University of São Paulo College of Agriculture "Luiz de Queiroz"

Reflectance spectroscopy vis-NIR and mid-IR applied for soil studies

Suzana Romeiro Araújo

Thesis presented to obtain the degree of Doctor in Science. Area: Soils and Plant Nutrition

Piracicaba 2013 Suzana Romeiro Araújo Agronomist

Reflectance spectroscopy vis-NIR and mid-IR applied for soil studies

versão revisada de acordo com a resolução CoPGr 6018 de 2011

Advisor: Prof. Dr. **JOSÉ ALEXANDRE MELO DEMATTÊ**

Thesis presented to obtain the degree of Doctor in Science. Area: Soils and Plant Nutrition

Piracicaba 2013

Dados Internacionais de Catalogação na Publicação DIVISÃO DE BIBLIOTECA - ESALQ/USP

Araújo, Suzana Romeiro

Reflectance spectroscopy vis-NIR and mid-IR applied for soil studies / Suzana Romeiro Araújo.- - versão revisada de acordo com a resolução CoPGr 6018 de 2011. - -Piracicaba, 2013.

182 p: il.

Tese (Doutorado) - - Escola Superior de Agricultura "Luiz de Queiroz", 2013.

1. Absorção 2. Análise do solo 3. Carbono 4. Espectroscopia 5. Metal pesado do solo 6. Modelagem de dados 7. Poluição do solo 8. Solos - Propriedades físico-químicas I. Título

> CDD 631.41 A663r

"Permitida a cópia total ou parcial deste documento, desde que citada a fonte - O autor"

Aos meus maiores exemplos, meus pais Luis Fernando e Maria Lea, **DEDICO**

AGRADECIMENTOS

Gostaria de agradecer ao Prof. José Alexandre Melo Demattê que possibilitou a realização deste trabalho com sua orientação, fornecendo infra-estrutura e favorecendo o desenvolvimento da pesquisa com apoio técnico e financeiro; aos membros do Programa de Pós Graduação em Solos e Nutrição de Plantas da ESALQ, Prof. Dr. Pablo Vidal Torrado e Prof. Dr. Luis Reynaldo F. Alleoni, a oportunidade oferecida; ao Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) e à Coordenação de Aperfeiçoamento de Nível Superior (CAPES), pela concessão das bolsas de doutorado no Brasil e exterior; Dr. Bo Stenberg pela supervisão e sugestões no trabalho durante o período de doutorado sanduíche na Swedish University of Agricultural Sciences (SLU), Skara, Suécia; Dra. Johanna Wetterlind (SLU) que com sua experiência e sensibilidade apoiou-me durante o período de estágio no exterior e muito contribuiu para o desenvolvimento deste trabalho, especialmente com as publicações; à Dra. Simone Vicente e aos funcionários do Departamento de Ciência do Solo, Luis Silva e a amiga Marina Colzato, pelo auxílio nas análises químicas; Todos os integrantes do Projeto Terra Preta em nome dos doutores Mats Söderström e Jan Erickson, meus sinceros agradecimentos. Agradeço aos colegas do grupo de pesquisa e orientação, atuais e ex-participantes, todas as sugestões no trabalho e também por agradáveis momentos compartilhados. Obrigada amigos da pós-graduação pela troca de experiências e prazeroso convívio durante esses anos em Piracicaba. Para finalizar, o meu agradecimento especial aos meus pais, à tia Flora e aos meus irmãos, Alexandre e Helena, que sempre apoiaram meus estudos e ensinaram-me a reconhecer Deus em todos os meus caminhos. Agradeço a Deus as bênçãos recebidas durante minha vida.

ACKNOWLEDGMENTS

I would like to thank Prof. José Alexandre Melo Demattê, whose supervision and encouragement of this research project made it all possible, by providing infrastructure and technical and financial support; the members of the Postgraduate Program in Soils and Plant Nutrition, for the opportunities they offered me; the National Council for Scientific and Technological Development (CNPq) and the Coordination for the Support and Evaluation of Graduate Education (CAPES) for providing doctoral scholarships both in Brazil and abroad; Dr. Bo Stenberg for his supervision and suggestions during the 'sandwich' doctorate (doutorado sanduíche) research at the Swedish University of Agriculture Sciences (SLU); Dr. Johanna Wetterlind (SLU), who with her experience and understanding during the overseas portion of the study contributed a great deal to this research, especially with regard to publications; all the members of the Projeto Terra Preta team, and especially Drs. Mats Söderström and Jan Erickson, to whom I am sincerely grateful; Dr. Simone Vicente and the staff of the Department of Soil Science, especially my friend Marina Colzato and Luis Silva, for their help with the chemical analyses. My special thanks to friends in the post-graduate program for all the experiences we shared and for their wonderful companionship during the last few years. I am deeply grateful to colleagues in the research and graduate school team, both current and past, for their suggestions regarding the study and for the many excellent times we shared. Finally, I owe a huge thanks to my family who have always supported my studies, and to God, for all of the blessings I have received throughout my life.

