

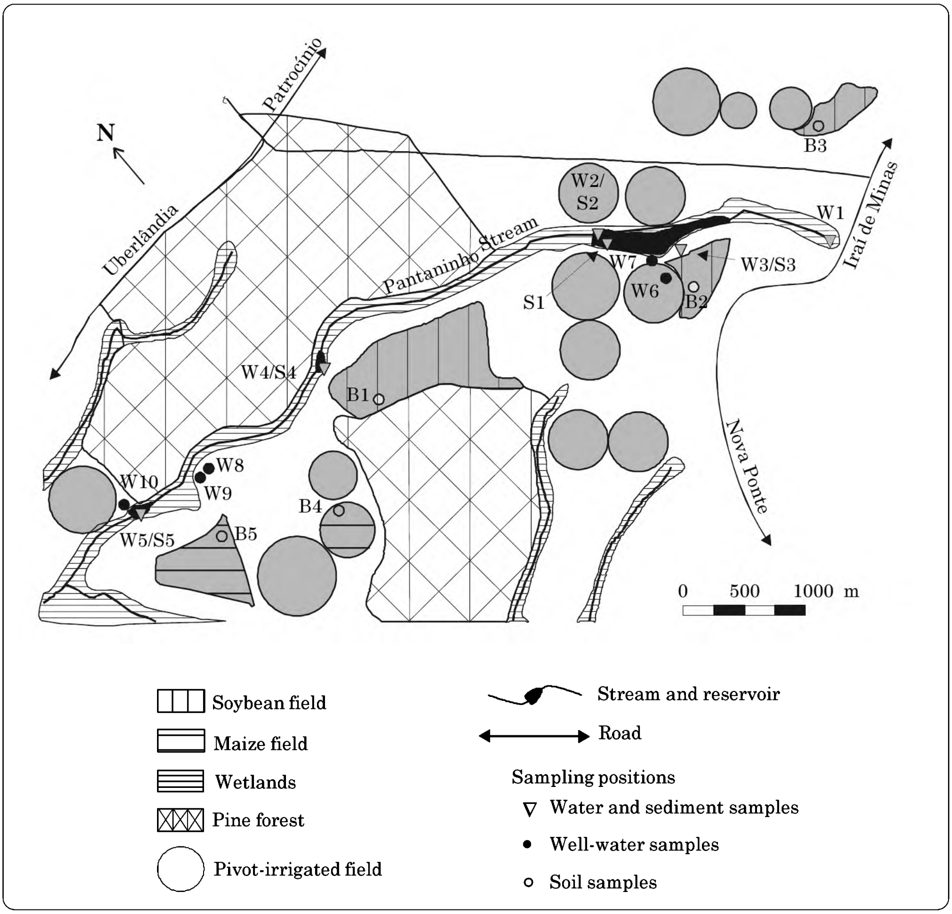

Figure 1. Microbasin of the Pantaninho stream, showing sampling sites for determining biocides levels in the savanna environment of central Brazil.

additional sediment sample was therefore taken at S1, where a small erosion creek led into a big reservoir. Samples of well water were taken at three farms within the valley at various depths, ranging from 5 to 60 m.

Soil samples were taken from soybean and maize fields (tilled, not tilled, and irrigated), which covered most of the cultivated area in this valley. In one maize field (B5), samples were taken as deep down as 70 cm to evaluate pesticide mobility.

## *Sampling*

***Surface-water samples.*** One-liter samples were taken from the top 20-cm layer of the stream water or reservoir water. The samples were collected in brown glass bottles, which had been rinsed with acetone and hexane and heated to 200 °C before being used. To minimize losses by adsorption, the bottles were rinsed three times with the water at the sampling site immediately before the sample was taken. The samples were then stored under ice (0-4 °C) until analysis at the Universidade Federal de Uberlândia (UFU).

***Sediment samples.*** At each sampling site, five single samples were taken at 1-m intervals along the banks of the stream or its reservoirs, using only the top 5 cm of sediments resting at no deeper than 50 cm in the water. Visible organic material was removed, and the samples pooled into one composite sample. All the composite samples were then stored in plastic bags under ice until they were air-dried for 3 days, then frozen at -20 °C until analysis at Bayreuth University (BU).

***Well-water samples.*** One-liter samples, collected in bottles similar to those used for the surface-water samples, were taken from the pumping hoses of each well. The well was first pumped for a short period to ensure that the water delivered was fresh. As for the other samples, these samples were stored under ice until analysis.

***Soil samples.*** Nine single samples of soil were taken from the top 5 cm in a 3 x 3 m grid (50-m side length), placed diagonally to treatment direction to avoid multiple samples from one treatment row. The samples were pooled into one composite sample for every field. At B5, deeper soil layers were sampled with a spade to 10 cm, then with an Edelmann-auger to 70 cm. To avoid contaminating the deeper soil samples with topsoil, only the inner core of the auger sample was used. Five single samples were taken in a 2-1-2 grid (50-m side length). The samples were stored in plastic bags, the insides of which had been previously conditioned by rubbing soil from the respective sample for 10 s, thus coating the plastic surface with soil particles. Samples were air-dried for 2 days and stored at -20 °C until analysis at BU.

## *Analytical methods*

The method used for extracting and analyzing biocides processed the 10 biocides commonly used (fluazifop-butyl, haloxyfop-methyl, trifluralin, monocrotophos, and λ-cyhalothrin for soybean; atrazine, chlorpyrifos, cyanazine, metolachlor, and simazine for maize) and the five following substances: alachlor, carbofuran, endosulfane-α, metribuzin, and triallate.

***Water samples.*** Researchers at the UFU used a solid-phase extraction (SPE) method (Laabs 1997) on the water samples. A sample was first filtered through fiberglass and, when necessary, a Whatman filter. It was then acidified to a pH of 3 and 30 g of KCl were added, and the whole sucked over glass columns, containing 2.5 g of C18, at an average flow rate of 150 mL/h. The cartridges were air-dried for about 20 min and stored at -20 °C for later analysis at BU. Suspended material (i.e., filtration residue) was air-dried for 30 min, packed in aluminum foil, and stored in the freezer until analysis.

At BU, the extraction cartridges were freeze-dried. Pesticides were eluted from the solid sorbent with hexane and ethylacetate (6 mL each). After the eluate was concentrated with a rotation evaporator, the sample was analyzed by gas chromatography (GC) and mass spectrometry (MS).

***Soil and sediment samples.*** Twenty-five-gram samples were extracted with 50 mL of a solution of acetone, ethylacetate, and water at a ratio of 2:2:1 (v/v) and shaken end-over-end for 4 h. After filtering through Schleicher & Schüll paper filters, 200 μL of toluene were added and the extract concentrated to about 10 mL by evaporation. The remaining water-toluene mixture was liquid/liquid extracted with 25 mL of methylene chloride. The procedure was repeated twice more with 25 mL of fresh methylene chloride. The organic phase was concentrated again and submitted directly to either GC/MS analysis (soil samples) or a clean-up flash-chromatography with AlOx/Florisil (sediment samples). The clean-up glass columns were wet packed in hexane with 1 g AlOx on top of 1 g Florisil (6% and 10% deactivated, modified after Balinova and Balinov 1991) and the elution of pesticides achieved with hexane and hexane/ethyl ether (1:2 v/v). The eluate was then concentrated and analyzed by GC/MS.

Suspended solids (i.e., filtration residues) of water samples were processed by the same method as for soil and sediment samples.

***Apparatus:*** A Hewlett Packard 6890 GC/MS was used to determine pesticides. Conditions were:

Column = fused silica HP-5 MS, 30 m;

Injector = 210 °C, hot-splitless injection;

Liner = cone-shaped borosilicate glass with glass-wool plug;

Oven = 82 °C, 3-ramp temperature program up to 280 °C, total time of 42.6 min; and

Transfer line = 280 °C.

The MS was operated in the selected-ion mode; three ions were monitored per substance. Quantification was done with HP-ChemStation software, using 3 to 7 point-fitting linears. The routine limits of determination were 0.05-0.25 µg/L for water samples and 1-5 µg/kg for soil samples.