RESUMO	13
ABSTRACT	15
1 INTRODUCTION	17
References	22
2 QUANTIFYING SOIL ATTRIBUTES VIA SPECTRAL LIBRARY: A NEW	V APPROACH
Abstract	27
2.1 Introduction	27
2.2 Materials and Methods	
2.2.1 Spectral library	
2.2.2 vis-NIR measurements	
2.2.3 Model development	
2.2.4 Validation	
2.3 Results and discussion	
2.3.1 Global calibrations: prediction accuracy obtained with PLS, BT and SVM	techniques.35
2.3.2 Clustered calibrations: PLS model performance	
2.3.2.1Clustering	
2.3.2.2 Clustered predictions	
2.3.2.3 Soil spectra	45
Conclusions	47
References	48
3 CHARACTERIZATION OF POTENTIAL AMAZONIAN DARK EARTH . PROXIMAL SENSING TECHNIQUES	AREAS WITH 55
Abstract	55
3.1 Introduction	55
3.2 Material and Methods	58
3.2.1 Description of studied region	58
3.2.2 Studied areas	59
3.2.2.1 Bom Futuro 2	59
3.2.2.2 Bom Futuro 6	60
3.2.3 Laboratory analysis	61
3.2.3.1 Chemical analyses	61
3.2.3.2 Spectroscopy measurements	62
3.2.4 Data analyses	62
3.2.4.1 Selecting samples	63
3.2.4.2 Statistical analyses	65

CONTENTS

3.3 Results and Discussion	67
3.3.1 Bom Futuro 2	67
3.3.1.1Chemical properties	67
3.3.1.2 Profiles characterization	71
3.3.1.3 Qualitative and exploratory vis-NIR analysis of the BF2 profiles	74
3.3.2 Bom Futuro six: pits and forest transect	78
3.3.2.1 Chemical properties	78
3.3.2.2 Qualitative and exploratory vis-NIR and mid-IR analysis of BF6 area	85
3.3.3 Modeling PLS regression models	89
Conclusions	104
References	104
4 SOIL ENVIRONMENTAL MONITORING: INVESTIGATING HEAVY METALS VIS-NIR AND MID-IR SPECTRAL REFLECTANCE	BY 113
Abstract	113
4.1 Introduction	113
4.2 Material and Methods	116
4.2.1 Soil characterization	116
4.2.2 Incubation experiment	120
4.2.2.1 Experiment I	120
4.2.2.2 Experiment II	121
4.2.3 Laboratory analysis	121
4.2.3.1 Analytical methods	121
4.2.3.2 Spectral measurement	123
4.2.4 Statistical analysis	124
4.3 Results and discussion	124
4.3.1 Exploratory analysis of the spectral data	124
4.3.2 Experiment I	130
4.3.2.1 Chemical data	130
4.3.2.2 Spectra data	133
4.3.3 Experiment II	141
4.3.3.1 Effects of Cr application on soils	141
4.3.3.2 Chemical sequential extraction for Metals	144
4.3.3.2.1Cromium	144
4.3.3.2.2 Iron	148
4.3.3.2.3 Manganese	149
4.3.3.2.4 Zinc	151
4.3.3.2.5 Lead	153

4.3.3.2 Spectral response of Cr in soils	155
4.3.3.3 Principal component analysis	164
4.3.3.4 Vis-NIR and mid-IR spectroscopy calibrations	166
Conclusions	176
References	177