## Results and Discussion

### *Water and sediments*

The results of the biocide analysis of water and sediment samples, which refer only to the 15 pesticides chosen for study, are shown in Table 1.

The drinking water from the farmers' wells did not contain residues of biocides, regardless of well depth. The surface-water samples were all contaminated with atrazine in relatively low concentrations (0.05-0.13 µg/L). At two sites (W2 and W3), concentrations exceeded limits set by the European Community (0.1 µg/L), but were well below the acceptable daily intake (ADI) values (0.7 µg/kg per day) set by the World Health Organization (WHO) for drinking water. In the filtration residues of water samples, no detectable residues of biocides were found.

At two sites of the stream (S2 and S4), residues of λ-cyhalothrin and simazine were detected in sediments taken from the stream's banks.

Because water and sediments were sampled only once, caution must be taken in interpreting the results. Determinations of pesticide concentrations in streams are well known to be influenced by sampling date in relation to the last rainfall and application of biocides. From streams of Vermont state, USA, atrazine contamination in runoff from fields of pulses was highest during the first three rain events after application. About one week after application, concentrations in water had dropped to 0.05-0.1 µg/L. A comparison of planting seasons showed that atrazine concentrations were highest when heavy rainfall occurred soon after the herbicide was applied (Gruessner and Watzin 1995). Another study showed that peak concentration of herbicides used for maize (atrazine and alachlor) in Shell Creek (a small river in Nebraska, USA) occur just before the maximum runoff, with a lower lag peak (at 1.5 days) after the main discharge (Spalding and Snow 1989).

In the Pantaninho microbasin, the last application of atrazine before sampling had been 20 days beforehand, with frequent rain events (2-10 per week) of high intensity in the

Table 1. Biocide concentrations in water (W) and sediment (S) samples taken from the Pantaninho stream and its reservoirs, savannas of central Brazil (sampling date = 12 December 1995).[a]

| Position | Site | Water concentration (µg/L) | Sediment concentration (µg/kg) |
|---|---|---|---|
| W 1 | Source of Pantaninho stream | Atrazine, 0.07 | — |
| S 1 | Big reservoir, left bank | — | n.d. |
| W/S 2 | Big reservoir, center of dam (W); both banks (S) | Atrazine, 0.13 | λ-cyhalothrin, 4.0 |
| W/S 3 | Pond at Sch. farm | Atrazine, 0.12 | n.d. |
| W/S 4 | Bridge over Pantaninho, left bank | Atrazine, 0.05 | Simazine, 3.2 |
| W/S 5 | Small reservoir, left bank | Atrazine, 0.09 | n.d. |
| W 6 | Well (5 m, Sch. farm) | n.d. | — |
| W 7 | Well (8 m, Sch. farm) | n.d. | — |
| W 8 | Well (6 m, G. farm) | n.d. | — |
| W 9 | Well (60 m, G. farm) | n.d. | — |
| W 10 | Well (14 m, S. farm) | n.d. | — |

a. n.d. = no detectable residues.

meantime. The measured atrazine concentrations do not therefore represent the peak concentrations of the herbicide in this stream, but rather the basic flux. Long-term monitoring of water concentrations would show whether the higher intensity and frequency of rain events, compared with temperate regions, leads to a greater loss of herbicides from agricultural soils in the *Cerrados*.

The farmers' wells did not contain any measurable biocide residues. The deeper underground water layers (5-60 m) are therefore not yet penetrated by contaminated water percolating from cultivated soils. As Ritter (1990) reported, the extensive contamination of underground and well water with atrazine in the maize-growing regions of the USA resulted from a slow movement of atrazine from shallow groundwater to deeper layers. A similar phenonomen is also to be expected in the Brazilian study area. Indeed, both simazine and atrazine seem to exhibit, overall, a high mobility within this savanna ecosystem (Figure 2), and may, in the long term, endanger aquatic life and drinking-water resources.

Our finding that atrazine was absent from the sediment samples agrees with those of other studies (Gruessner and Watzin 1995; Pereira and Rostad 1990), which observed that this herbicide is almost exclusively transported in the dissolved state. Spalding and Snow (1989) suggest that, even if atrazine is transported into the stream adsorbed to solid particles, it desorbs rapidly once it is in the water. The contamination of sediments at two points, albeit at low rates, with λ-cyhalothrin and simazine (water solubility = <4 mg/L) is probably a result of erosion. Biocides that have a water solubility of less than 10 mg/L are thought to be lost from fields by being transported mainly on eroded material. In contrast, pesticides with greater solubility (e.g., atrazine at 28 mg/L) tend to move in the dissolved state (Ghadiri and Rose 1993).

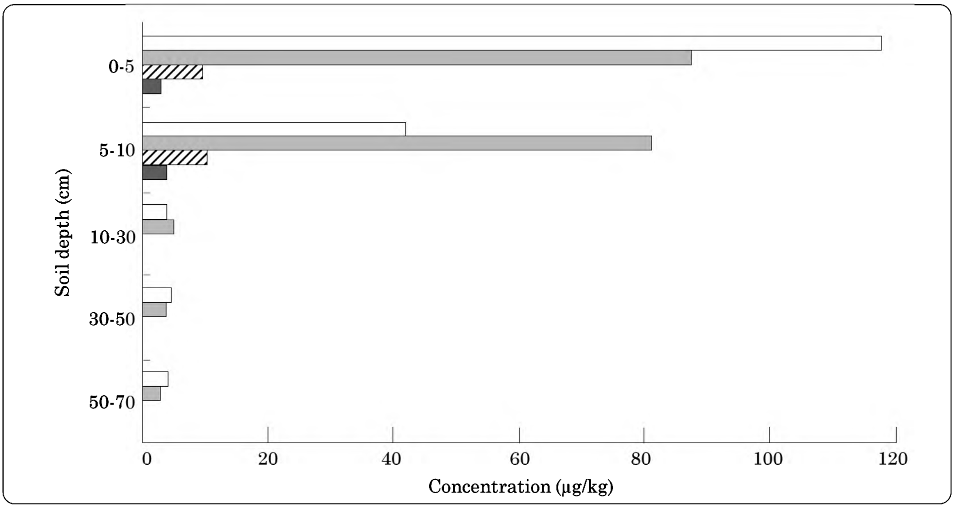

Figure 2. Distribution of pesticides in a depth profile of a soil under maize (n = 2), Pantaninho valley, savannas of central Brazil. (□ = simazine; □ = atrazine; ▨ = trifluralin; ■ = metolachlor.)

Consequently, the carefully executed measures to control erosion in the Pantaninho valley may have prevented the input of large quantities of highly contaminated topsoil into streams, thus resulting in very low levels of hydrophobic pesticides in the sampled sediments.

## Soil

The basic properties and history of biocide applications of the investigated soils are summarized in Table 2. All soils can be classified as Ferralsols, or Oxisols (FAO 1990).

The pesticide contents of the soils can be seen in Figures 3 (maize fields) and 4 (soybean fields). The herbicides typically used for maize (atrazine and simazine) were detected in concentrations between 80 and 180 µg/kg in the topsoil at 20 to 35 days after application. The insecticide chlorpyrifos was present at site B4 at concentrations of about 100 µg/kg, 18 days after use.

Table 2. Basic properties and history of biocide applications of soils sampled in the Pantaninho valley, savannas of central Brazil.

| Site | Crop[a] | $pH_{KCl}$ | $C_{org}$ (%) | Texture[b] | Biocide treatment (days after application) |
|---|---|---|---|---|---|
| B1 | Soybean (nt) | 6.2 | 2.0 | Clayey loam | Fluazifop-butyl, λ-cyhalothrin (0) |
| B2 | Soybean (nt) | 6.0 | 2.0 | Clayey loam | λ-cyhalothrin (6) |
| B3 | Soybean (nt) | 6.4 | 2.5 | Clay | Monocrotophos (8) |
| B4 | Maize (irrigated) | 6.7 | 3.4 | Silty loam | Atrazine, simazine (35), chlorpyrifos (18) |
| B5 | Maize (tilled) | 7.2 | 2.9 | Clayey loam | Atrazine, simazine (20) |

a. nt = not tilled.
b. Texture determined by finger test.

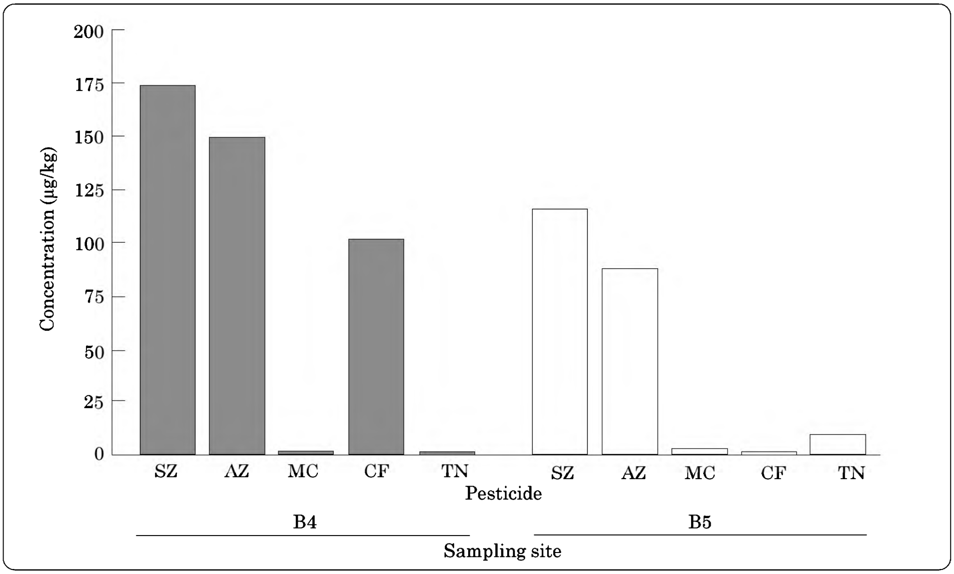

Figure 3. Pesticide concentrations in the topsoil (0-5 cm) of maize fields (n = 2), Pantaninho valley, savannas of central Brazil. SZ = simazine; AZ = atrazine; MC = metolachlor; CF = chlorpyrifos; TN = trifluralin.

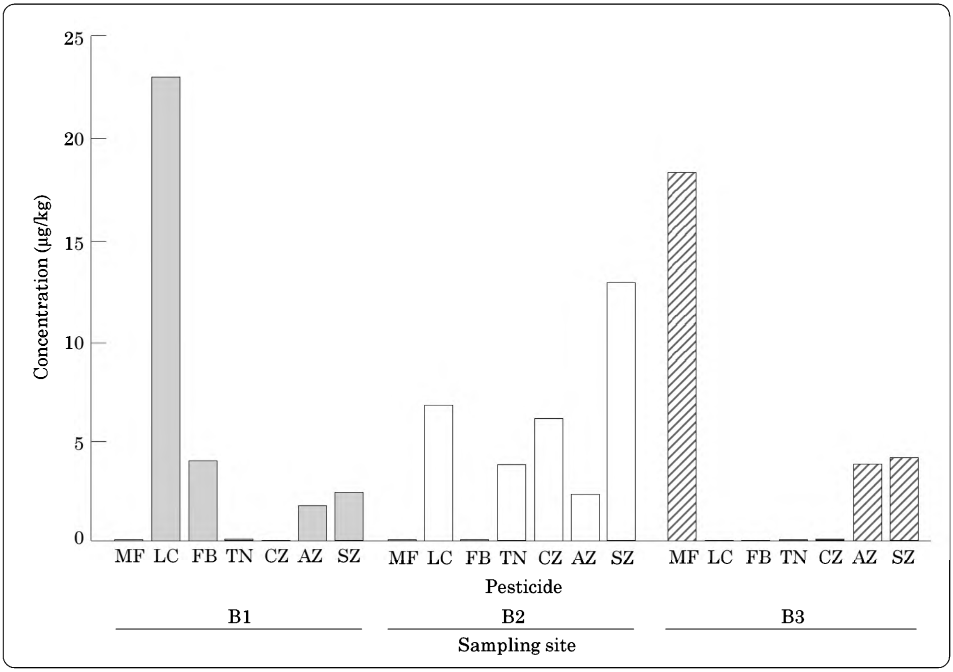

Figure 4. Pesticide concentrations in the topsoil (0-5 cm) of soybean fields (n = 2), Pantaninho valley, savannas of central Brazil. MF = monocrotophos; LC = λ-cyhalothrin; FB = fluazifop-butyl; TN = trifluralin; CZ = cyanazine; AZ = atrazine; SZ = simazine.

Trifluralin, a typical herbicide for tilled soybean fields, and metolachlor, a herbicide used for maize, were also detected in the topsoil of one maize field at concentrations of 8 and 3 µg/kg, respectively.

The topsoil concentrations of triazine are comparable with those found by Nakagawa et al. (1996) in his studies of atrazine dissipation in a deep red Latosol in the Brazilian state of São Paulo, where 130 µg/kg atrazine remained after maize was harvested. In Spain, which has a Mediterranean climate, concentrations of triazine residues in topsoils after maize is harvested are between 40 and 150 µg/kg (Sánchez-Brunete et al. 1994). Compared with temperate regions, where as much as 200 µg/kg of atrazine are found 6-8 months after the last application (Huang and Pignatello 1990), the residues found in the *Cerrados* soils look quite low. Even so, the frequent contamination of groundwater with atrazine in Spain and Italy (van den Berg and van den Linden 1994) warns of the potential danger for the *Cerrados* environment.

The somewhat high levels of residues of herbicides (150-175 µg/kg) and insecticides (100 µg/kg) in irrigated soil (B4) in the Pantaninho valley provide an anomaly. The more constantly moist conditions should stimulate microbial activity, and thus encourage a more intensive decomposition of biocides in the soil (Hurle 1982). One explanation for the anomalously high biocide concentrations might be that these same moist conditions stimulate a more intense weed and insect growth, thus obliging farmers to use higher application rates to combat the pests.

At site B5 (where samples were taken at depth in a nonirrigated maize field), the residues of trifluralin and metolachlor were probably carried over from the previous year. In the year of the study, no biocides were applied to the surrounding fields, thus ruling out spray drift contamination of the studied site. These herbicides therefore seem to persist, even under in tropical conditions.

Figure 4 shows that the highest concentrations (6-25 µg/kg) of the insecticides λ-cyhalothrin and monocrotophos were found in tilled soils under soybean, whereas, in the untilled fields of soybean, the herbicide fluazifop-butyl was detected at very low levels (2-3 µg/kg). Three triazines (cyanazine, atrazine, and simazine) were also present in the soybean plots, both tilled and untilled, at concentrations between 1 and 11 µg/kg.

The very low concentrations of fluazifop-butyl result from its rapid hydrolization to fluazifop acid. This metabolite is biocidally active and persists much longer than the original herbicide (Hornsby et al. 1996). An evaluation of the concentration levels of fluazifop-butyl makes sense only if its main metabolite is included. Because fluazifop acid can be measured only by the GC technique after a derivation, it was not included in this study.

The concentrations of λ-cyhalothrin (6 h after application) and monocrotophos (8 days after application) indicate that these two insecticides are less persistent than chlorpyrifos. Nevertheless, the high water solubility of monocrotophos raises the question of whether this highly toxic insecticide is mobile enough to reach underground or surface waters, despite being readily degradable. The three triazines present in the soils under soybean were probably carry-over residues, because no maize herbicides had been used within 100 m around the sampling site. The fact that the triazines were detected suggests that they too show a persistence similar to that of trifluralin and metolachlor, and may constitute a problem, in the long term, through leaching.