RESUMO

Espectroscopia de reflectância vis-NIR e mid-IR aplicada ao estudo de solos

Para o planejamento agrícola e o monitoramento ambiental são necessárias informações sobre os solos. As análises de solos realizadas através de métodos convencionais em laboratório são normalmente caras e demoradas. Além disso, geram resíduos químicos que caso não sejam dispostos e/ou tratados adequadamente, podem contaminar o ambiente. Nas últimas décadas a espectroscopia de reflectância difusa na região do visível e infravermelho próximo (vis-NIR, 400-2500 nm) do espectroeletromagnético tem se mostrado uma alternativa viável para analisar atributos de solo de maneira rápida. Para tanto, a informação espectral é matematicamente extraída do espectro e métodos multivariados são usados afim de correlacioná-la com as propriedades do solo. Entretanto, ainda são poucos estudos de solos em que a espectroscopia de reflectância na região do infravermelho médio (mid-IR, 4000-400 cm⁻¹) foi usada. Objetivaram-se com este trabalho investigar a viabilidade da utilização de dados espectrais vis-NIR e mid-IR de solos e métodos quimiométricos para predizer as propriedades dos mesmos, a fim de reduzir o número de análises convencionais de terra. As relações existentes entre características espectrais e propriedades físico-químicas de solos tropicais foram avaliadas em três estudos distintos com solos (i) de uma biblioteca espectral (Capítulo 1), (ii) da região amazônica (Capítulo 2) e, (iii) contaminados com metais pesados e lodo de curtume (Capítulo 3). Foi possível identificar faixas espectrais nas regiões do vis-NIR e mid-IR relacionadas às feições de absorção características da água, óxidos de ferro e minerais de argila. No capítulo 1 os modelos de predição vis-NIR de argila e matéria orgânica do solo apresentaram elevada acurácia. Isto reflete a influência direta destas propriedades do solo na sua resposta espectral. A divisão da biblioteca espectral em subgrupos menores baseada nas características espectrais foi eficiente na quantificação de atributos de solos tropicais. Outra alternativa foi usar o método de regressão de árvores para o conjunto total de dados. No capítulo 2, os modelos de predição mid-IR foram mais precisos que os vis-NIR. Os modelos de carbono orgânico do solo e capacidade de troca catiônica obtidos pela regressão pelo método dos mínimos quadrados parciais permitiram a reprodução do padrão espacial destas propriedades na área estudada (r > 0.81); e puderam ser aplicados em uma área geográfica diferente, em amostras de solos desconhecidas. No capítulo 3, a adsorção de metais em constituintes dos solos provocou mudanças nas curvas espectrais dos mesmos, mostrando diferenças entre solos altamente contaminados por metais pesados e solos livres de contaminação. Os teores de Cr (semi-total) no solo pode ser predito através da espectroscopia de reflectância vis-NIR-mid-IR e regressão por mínimos quadrados parciais. Fe e Mn também foram preditos com acurácia usando dados vis-NIR. Em geral, os modelos de predição vis-NIR de metais pesados foram mais precisos que o mid-IR. A vantagem da utilização do sensor vis-NIR está no preparo mais simples de amostras e na possibilidade de utilizá-lo diretamente no campo.

Palavras-chave: Espectroscopia de solo; Contaminação de Solos; Carbono orgânico do solo; Terra preta de índio; Regressão PLS, Máquina de vetor suporte, Árvores de regressão; Biblioteca espectral.

ABSTRACT

Reflectance spectroscopy vis-NIR and mid-IR applied for soil studies

Effective agricultural planning and environmental monitoring requires basic soil information. However, analyzing soil properties by conventional methods is often expensive and time consuming. In addition, these analyses result in chemical residues, which may be environmentally hazardous. In recent decades near-infrared diffuse reflectance spectroscopy (400-2500 nm) has been shown to be a viable alternative for rapidly analyzing soil properties. Information needs to be mathematically extracted from the spectra in order to correlate them with soil properties, and multivariate statistics are often used to calibrate soil prediction models. However, soils evaluated by the mid-IR region (4000 to 400 cm⁻¹) warrants new studies. The primary aim of this study was to investigate the feasibility to use soil spectral data and chemometrics methods to predict soil properties, in order to reduce the number of conventional soil analyses. The understanding of the relationships between spectral characteristics and the physic-chemical properties of soils were evaluated in three different studies with soils of: (i) spectral library (Chapter 1), (ii) amazonian region (Chapter 2), (iii) soils contaminated with heavy metals and tannery sludge (Chapter 3). It was possible to identify regions of the vis-NIR and mid-IR spectra that showed absorption features due to water, iron oxides, and clay minerals. In Chapter 1 the predicted models for clay and soil organic matter showed high accuracy. It reflects the influence of the direct spectral responses of these properties in the NIR. The division of the large library into smaller subsets based on variation in the spectra characteristics was the best alternative to quantify soil attributes in tropical soils by Partial Least Square regressions. Another alternative would be to use Boosted regression trees for the whole library. In Chapter 2, the mid-IR predicted models outperformed the vis-NIR. Comparison of the interpolation results revealed that the predictions of the PLS regression (mid-IR and vis-NIR) adequately reproduced the spatial pattern of the properties evaluated, especially soil organic carbon and cation exchange capacity and, had the ability to predict the soil properties of unknown samples from a different geographical location. In Chapter 3, the metals adsorption to soil constituents caused expressive changes in soil spectral curves, showing spectral differentiation between highly contaminated soil and soils that are relatively contaminant-free. The results indicate that the Cr pseudo-total content can be predicted by spectroscopy reflectance with both sensors data. Fe and Mn also can be predicted accuratley by vis-NIR. The vis-NIR models outperformed the mid-IR. Besides these results, the vis-NIR instrument has less complicated sample and can be used directly in the field using portable spectrorradiometers.

Keywords: Soil spectroscopy; Soil contamination; Soil organic carbon; Terra preta de índio; PLS regression, Support vector machine learning, Boosted regression trees; Spectral library.

1 INTRODUCTION

Once focused primarily on productivity, agriculture today has several different objectives. These include the diminution of production costs, minimizing the environmental impact of croplands and productive systems, and maximizing the final product quality. Among others, developing sustainable and highly productive agriculture requires information about soils, which are considered to be a finite, non-renewable resource in the short term (SOUZA JUNIOR; DEMATTÊ; ARAÚJO, 2011).

Soils are a complex, heterogeneous system made up of organic compounds in various stages of decomposition, mineral particles of various sizes deriving from the weathering of rocks and sediments, and gaseous and liquid components. They play a crucial role in the sustainability of the terrestrial ecosystem, provide habitat for a large number of organisms, and are responsible for plant growth, decomposition, and microbial biomass recycling (ALLOWAY, 1995). For the microorganisms, animals, protozoa, fungi, and plant roots that inhabit soils, edaphic conditions can be highly variable at small scales, changing from aerobic to anaerobic, wet to dry, and nutrient-rich to nutrient-poor.

Physical and chemical analyses of soil samples are one of the tools used to characterize soil quality, and consequently to provide proper amounts of soil fertilizers and prevent environmental pollution. Silva et al. (2001) have estimated that the number of conventional soil analyses carried out in Brazil reached 1 million samples in 2001. In 2011, the Soil Chemistry Analysis Laboratory of the *Escola Superior de Agricultura Luiz de Queiroz* (ESALQ) received approximately 21000 soil samples for classification and fertility analyses. This laboratory is just one of 118 members of the Proficiency-Tested Laboratories for Soil Analysis for agricultural applications, organized by the *Instituto Agronômico de Campinas* (IAC) in the state of São Paulo. The results of soil analyses are used to classify soils, indicate proper levels of fertilization and soil correctives, monitor environmental conditions, and other related activities.

In the context of environmental monitoring, soil pollution is known to be a serious problem around the world, largely due to the use of soils in agriculture, and because it can lead to the pollution of surface waters via erosion and the pollution of both groundwater and surface water as metals migrate through moist soils due to gravity. There is growing interest in using soils as an alternative means of helping manage environmental pollution. For example, soils are increasingly used to dispose of potentially polluting wastes such as tannery sludge. Using these residues in agriculture is one option for their disposal, since they have high levels of N. Soil analyses are a fundamental tool in such processes.

Management strategies for soil fertilizers and correctives often take the form of precision agriculture (PA), which requires information on the spatial variation of soil attributes in the field. Advances in PA over the last 20 years, thanks to global satellite navigation systems, geographical information systems, and technologies of variables rates, have increased demand for agricultural soil mapping that aims to provide, for example, high-resolution spatial information regarding soils and plants. PA that relies on knowledge about the spatial variation of chemical and physical soil attributes in the field thus requires high-density sampling (SILVA et al., 2010) and a large number of conventional soil analyses (WEBSTER; OLIVER, 1992). While some researchers have studied how to reduce the number of physical and chemical soil analyses (e.g. WETTERLIND et al., 2008), PA remains a high-cost venture in Brazil, and the high-resolution sampling it requires is one of various obstacles to its implementation by farmers.