At site B5, sampling at different depths was performed to assess the mobility of atrazine and simazine within the soil. Figure 2 shows how the triazines were distributed across the different soil layers. The highest concentrations (40-120 µg/kg) of atrazine and simazine were restricted to the top 10 cm of the soil. In the deeper soil layers, the triazines were detected in concentrations between 2 and 4 µg/kg to as deep as 70 cm. Carry-over residues of metolachlor and trifluralin were found in the top 10 cm of the soil in concentrations of 2-8 µg/kg.

The triazines' continuity throughout the soil profile indicates that they possess a high mobility within this Ferralsol. Their dangerous leaching properties have been well documented for temperate regions (Ritter 1990; Skark and Zullei-Seibert 1995), and have led to atrazine being legally banned in Germany (Heintz and Reinhardt 1993). Because the microbial decomposition in subsoil layers (>50 cm) is very slow (Fomsgaard 1995), biocide residues below the root zone may persist over time and thus pose a threat to shallow groundwater. If pesticide residues are detected continuously down to the water table, then underground water contamination is proven (Huang and Frink 1989). Further studies are needed to discover if, in the *Cerrados*, continuous cropping and use of triazines have the potential to contaminate underground and surface waters.

## Summary and Conclusions

We measured biocide concentrations in soil, sediments, and water samples of a small microbasin in the *Cerrados*. Pesticides were detected at medium concentrations in soils and at low concentrations in water and sediments. Carry-over residues in soils were also found and measured for atrazine, simazine, cyanazine, metolachlor, and trifluralin.

Results show that, at sampling, only low levels of contamination were found in different sections of the catchment. Nevertheless, as demonstrated by the presence of carry-over residues, several herbicides can persist in soils under tropical conditions. Of the applied insecticides, chlorpyrifos seems to be the most persistent. The presence of atrazine in surface waters 3 weeks after the last application indicates that, at least, this chemical is sufficiently persistent and mobile to be transported to streams. The mobility of simazine and atrazine across a soil profile points out the need to determine leaching rates under the *Cerrados*' environment. The higher application and leaching rates in irrigated fields also need further research. The final goal for monitoring biocides in the *Cerrados* must be to identify those mobile and persistent pesticides that should be banned or restricted.

## Acknowledgments

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# Chapter 19

# General Conclusions

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## Abstract

The objective of the studies described in this book was to generate knowledge on the dynamics of soil organic matter and physical processes in different agricultural systems currently operating in the savannas of Latin America, principally the Brazilian *Cerrados*. These studies included the identification of indicators of soil degradation and improvement. Here, we synthesize the main conclusions, discuss their relevance to the well-drained acid-soil savannas of the tropics, and suggest areas for future research. Highlights of the chapters on research activities are also presented.

## Dynamics of Soil Organic Matter in Different Agricultural Systems

### *General effects*

As a component in the Oxisols of the Brazilian savannas (also known as the *Cerrados*), soil organic matter (SOM) plays a key role in regulating both the physical and chemical properties of these soils. Humified organic matter (OM) is responsible for most soil fertility, because it provides most of the exchange sites and controls the formation of stable microaggregates that give Oxisols their favorable structure via the strong attraction between the negatively charged humic matter and the positively charged oxyhydroxides. Nitrogen is also mainly bound to SOM in these soils. Moreover, because of the P-deficiency conditions, most of the demand for P is met by organic phosphorus forms. Management-induced SOM losses will therefore affect, at the same time, both the physical and chemical properties of the soils.

The composition of SOM in Brazilian Oxisols is similar to that of different soil types in other regions. That is, it shows comparable proportions of polysaccharides, lignin, dissolved organic carbon, and particulate organic matter (POM). Levels of microbial activity are also comparable (Chapters 8 and 16).

The observed losses of SOM in selected Oxisols after 10 to 20 years of cropping is mainly associated with a loss of POM, whereas the humified matter bound to the clay fraction is only slightly altered. Hence, the ability of SOM to serve as nutrient sink and source is not yet drastically reduced. But, if current land management

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practices continue, then the humified fractions will eventually decrease because the inputs of fresh humified matter are reduced as the mineralization of humic matter continues.

On loamy Oxisols, the loss of POM reduces large water-stable aggregates, despite the fact that polysaccharides are more important for aggregate stability. On clayey Oxisols, the reduction of POM is less significant because of the overall higher SOM contents. Yet, it must be expected that continued depletion of POM will ultimately lead to a loss of polysaccharides and thus of aggregate stability in loamy and clayey Oxisols.

Phosphorus dynamics in Oxisols are similar to those of other highly weathered soils in which bioavailable fractions are very small (Chapters 13 and 14). Biological competition for the small amounts of orthophosphate in solution is therefore high and, thus, P cycling in the soil is accelerated. Fertilization increases the labile inorganic P fraction and reduces the competition for P, although biological cycling continues to be high. Some of the applied P is lost to oxyhydroxides, depending on the clay content and on management. Tree plantations are apparently very efficient in maintaining fertilizer P available to plants, whereas crops and pastures need regular P amendments to keep available P high.

### *Soil fractionation*

The particle-size separates fractionate organic compounds and organic P along a biological gradient from undecomposed to highly humified OM with decreasing particle size. Inorganic P also follows a mineralogical gradient to increasing recalcitrance in the fine fractions. Therefore, soil processes are best studied in these primary organo-mineral complexes. Land-use changes are most apparent in the particulate, and therefore more labile, fractions. Because separating the sand fraction is easy for most laboratories, we propose that organic carbon in the 20-50-µm fraction should be used to characterize the effects of land-use changes on Brazilian Oxisols.

Fractionation into a labile and stable fraction with potassium permanganate similarly allows for the study of SOM and nitrogen dynamics and is highly sensitive to land-use change. This method is equally simple to apply on a routine basis in most laboratories.

### *Management effects*

The impact of management systems on Oxisols is variable and depends on the clay content of the soil. Cropping systems are strongly affected by seedbed preparation and liming, which compact the soil and apparently diminish the number of rapidly draining macropores. Concomitantly, the number of mesopores, which are important for the plant's water supply, increases. Moreover, the use of machinery depletes OM and thus reduces aggregate stability and soil fertility. These effects are more accentuated in loamy than in clayey soils. In the systems studied, the loss of SOM is restricted to particulate forms and subsequent change to more sustainable land-use forms will replenish this loss, but in the long term, humified matter will also be affected if cropping continues without rotation. Soils degraded beyond this point may not be productive because applied nutrients are not retained and aggregation may break down completely.

Soils under pastures are able to maintain or increase their SOM contents, compared with soils under native savanna. However, productivity is low on degraded pastures, because of insufficient P supply. Regular P additions are therefore necessary to maintain high pasture productivity.

On recuperated pastures and crop/pasture rotations, especially the legume-based pastures with *Stylosanthes* or *Arachis*, high productivity is established rapidly (Chapter 3). This also leads to an amelioration of soil physical and chemical properties. Nitrogen (N) availability is increased as a result of N fixation by the legumes. The increased biomass production also has a positive effect on root development and thus on aggregate stability. This is of greater relevance to loamy soils where roots are more important to aggregation than to clayey soils.

Management effects from eucalyptus and pine reforestation are not directly comparable. Pine reforestation results in an accumulation of a thick organic layer and the beginning of podzolization in a relatively short time. As a result of the impeded incorporation of litter, and because mineralization processes continue, POM is lost. This decreases the number of large macroaggregates but has no consequence on total macroaggregation. Further research is needed to ascertain whether the litter is rapidly incorporated into the mineral soil after clearfelling or is retarded because of the pine's low litter quality.

In contrast, under eucalyptus, the litter is rapidly incorporated and organic carbon content even increases as a result of the higher litterfall, compared with the savanna control. Any future land-use change after eucalyptus may therefore benefit from better aggregation and higher biological activity than after savanna. In both tree plantation systems, applied P is kept available to plants through high internal P cycling.

### *Considerations for sustainable management*

Sustainable management must aim to keep organic carbon contents high. This can be achieved by rotating between cropping systems and pastures (as proposed by CIAT and others) or planting tree plantations. The desirable frequency of rotations depends on the soil's clay content: clayey soils can be cropped for longer periods without substantial losses of OM than sandy soils.