Current analytical techniques allow one to determine very low quantities of elements in a variety of matrices, such as water, sediments, soils, and plant and animal tissues. These techniques have drawbacks, however, including the high price of soil analyses. Another problem is that common physical and chemical analyses of soils produce wastes, some of which are rich in metals, acids, and sodium. If these wastes are not treated and/or disposed of properly, they themselves can pollute soils and surface waters. For this and other reasons, there is increasing interest in developing alternative procedures to analyze soils.

One promising approach is the application of proximal sensing, and in particular reflectance spectroscopy associated with spectral absorption features analysis. NIR spectroscopy, for example, is receiving significant attention from environmentalists for its capacity to monitor changes in the quality of waterways and lakes, and the effects of disposing of material in soils such as manure and sludge. Without entering into contact with the substance, reflectance spectroscopy uses sensors to study electromagnetic radiation as a function of the wavelength that is reflected, emitted, or scattered by a gas, liquid, or solid (CLARK, 1999). Proximal sensors can be used in the field or in the laboratory, where spectral data are acquired under controlled conditions, without atmospheric interference or variation in lighting. The advantage of proximal sensors, both in the field and in the laboratory, is their ability to collect soil information with a higher spatial resolution than conventional techniques. Compared to remote sensing techniques (e.g., satellite images), proximal sensors permit researchers to collect data about superficial and subsurface soils (VISCARRA

ROSSEL et al., 2009). Examples of proximal sensors include those that measure the electrical conductivity (SUDDUTH et al., 2005) and mechanical resistance (ADAMCHUK et al., 2008) of soils, ground-penetrating radars that measure soil moisture (LUNT et al., 2005), acoustic sensors that measure compaction layers (GRIFT et al., 2005), electrochemical sensors that measure pH (ADAMCHUK et al., 2006), and diffuse reflectance spectroscopy in the vis-NIR-MIR regions (350 - 25000 nm) of the electromagnetic spectrum that predicts soil composition and various other attributes (e.g. ARAÚJO, 2008; VISCARRA ROSSEL et al., 2006;. DEMATTÊ et al., 2004; ISLAM et al., 2003; UDELHOVEN et al., 2003; CHANG et al., 2001).

Diffuse reflectance spectra (vis-NIR-MIR) contain a mixture of chemical and physical information. The physical portion is associated with the influence of particle size and surface structure on diffuse reflectance (DAHM; DAHM, 2004), while the chemical portion is related to the absorption energy by molecular bands. Absorption in the NIR region of the electromagnetic spectrum occurs due to overtones and combinations of fundamental vibrations of the OH, CH, NH, CO, CN, and NO groups in the mid-region. Depending on the soil components, radiation will cause molecular bonds (stretching and distortions) to vibrate, thereby causing them to absorb at various levels, one quantum of specific energy. Since the quantum de energy is directly related to the frequency, the resulting absorption spectrum takes a characteristic form that can be used for analytical purposes (MILLER, 2004). As a result, energy levels are affected by the surrounding environment, such as the functional group, neighboring molecules, and hydrogen. This means that a particular molecule only absorbs light of certain wavelengths, which allows the identification of molecules or substances due to different absorption patterns (EPHIPHANIO et al., 1992). Water, for example, has a strong influence on NIR spectra around 1400 and 1900 nm. Organic molecules generally include many molecular bonds that absorb in the NIR region. Clay minerals also have fundamental spectral characteristics in the NIR and MIR regions (VISCARRA et al., 2009; CLARK et al., 1990; HUNT, 1977).

Spectral attributes of soils thus represent a cumulative property of the intrinsic spectral attributes of the heterogeneous combinations of mineral and organic material and soil humidity levels present in soils (STONER; BAUMGARDNER, 1981). Thus, absorption features analysis uses diagnostic absorption bands in the reflectance spectrum that are the result of specific dielectric properties of the material. These wavelength-dependent properties generate a unique spectral reflectance signature from which materials can be described and distinguished (CLARK 1995; BEN-DOR et al. 1999).

Some authors have argued that the shape of spectra can provide valuable information about the chemical, physical, and mineralogical attributes of soils (e.g. DEMATTÊ et al., 2004; BEN-DOR et al., 2008; STENBERG et al., 2010). This possibility of linking spectral variation to specific absorption phenomena makes reflectance spectroscopy an important tool for studying the composition of soils in the laboratory. According to Shepperd and Walsh (2007), sensor sensing is one of the most efficient, cost-effective, and easily implemented analytical techniques, because when combined with calibrated statistical models it permits estimates of physical, chemical, and biological attributes from a single spectral reading of soil (McBRATNEY; MINASNY; VISCARRA ROSSEL, 2006).