As with cropping systems, pastures need regular fertilization, especially with P, to remain productive and to exert their positive influence over aggregate stability and SOM. Legume-based pastures increase N availability in the soil and improve pasture quality, thus leading, simultaneously, to higher cattle productivity and improved soil quality.

Eucalyptus plantations can be considered as a possible alternative to pastures in rotation systems because SOM contents increase and P is kept bioavailable. In contrast, no positive effects on the soil or the OM can be obtained under pine forests, apart from a comparatively high bioavailable P.

## Soil Quality Indicators for Acid-Soil Savannas

As agricultural production intensifies to meet the needs of the world's burgeoning population increasing pressure is put on natural resources such as soil, air, and water. Land degradation is occurring at an alarming scale, with nearly 1 billion hectares of agricultural land severely or moderately degraded (Oldeman 1994). Although degradation usually occurs over time, it can also occur rapidly, for example, during storm events and landslides. The recuperation of degraded soil is, however, always slow and costly. Land users and policymakers therefore need sets of indicators to monitor the state of the land and provide early warning of degradation so timely decisions can be made to reverse or prevent further degradation.

Soil is now viewed as a dynamic living resource whose condition is vital to both agriculture and to ecosystem functioning. Because of its regulating roles in biogeochemical nutrient cycles, as a conditioner of the amounts and quality of water available to agricultural plants and, as a filter and decomposer of agrochemical contaminants and other wastes, the soil is a key natural resource for our future survival. We need to husband this essentially nonrenewable resource (at least in terms of a farmer's lifetime) with increasing skill and foresight to prevent further degradation and loss of agricultural production potential.

Society already has in place indicators and standards for air and water quality, but soil has been neglected. The need for soil quality indicators (SQIs) is now increasingly recognized by scientific and policymaking communities, and several publications, giving background information, are now available (Doran et al. 1994; Doran et al. 1996; Pankhurst et al. 1997; Pierri et al. 1995).

Soil quality has had many definitions. Here, we use Doran and Parkin's definition (1994):

> "Soil quality is the capacity of the soil to function, within ecosystem and land-use boundaries, to sustain biological productivity, maintain environmental quality and promote plant, animal and human health".

"Soil health", sometimes used interchangeably with "soil quality", is defined after Doran and Safley (1997):

> "The continued capacity of soil to function as a vital living system, within ecosystem and land-use boundaries, to sustain biological productivity, promote the quality of air and water environments, and maintain plant, animal and human health".

To distinguish between these, current thinking follows the premise that the term "soil quality" is appropriate when the intended use of the soil is specified (Pankhurst et al. 1997b). Essentially, the term "soil health" differs from "soil quality" in that it (1) includes a time function, and (2) recognizes that soil is a vital living system.

Because soil represents a unique balance between physical, chemical, and biological factors, SQIs should also be made up of combinations of these factors, particularly where parameters can be identified that integrate all three factors and their functions.

An example may be the rate of water infiltration, which is dependent on the soil's physical structure (particularly texture), chemistry (relationships between soil surfaces, particularly clays), and porosity (which can be affected by the activity of soil biota).

To be useful to a variety of users, including farmers, extension workers, and policymakers, SQIs should, according to Doran and Safley (1997) and Beare et al. (1997), be:

1. Relatively easy and practical to use under field conditions by farmers,

extension workers, specialists, and scientists.

2. Relatively precise and easy to interpret.
3. Cost-effective to measure.
4. Sensitive enough to variations in management and climate to reflect the effects of these on long-term changes, but not so sensitive as to be influenced by short-term weather patterns.
5. Able to integrate soil physical, chemical, and biological properties and processes, and serve as basic inputs for estimating soil properties or functions that are more difficult to measure directly.
6. Able to correlate well and in a predictable way with ecosystem processes, plant and animal productivity, and soil health.
7. Able to be used as components of existing soil databases.

The selection of a suitable set of SQIs and the development of their use in a soil quality monitoring system (or SQMS) requires the following activities (Beare et al. 1997):

1. Identify suitable SQIs.
2. Develop a monitoring system for soil quality.
3. Obtain acceptability for the SQMS by users.
4. Monitor agricultural systems and their sustainability.

The work reported here mainly focuses on the first phase of this process, that is, identifying soil quality indicators that are suitable for sustainable agricultural systems for the acid Oxisols of the Latin American savannas, including crop and livestock production.

Usually, two approaches have been used to evaluate sustainable agricultural systems. The first is *comparative assessment*, where the performance of one system is compared with that of other systems. Normally, a reference system such as the native climax vegetation is included in these comparisons. The other approach is *dynamic assessment*, where the changes in system performance are monitored over time. Because of time limitations, we used the first approach to compare systems and develop a set of sensitive indicators of changes in soil quality for a set of different land-use systems in the Brazilian *Cerrados* and the Colombian *Llanos*.

A wide range of potential SQIs are available and to limit this range we had to identify the predominating biophysical constraints in the targeted agricultural system. In the savanna agroecosystem of Latin America, these constraints are:

1. Loss of SOM.
2. Limited water availability during dry periods of the wet season.
3. Compaction and surface sealing.
4. Wind and water erosion.
5. Depletion of soil nutrients.
6. Acidification and associated aluminum toxicity.
7. Weed infestation.

## List of Potential Indicators Identified

Taking into account the factors mentioned above, we identified a list of potential SQIs from the research described in this book and from other studies conducted in the Colombian *Llanos* (Table 1). Table 1 also indicates the methodology used, ease of use, otential soil quality indicators for Oxisols in the Brazilian and Colombian savannas.

| | Methodology | Ease of use[a] | Sensitivity to land-use change[a] | Suitability for on-farm use[a] | Ge suit |
|---|---|---|---|---|---|
| avannas | | | | | |
| e size distribution and stability | Aggregate stability | ++ | +++ | - | |
| le organic carbon | Lab. extractions and colorimetry | ++ | ++ | - | |
| anate-extractable N | Lab. extractions and colorimetry | ++ | ++ | - | |
| C-to-total C ratio | Microbial biomass | + | ++ | - | |
| easily accessible POM | Organic matter fractionation | ++ | ++ | - | |
| savannas[b] | | | | | |
| ltration rates | Ring infiltrometer | +++ | + | - | |
| m biomass | Soil sampling and manual sorting | ++ | +++ | + | |
| m-to-termite ratio | Soil sampling and manual sorting | ++ | +++ | + | |
| | pH strips | +++ | + | + | |
| | Pore size analysis | + | ++ | - | |
| on | Hand-held penetrometer | +++ | ++ | ++ | |
| gth | Hand vane tester | +++ | ++ | + | |
| eability | Laboratory | ++ | ++ | - | |
| conductivity | Laboratory determinations | ++ | ++ | - | |
| osity | Tension table | ++ | ++ | - | |
| | Field determination | ++ | + | - | |

f easiness, suitability, and sensitivity are - = nil; + = low; ++ = fair; +++ = high.

tion from CIAT annual reports (1997, 1998); Thomas et al. (1996).

sensitivity to land-use change, and suitability for on-farm use.

The list of potential SQIs derived from this study can be incorporated into a SQMS, together with basic or standard measurements such as bulk density, pH, depth of soil and roots, water content, soil temperature, total C and N, electrical conductivity, and mineral N (Doran and Parkin 1994). The exact choice of scientific parameters will depend on land use, soil type, and key soil processes relevant to the particular land use and climate.

If the ultimate objective is to develop a SQMS that can be used by land users themselves, attempts should be made to incorporate indigenous SQIs into the monitoring system. The mix of indigenous and scientific parameters will vary with the monitoring objectives of different users, for example, farmers, extension workers, or policymakers. Soil quality indicators that are integrative are likely to be more useful for land users than a measurement of, say, inorganic soil N. This is because many of the indicators used by farmers are also integrative, such as soil color, soil structure, crop yield, and occurrence of specific weed species. Indicators that can scale up findings from the plot, field, or farm to the watershed, region, or nation should also be considered. Examples of these include crop yields and their trends, land cover, land-use intensity, and nutrient balances (Pierri et al. 1995).

The next phase in establishing a SQMS for acid-soil savannas should include the following steps:

1. Developing guidelines for establishing a monitoring system; identifying partners, farmers, and community groups; making agreements on the list of SQIs that are appropriate to given conditions.
2. Obtaining information on soil properties, critical values, and ranges of the indicator parameters.
3. Establishing simple descriptions of the methods involved for each indicator.
4. Developing guidelines to interpret results from the use of indicators.
5. Preparing management recommendations for stopping or reversing soil degradation.

## Further Research Needs

1. Increase the component options of crops and pastures in crop/pasture rotations to maximize the synergistic effects on production and soil quality.
2. Increase diffusion of alternative farming systems, SQIs, and SQMS among producers and identify difficulties of structural changes in macroeconomics and policies.
3. Study the interactions among SOM, plowing, and liming on soil aggregation, clay dispersion, compaction, and water-retention capacity under different land-use systems and thus optimize the positive effects of plowing on the water-retention characteristics and diminish SOM losses.
4. Conduct follow-up research on preliminary results that showed strong seasonal variations of the effects of land use on SOM and nutrient dynamics.
5. Increase knowledge on microbial parameters in the Brazilian savanna ecosystem, particularly as microorganisms affect most of the SOM dynamics in the soils of this ecosystem.

6. Quantify termite-induced changes in SOM stocks and nutrients at the field and landscape levels to evaluate their influence on the ecosystem.

7. Identify and monitor mobile and persistent (and thus hazardous) biocides, and have them banned or restricted. This is especially important for irrigated systems.

8. Determine the ranges and critical values for sets of SQIs.

9. Incorporate farmer knowledge on soil quality into an SQMS and determine the appropriate guidelines for use and interpretation of SQI results.

## Highlights of Research

### *Chapter 3: Agropastoral systems based on legumes: an alternative for sustainable agriculture in the Brazilian* **Cerrados**

1. Agropastoral systems have the potential to increase productivity and improve soil properties while reducing the risks of degradation. The impact of these systems is greatest when *Stylosanthes guianensis* cv. Mineirão and *Arachis pintoi* BRA-031143 are included.

2. *Stylosanthes guianensis* cv. Mineirão is a legume that is adapted to low-fertility soils and can be easily established in rice/pasture systems to renovate degraded pastures, without demanding high inputs. In addition to improving the diet of grazing animals, it can increase N availability in the soil-plant system and allow better pasture establishment.

3. In contrast, *A. pintoi* BRA-031143 is a legume that is better adapted to more intensive production systems with higher inputs. It is relatively tolerant of competition for light and nutrients and has a good ability to cover ground, once it is established. These attributes are appropriate for rotational use with crops and as a ground cover for direct planting systems.

4. The integration of crop and livestock activities on-farm is a relatively recent innovation for producers in the *Cerrados*. Those producers who are using the system are seeing the economic and environmental advantages of this technology, but its widespread adoption depends on the ability of both grain producers and cattlemen to adapt to the requisite structural changes. Researchers, for their part, need to increase the component options of crops and pastures and identify an adequate management system to maximize the synergistic effects on production and on soil quality.

### *Chapter 4: Physical and chemical properties of selected Oxisols in the Brazilian* **Cerrados**

1. Soil organic matter can be considered the key compound for soil fertility and soil stability in the Brazilian Oxisols because it serves as an important nutrient sink and source, and controls clay dispersion in terms of the specific charge characteristics of Fe and Al oxyhydroxides.

2. Management significantly affects soil compaction, altering pore-size distribution and leading to a reduced number of macropores and an increased number of mesopores in cropped soils. Considering the typically low amount of

plant-available capillary water, the increase in mesoporosity must be considered as positive because it increases the amount of water available to crops.

### *Chapter 5: Distribution of water-stable aggregates and aggregating agents in Oxisols of the Brazilian* Cerrados

1. Whether a land-use change leads to a significant alteration of aggregate stability depends not only on the kind of management and implements used but also on the soil's clay content.

2. The main aggregating effects are attributed to polysaccharides, because any direct effects of Fe and Al oxyhydroxides could not be shown.

3. In soils with low clay contents, the entangling of roots also plays a significant role in aggregation, making it necessary to distinguish between aggregation associated with POM and polysaccharide-bound aggregation.

### *Chapter 6: Aggregation studied by laser diffraction in relation to plowing, soil organic matter, and lime in the Brazilian* Cerrados

1. Plowing significantly reduces the number of macroaggregates and increases the number of microaggregates in the soil.

2. Whether liming has a disaggregating effect in soils depends on tillage practices and the SOM content. For example, liming will result in decreased macroaggregation and a destabilized soil structure only if SOM contents are low as a result of regular tillage.

### *Chapter 7: Short-term variation in aggregation and particulate organic matter under crops and pastures*

1. Despite the general belief that aggregation in Oxisols is stable, peds of the clayey Oxisol studied were relatively fragile and sensitive to cropping.

2. Easily accessible POM is an important and active carbon pool in Oxisols. The POM content of soil increases with agricultural activity. Under pastures and, especially, under cropping systems, plant residues accumulate in soil predominantly as free POM. Under native savanna, however, a higher proportion of POM is occluded within peds, probably resulting in overall lower turnover rates.

3. The capacity to distinguish between free and easily accessible POM can function as a sensitive indicator of short-term effects of land management on C and N dynamics and availability.

### *Chapter 8: Soil organic matter in Oxisols of the Brazilian* Cerrados

1. Soil organic matter in Oxisols of the *Cerrados* shows similar characteristics to that in other soil types under different environmental conditions.

2. Polysaccharides and lignin dynamics are strongly related to the habitable pore space and thus to water-retention characteristics.

3. Land-use effects are rather small in whole-soil samples but are more pronounced in the sand fractions, especially that of the very fine sand (20-50 µm).

4. Continuous cropping results in significant losses of POM, but minor losses of humified OM. Hence, subsequent change to a land-use system with high litter input, such as pastures and eucalyptus plantations, will rapidly replenish the lost labile carbon pool.

5. Because of its low quality, litter under pine forms a thick organic layer that does not readily become incorporated into the mineral soil and, because OM continues being mineralized, POM is quickly reduced. Whether land-use change effects a rapid incorporation of the organic layer is still to be clarified.

### *Chapter 9: Soil organic carbon, carbohydrates, amino sugars, and potentially mineralizable nitrogen under different land use systems in Oxisols of the Brazilian* Cerrados

1. Land-use effects are most apparent in the sand fractions, especially that of the very fine sand (20-50 µm). Soils under pastures show strongly enriched contents of sugars, amino acids, and potentially mineralizable N ($N_{pot}$), whereas soil under pine plantations are clearly depleted, compared with soil under native savanna.

2. When degraded pastures are reclaimed by re-sowing pastures, whether of grass alone or grass/legume, a rapid increase of amino acids and $N_{pot}$ can be achieved over 3 years, especially under legume-based pastures.

3. Amino acids represent an important component of mineralizable N and are therefore sensitive indicators of N availability.

### *Chapter 10: Carbon fractions as sensitive indicators of quality of soil organic matter*

1. Extracting labile soil organic carbon with water (WEOC) and permanganate (PEOC) is easy and constitutes a valuable screening method for comparing the short-term effects of land-use systems on biological activity and nutrient availability in the *Cerrados*.

2. The WEOC and PEOC correlate better with C and N mineralization than with total and stable carbon. They are also clearly influenced by the mineralization flush at the beginning of the rainy season.

### *Chapter 11: Labile N and the nitrogen management index of Oxisols in the Brazilian* Cerrados

1. The nitrogen management index (NMI) is a good indicator of N availability but gives no information about the total amount of N in soils.

2. In land-use system analyses, total N and labile N can be used together to simply and quickly evaluate the soil's N status.

3. Labile N, and thus the availability of N, increases under legume-based pastures and legume-based pasture/crop rotations, compared with under native savanna, but is reduced under continuous cropping with soybean, a nitrogen-fixing crop.