In fact, vis-NIR reflectance spectroscopy of soils together with chemometric methods allow one to quantify various physical attributes (clay, sand, and silt), chemical attributes (CEC; pH; organic, inorganic, and total C; MO; Ca; N; K; Mg; As; Fe; Hg; Pb; S; Sb), and mineralogical attributes (kaolinite, gibbsite, montmorillonite, and iron oxides) of soils (KEMPER, SOMMER, 2002; VISCARRA ROSSEL et al., 2009; WETTERLIND et al., 2008; STENBERG et al., 2010). However, very little is known about how the medium infrared (MIR: 2500 - 5000 nm), thermal (TIR: 8000 - 14000 nm), and far (FIR: 15000 - 25000 nm) regions of the electromagnetic spectrum can contribute to the evaluation of Brazilian soils. In this thesis we named this range as mid-IR (2500-25000 nm). According to Viscarra Rossel et al. (2008), these wavelengths contain a large amount of information that has not yet been explored.

Another advantage of this soil analysis technique regards the ability to store digital data of analyzed spectra in real time. This raises the possibility of developing databases known as spectra libraries, which serve as standard references for developing and applying SR techniques at various scales, from field to space-based sensors. These libraries also facilitate the evaluation of predictive models of soil attributes, and serve as standards for pedological studies and soil classification (RIZZO, 2011; BELLINASO, DEMATTÊ, ARAÚJO, 2010; VISCARRA ROSSEL et al., 2008). Since April/2008, a world soil spectroscopy group was established by Viscarra Rossel (http://groups.google.com/group/soil-spectroscopy), who gathered soil spectra and corresponding attribute database providing soil-NIRS capability to all. This initiative was based on the idea that the NIRS approach in soil sciences was well established and feasible and that it should be more broadly collaborative.

This thesis examines some applications of vis-NIR (350-2500 nm) and mid-IR (4000-400 cm⁻¹ or 2500-25000 nm) spectroscopy and spectral libraries, such as estimating soil attributes via a variety of statistical techniques, and discusses their advantages and disadvantages in relation to conventional soil analysis methods. Soil is a complex mixture of components with different spectral properties. Each spectral component possesses unique eletronic transitions (caused by its atoms) and vibrations and molecular stretching (caused by structural groups of the atoms), leading to different spectral signatures in some spectral bands. Since it is known that the reflectance spectrum of soils is a linear combination of the spectral signatures of its components, weighted by their abundances, it is hoped that information regarding soil components can be obtained from spectral curves.

The primary aim of this study was to compare soil information obtained through conventional analytical methods with those obtained via vis-NIR and mid-IR reflectance spectroscopy of soils via statistical models, in order to reduce the number of conventional soil analyses required to monitor soils of areas polluted with heavy metals, to measure soil fertility, and to otherwise characterize soils. We also aim was to understand the relationships between spectral attributes and the chemical and physical attributes of the studied soils.

The specific objectives were:

Chapter I: Quantifying soil attributes via spectral library: a new approach

(i) Explore the possibility of enhancing predictions of OM and clay content in a large Brazilian soil spectral library by dividing it into smaller sub-libraries based on their vis-NIR spectra. In the process, we also tested the effect of three different pre-treatments of the spectra; continuum removal, first derivative, and mean normalization before dividing the library; (ii) compare the predictive performance of the sub-models with global models using PLSR and two multivariate data-mining techniques: boosted regression trees (BT) and support vector machines (SVM).

Chapter II: Characterization of potential Amazonian Dark Earth areas with proximal sensing techniques

(i) Characterize the chemical and spectroscopic (visNIR and mid-IR) attributes of these soils and compare the results with those of other studies from the region; (ii) identify parameters of spectral variation (e.g., band depth, reflectance intensity) associated with soil attributes content; (iii) explore the possibility of predicting soil properties based on spectral characteristics and Partial Least Square (PLS) regression. We also tested whether PLS models generated with soil data from one geographical area could be applied to soil data from another area. Successful results from this study would support the hypothesis that ADE mapping can be facilitated by spectroscopy techniques even when ADE occurs in small patches. This technique could improve and facilitate archaeological work, by helping identify locations where sampling and excavations should focus. The extent of these patches of high-fertility epipedons is of local and regional importance, and has been considered an indication of sustainable historical land use (SMITH, 1980; GLASER, 2000).