### *Chapter 12: Characterizing labile and stable nitrogen*

1. Amino acids and amino sugars form a substantial part of permanganate-extractable nitrogen (PEN), but two-thirds of PEN constitute "unknown" N. Stable N has lower proportions of amino

acids and amino sugars, and the proportion of “unknown” N is even greater. A structural difference between PEN and stable N is therefore hypothesized.

2. Possibly, PEN and stable N are separated spatially, with PEN outside and stable N inside the microaggregates, so that stable N is also physically protected from microbial breakdown.

### *Chapter 13: Phosphorus fractions under different land-use systems in Oxisols of the Brazilian* Cerrados

1. Under natural conditions of strong phosphorus deficiency, organic phosphorus ($P_o$) contributes strongly to plant nutrition, confirming the general concepts of P dynamics in highly weathered soils.

2. Fertilization elevates inorganic phosphorus ($P_i$) but has only small effects on $P_o$. The increase of fertilizer $P_i$ is most accentuated in the bioavailable fraction and lowest in the recalcitrant fraction. Therefore the ratio of bioavailable $P_i$ to $P_o$ appears to effectively reflect the P status of the land-use systems, with P deficiency increasing in the order crop << reforestation < degraded pasture < native savanna, independently of soil type.

3. Soils under tree plantations maintain high quantities of bioavailable P by efficient recycling, while under crops and pastures, P tends to accumulate in recalcitrant P forms. Possibly, the adsorption of P to oxyhydroxides is reduced at the more acid forest sites because of increased complexation of Fe and Al oxides with organic acids.

### *Chapter 14: Phosphorus pools in bulk soil and aggregates of differently textured Oxisols under different land-use systems in the Brazilian* Cerrados

1. The percentage of total P that is plant-available is smaller in clayey than in loamy Oxisols.

2. Land use influences the total P concentrations under tree plantations and continuous cropping, but not under pastures.

3. Fertilizer P accumulates in labile and medium-labile forms. In loamy Oxisols, $P_i$ concentrations are higher under crops than under native savanna, and fertilization compensates for the loss of $P_o$. In clayey Oxisols, P fertilization results in an accumulation of inorganic and organic fractions as a result of higher microbial activity.

4. Large macroaggregates in loamy Oxisols contain physically protected $P_o$, whereas in clayey Oxisols, P concentrations in macroaggregates do not differ from those of bulk soil. The physically protected $P_o$ accumulates more as stable orthophosphate monoesters in the loamy Oxisols than as orthophosphate diesters, which are more easily hydrolyzed.

### *Chapter 15: Acid monophosphatase: an indicator of phosphorus mineralization or of microbial activity? A case study from the Brazilian* Cerrados

1. Potential acid monophosphatase activity (PAMA) in the *Cerrados* is much higher in clayey than in loamy Oxisols. It responds to land-use changes within a few years. In soils under crops and pine, PAMA is significantly lower than under native savanna. The highest levels

of activity are found in clayey Oxisols under pasture.

2. According to data on phosphatase activity, pasture/crop rotations could form a better alternative to conventional systems. When fertilized regularly, the crop component leads to an accumulation of $P_i$, whereas the pasture component stimulates microbial activity and OM accumulation.

3. Correlations of PAMA with soil microbial activity and with soil C were significantly higher than with moderately labile P fractions, meaning therefore that it cannot serve to measure actual P mineralization rates in the given systems. However, it does indicate the soil's potential to mineralize available phosphomonoesters.

### *Chapter 16: Microbial biomass, microbial activity, and carbon pools under different land-use systems in the Brazilian* **Cerrados**

1. Land management strongly influences soil microbiology: microbial carbon declines under cropping and pine, whereas the establishment of pastures seems to stimulate microbial activity.

2. Water-extractable organic carbon (WEOC) is possibly the most important C source for microbes. It consists mainly of root exudates and litter degradation products. Root density, OM input, and soil cover are therefore hypothesized to have the greatest influence over microbial biomass C ($C_{mic}$).

3. The $C_{mic}/C$ ratio can be used to indicate sustainability with regard to future soil organic carbon development. According to this ratio, the pasture system is sustainable, whereas the cropping systems and reforestation are not.

4. In summary, results show that findings obtained in other regions of the world can also be applied to soils of the *Cerrados*. Yet, further research is needed, especially on the function of WEOC as a key link between $C_{mic}$ and land management, and on the possible differences in soil microbiology between varying pasture systems.

### *Chapter 17: Organic matter in termite mounds of the Brazilian* **Cerrados**

1. Termite mounds in the *Cerrados*, inhabited by *Armitermes* and *Dihoplotermes* spp., have higher SOM contents than the surrounding Oxisols. In all size separates of the termite mounds, SOM is less decomposed than in the surrounding soil, as indicated by higher lignin contents, lower ratios of acids-to-aldehydes of the vanillyl and syringyl structural units of lignin, and lower ratios of microbial to plant-derived monosugars.

2. Termites of the Brazilian *Cerrados* selectively enrich fresh and partly decomposed OM for their mounds, which then become a temporary, but important, carbon and N sink in this tropical ecosystem.

### *Chapter 18: Pesticides in soil, sediment, and water samples from a small microbasin in the Brazilian* **Cerrados**

1. Pesticides were detected at medium levels of concentrations in soils and at low concentrations in water and sediments. Carry-over residues in soils were measured for atrazine, cyanazine, simazine, trifluralin, and metolachlor.

2. At sampling, no high contamination levels were found in any of the investigated sections of

the catchment of a small stream. Nevertheless, as demonstrated by carry-over residues, several herbicides persisted for long periods in the soils, even though under tropical conditions.

3. Of the applied insecticides, chlorpyrifos seems to persist the most in the studied soils.

4. The presence of atrazine in surface waters 3 weeks after the last application indicates that, at least, this compound is persistent and mobile enough to be transported to streams. The observed mobility of simazine and atrazine within a soil profile demonstrate the need to determine leaching rates in the *Cerrados* environment. Especially irrigated fields, which have higher application and leaching rates, should be included in further research.

5. The final goal of monitoring biocides in the *Cerrados* must be to identify those mobile and persistent (and thus potentially dangerous) pesticides, which should be banned or restricted in their use.

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# Acronyms and Abbreviations Used in the Text

## Acronyms

| | |
|---|---|
| ASA | American Society of Agronomy |
| BITÖK | Bayreuther Institut für Terrestrische Ökosystemforschung, Germany |
| BMZ | Bundesministerium für Wirtschaftliche Zusammenarbeit und Entwicklung, Germany |
| BU | Bayreuth University, Germany |
| CGIAR | Consultative Group on International Agricultural Research, USA |
| CNPAF | Centro Nacional de Pesquisa de Arroz e Feijão (*of* EMBRAPA) |
| CPAC | Centro de Pesquisa Agropecuária dos Cerrados (*of* EMBRAPA) |
| CSSA | Crop Science Society of America |
| EMBRAPA | Empresa Brasileira de Pesquisa Agropecuária |
| FAO | Food and Agriculture Organization of the United Nations, Italy |
| GTZ | Deutsche Gesellschaft für Technische Zusammenarbeit, Germany |
| IITA | International Institute of Tropical Agriculture, Nigeria |
| ISCO | International Soil Conservation Organisation, Germany |
| ISSSG | Institute of Soil Science and Soil Geography (*of* BU) |
| MAS | Management of Acid Soils (*of* SWNM *of the* CGIAR) |
| ORSTOM | Institut français de recherche scientifique pour le développement en coopération, France |
| POTAFOS | Associação Brasileira para Pesquisa da Potassa e do Fosfato |
| SCS | Soil Conservation Service (*of the* USDA) |
| SNLCS | Serviço Nacional de Levantamento e Conservação de Solos (*of* EMBRAPA) |
| SPI | Serviço de Produção de Informação (*of* EMBRAPA) |
| SSSA | Soil Science Society of America |
| SWCS | Soil and Water Conservation Society, USA |
| SWNM | Soil, Water, and Nutrient Management (*systemwide program of the CGIAR*) |
| UFU | Universidade Federal de Uberlândia, Brazil |

| | |
|---|---|
| UNESCO | United Nations Educational, Scientific, and Cultural Organization, France |
| UNESP | Universidade Estadual de São Paulo, Brazil |
| USDA | United States Department of Agriculture |
| WHO | World Health Organization, Switzerland |

## Abbreviations

| | |
|---|---|
| (Ac/Al)$_s$ | acid to aldehyde ratio for syringyl units |
| (Ac/Al)$_v$ | acid to aldehyde ratio for vanillyl units |
| (Ac/Al)$_{v,s}$ | mass ratio of acid-to-aldehyde for vanillyl and syringyl units |
| ADI | acceptable daily intake (of biocides in drinking water) |
| Al$_d$ | dithionite-extractable pedogenic aluminum;<br>dithionite-extractable aluminum oxide or hydroxide |
| Al$_o$ | oxalate-extractable pedogenic aluminum;<br>oxalate-extractable aluminum oxide or hydroxide |
| (ara+xyl) | arabinose + xylose (sugars synthesized by plants) |
| a:r:s | angular to round to iron-stained (of fine-sand grain types) |
| AS | amino sugars |
| Aw | tropical climate with wet and dry seasons, typical of savanna areas (*from Köppen's classification of world climates*) |
| AZ | atrazine (herbicide) |

| | |
|---|---|
| BP | before the present |
| BS | base saturation |

| | |
|---|---|
| C3, C4 | photosynthetic pathways in plants |
| $C_{mic}$ | soil microbial carbon |
| $C_t$ | total carbon |
| C F1, C F2 | continuous cropping systems (C) fertilized (F) at low (1) and conventional (2) rates |
| CC | continuous cropping |
| CCN | continuous cropping with no tillage |
| CCT | continuous cropping with conventional tillage |
| CEC | cation-exchange capacity |
| CEC$_e$ | effective cation-exchange capacity |
| CEC$_p$ | potential cation-exchange capacity |
| CF | chlorpyrifos (insecticide) |
| CMI | carbon management index |
| C/N | carbon-to-nitrogen ratio |
| CPs | cellulosic polysaccharides |
| cv. | cultivar |
| CZ | cyanazine (herbicide) |

| | |
|---|---|
| DCB | dithionite-citrate-bicarbonate (used to extract Fe$_d$ and Al$_d$) |
| DMS | dimethyl sulfide |
| DMSO | dimethyl sulfoxide |
| DP | degraded pasture |

| | |
|---|---|
| e. a. | easily accessible |
| ECPs | extracellular polysaccharides |
| EU | *Eucalyptus citriodora* Hook (tree used in reforestation) |

| | |
|---|---|
| F | forest |
| FB | fluazifop-butyl (herbicide) |
| Fe$_d$ | dithionite-extractable pedogenic iron;<br>dithionite-extractable ferric oxide or hydroxide |
| Fe$_o$ | oxalate-extractable pedogenic iron;<br>oxalate-extractable ferric oxide or hydroxide |
| Fe$_t$ | total iron |
| (fuc+rham) | fucose + rhamose (sugars synthesized by microorganisms) |
| (gal+man) | galactose + mannose (sugars synthesized by microorganisms) |

| | |
|---|---|
| GC | gas chromatography |
| GL | improved grass/legume pasture |
| GlucN/Mur ratio | ratio of glucosamine to muramic acid (amino sugars found in fungi and bacteria, respectively) |
| GMD | geometric mean diameter (of soil aggregates) |
| HSD | honestly significant difference (in statistics) |
| ICP-AES | inductively coupled plasma-atomic emission spectroscopy |
| LC | λ-cyhalothrin (insecticide) |
| LI | lability index |
| LMA | large macroaggregates (of soil) |
| LN | lability of nitrogen |
| Ma | millions of years ago (in geology) |
| MA | macroaggregates (of soil) |
| MANOVA | multiple analysis of variance (statistics) |
| MAP/MAT | ratio of mean annual precipitation to mean annual temperature |
| masl | meters above sea level |
| MBTH | 3-methyl-benzothiazonlinone-hydrazone-hydrochloride<br>(a reagent for polysaccharides) |
| MC | metolachlor (insecticide) |
| MF | monocrotophos (insecticide) |
| MIC | microaggregates (of soil) |
| MS | mass spectrometry |
| MWD | mean weight diameter (of soil aggregates) |
| $N_i$ | inorganic nitrogen |
| $N_{labile}$ | labile nitrogen |
| $N_{pot}$ | potentially mineralizable nitrogen |
| $N_s$ | stable nitrogen |
| $N_t$ | total nitrogen |
| NCPs | noncellulosic polysaccharides |
| n.d. | not determined;<br>not detected |
| n.m. | not measured |
| NMI | nitrogen management index |
| NMR | nuclear magnetic resonance spectroscopy |
| NPI | nitrogen pool index |
| NS | native savanna |
| nt | not tilled |
| OM | organic matter |
| P F2 | legume-based pasture (P) fertilized (F) at conventional rates (2) |
| $P_{HCl}$ | phosphorus extractable with hydrogen chloride |
| $P_{Hedley}$ | phosphorus extracted by Hedley's sequential extraction method |
| $P_i$ | inorganic phosphorus |
| $P_{NMR}$ | total phosphorus as measured by NMR |
| $P_o$ | organic phosphorus |
| $P_{res}$ | residual phosphorus |
| $P_{SW}$ | total phosphorus as determined by Saunders and William's digestion method |
| PAMA | potential acid monophosphatase activity |
| PC F1, PC F2 | legume-based pasture/crop rotations (PC) fertilized (F) at low (1) and conventional (2) rates |
| PEN | permanganate-extractable nitrogen |
| PEOC | permanganate-extractable organic carbon |
| PG | improved pure-grass pasture |
| pH | symbol for the degree of acidity or alkalinity of a solution; hydrogen ion concentration |
| $pH_{H_2O}$ | pH as measured by water |
| $pH_{KCl}$ | pH as measured by potassium chloride |
| $^{31}P$ NMR | $^{31}P$ nuclear magnetic resonance spectroscopy |
| POC | particulate organic carbon |
| POM | particulate organic matter |
| PV | pore volume |
| PZC | point of zero net charge |

| | |
|---|---|
| sat. | saturated |
| SEM | scanning electron microscope |
| SMA | small macroaggregates (of soil) |
| SPE | solid-phase extraction method for analyzing biocides |
| SOC | soil organic carbon |
| $SOC_s$ | not-extractable or stable soil organic carbon |
| $SOC_{sand\text{-}free}$ | sand-free soil organic carbon |
| $SOC_t$ | total soil organic carbon |
| SOM | soil organic matter |
| SQIs | soil quality indicators |
| SQMS | soil quality monitoring system |
| ssp. | subspecies |
| S/V | ratio of sum of syringyl units to sum of vanillyl units |
| SZ | simazine (herbicide) |
| TN | trifluralin (herbicide) |
| tr. | traces (of elements) |
| VSC-lignin | amount of lignin characterized by the sum of vanillyl (vanillin and vanillic acid), syringyl (syringaldehyde and syringic acid), and cinnamyl (ρ-coumaric and ferulic acid) units |
| WDC | water-dispersible clay |
| WEOC | water-extractable organic carbon |
| WSA | water-stable soil aggregates |
| XRD | x-ray diffraction;<br>x-ray diffractogram |

# Chemical Elements: List of Symbols Used in the Text

| | |
|---|---|
| Ac | Actinium |
| Al | Aluminum |
| B | Boron |
| Ba | Barium |
| C | Carbon |
| Ca | Calcium |
| Cl | Chlorine |
| Cu | Copper |
| F | Fluorine |
| Fe | Iron |
| H | Hydrogen |
| K | Potassium |
| Mg | Magnesium |
| Mn | Manganese |
| N | Nitrogen |
| Na | Sodium |
| O | Oxygen |
| P | Phosphorus |
| S | Sulfur |
| Si | Silicon |

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