Chapter III: Environmental monitoring of soils: evaluating heavy metal pollution with vis-NIR and mid-IR spectral reflectance

(i) evaluate over time Cr, Pb and Zn in three soils contaminated by salts commonly used in the industry; (ii) identify parameters of spectral variation (vis-NIR and mid-IR) associated to heavy metals in soils and explore their viability in the evaluation of contaminated soils; (iii) evaluate through sequential extraction procedures, soils contaminated with tannery sludge (solid), after 90 days of application; (iv) investigate the feasibility to use soil spectral data and chemometrics methods to predict metals in soils. Although pure metals do not absorb in the vis-NIR and mid-IR regions of the spectroelectromagnetic they can be detected by their co-variation with spectrally active components in this range (STENBERG et al., 2010). Thus, this approach starts from the premise that the spectrally assigned position of minerals varies with chemical composition and surface activity (BEN-DOR et al., 1999)

Knowledge about the spectral attributes of soils is an important pre-requisite for a more efficient use of remote and proximal sensor products over a broad range of applications. There is still no universal formula for analyzing spectral data from all soil and sensor types. It is our hope that this study will contribute to the understanding of the effects of spectral interactions among some components of Brazilian soils, given that the nature of spectral analysis offers a possible solution to the problems posed by conventional soil analyses.

References

ADAMCHUK, V.I.; HUMMEL, J.W.; MORGAN, M.T.; S.K, UPADHYAYA. On-the-go soil sensors for precision agriculture. **Computers and Electronics in Agriculture**, London, v.44, p.71–91, 2007.

ARAÚJO, S.R. Sensoriamento remoto laboratorial na detecção de alterações químicas no solo pela aplicação de corretivos. 2008. 130p. Dissertação (Mestrado em Solos e Nutrição de Plantas) – Escola Superior de agricultura "Luiz de Queiroz", Universidade de São Paulo, Piracicaba, 2008.

BELLINASO, H.; DEMATTÊ, J.A.M.; ARAÚJO, S.R.A. Soil spectral library and its use in soil classification. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 34, p. 861-870, 2010.

BEN-DOR, E.; IRONS, J.R.; EPEMA, G. Soil Reflectance. In: RENCZ, A.N. (Ed.). **REMOTE SENSING for the Earth Sciences**. Canada: John Wiley, 1999. cap. 3, p. 111-188.

CHANG, C.W.; LAIRD, D.A.; MAUSBACH, M.J.; HURBURGH J.C.R.. Near-infrared reflectance spectroscopy principal components regression analysis of soil properties. **Soil Science Society of America Journal**, Madison, v. 65, p. 480-490, 2001.

CLARK, R.N. Remote sensing for the earth sciences In: RENCZ, A.N. (Ed.) **Manual of remote sensing**. New York: John Wiley, 1999. v.3 chap1: Spectroscopy of rocks and minerals, and principles of spectroscopy: p. 3–58.

CLARK, R.N.; ROUSH, T.L. Reflectance spectroscopy: quantitative analysis techniques for remote sensing applications. **Journal of Geophysical Research**, Washington, v. 89, p. 6329–6340, 1990.

DAHM, D. J.;DAHM, K. D. Interpreting Diffuse Reflectance and Transmittance – A Theoretical Introduction to Absorption Spectroscopy of Scattering Materials NIR Publications, Chichester, UK. 2004.p346.

DEMATTÊ, J.A.M.; CAMPOS, R.C.; ALVES, M.C.; FIORIO, P.R.; NANNI, M.R. Visible-NIR reflectance: a new approach on soil evaluation. **Geoderma**, Amsterdam, v. 121, n. 2004, p. 95-112..

EPIPHANIO, J.C.N.; FORMAGGIO, A.R.; VALERIANO, M.; OLIVEIRA, J.B. **Comportamento espectral de solos do Estado de São Paulo.** São José dos Campos: INPE, 1992. 131p.

GLASER, B.; BALASHOV, E.; HAUMAIER, L.; GUGGENBERGER, G.; ZECH, W. Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. **Organic Geochemistry**, Bristol, v. 31, p. 669-678, 2000.

GRIFT, T.E.; TEKESTE, M.Z.;RAPER, R.L. Acoustic compaction layer detection. **Transactions of the ASAE**, St.Joseph, v. 48, n.5, 1723-1730, 2005.

HUNT, G.R. Spectroscopic properties of rocks and minerals. In: CARMICHAEL, R.S. (Ed.). Handbook of physical properties analysis of of rocks. Boca Raton: CRC Press, 1982. p.295–385

ISLAM, K.; SINGH, B.; McBRATNEY, A. Simultaneuous estimation of several properties by ultra-violet, visible, and near-infrared reflectance spectroscopy. **Australian Journal of Soil Research**, Sidney, v. 41, p. 1101-1114, 2003.

LUNT, I.A.; HUBBARD, S.S.; RUBIN, Y. Soil moisture content estimation using groundpenetrating radar reflection data. **Journal of Hydrology, New Zealand, v.** 307, n.1/4, p. 254-269, 2005.

MILLER, C.E. Chemical principles of near-infrared technology. In: WILLIAMS, P. (Ed.) **Near-Infrared Technology in the Agricultural and Food Industries.** Minnesota: American Association of Cereal Chemists, 2004. p. 19-37.

RIZZO, R. **Técnicas espectroscópicas e atributos do terreno mapeamento digital de solos**. 2011. 171p. Dissertação (Mestrado em Solos e Nutrição de Plantas) – Escola Superior de agricultura "Luiz de Queiroz", Universidade de São Paulo, Piracicaba, 2011.

SILVA; C.A.; BERNARDI, A.C.C.; VAN RAIJ, B. **Infra-estrutura e qualidade das análises de solo realizadas em laboratórios de fertilidade do Nordeste participantes do PAQLF**. Rio de Janeiro: EMBRAPA, 2001. 4p. (Circular Técnica, 11).

SHEPHERD, K.D.; WALSH, M.G. Infrared spectroscopy - enabling an evidence-based diagnostic surveillance approach to agriculture and environmental management in developing countries. **Journal of Near Infrared Spectroscopy**, Chichester, v. 15, p. 1-19, 2007.

SMITH, N.J.H. Anthrosols and human carrying capacity in Amazonian. Annals of the Association of American Geographers, New York, v. 70, p. 553-566, 1980.

SOUSA JÚNIOR, J.G.; DEMATTÊ, J.A.M.; ARAÚJO, S.R. Modelos espectrais terrestres e orbitais na determinação de teores de atributos dos solos: Potencial e custos. **Bragantia**, Campinas, v.70, p. 610-621, 2011.

STENBERG, B.O.; VISCARRA ROSSEL, R.A.; MOUAZEN, A.M.; WETTERLIND, J. Visible and Near Infrared Spectroscopy in Soil Science. In: SPARKS, D.L. (Ed.). Advances in Agronomy, Burlington, v. 107, p. 163-215, 2010.

STONER, E.R.; BAUMGARDNER, M.F.; BIEHL, L.L.; ROBINSON, B.F. Atlas of soil reflectance properties. West Lafayette: Purdue University, 1980. 75p.

SUDDUTH, K.A.; DRUMMOND, S.T.; KITCHEN, N.R. Accuracy issues in electromagnetic induction sensing of soil electrical conductivity for precision agriculture. **Computers and Electronics in Agriculture**, Amsterdam, v. 31, p. 239–264, 2001.

UDELHOVEN, T.;EMMERLING, C.;JARMER, T. Quantitative analysis of soil chemical properties with diffuse reflectance spectrometry and partial least-square regression: A feasibility study. **Plant Soil**, Dordrecht, v.251, p.319–329, 2003.

VISCARRA ROSSEL, R.A.; McGLYNN, R.N.; McBRATNEY, A.B. Determining the composition of mineral-organic mixes using UV–vis-NIR diffuse reflectance spectroscopy, **Geoderma**, Amsterdan, n.137, p. 70–82, 2006.

WEBSTER, R.; OLIVER, M.A. Sample adequately to estimate variograms of soil properties. **European Journal of Soil Science**, v.43, p.177-192, 1992.

WETTERLIND, J.; STENBERG, B.; SODERSTROM, M. The use of near infrared (NIR) spectroscopy to improve soil mapping at the farm scale. **Precision Agriculture**, New York, v.9, p. 57–69, 2008.

2 QUANTIFYING SOIL ATTRIBUTES VIA SPECTRAL LIBRARY: A NEW APPROACH

Abstract

Effective agricultural planning requires basic soil information. In recent decades nearinfrared diffuse reflectance spectroscopy (NIRS) has been shown to be a viable alternative for rapidly analyzing soil properties. We studied 7171 samples of seven different soil types collected from several regions of Brazil and varying in OM (0.2 - 10.3 %) and clay content (0.2 - 99.0 %). The aim was to explore the possibility of enhancing the performance of NIRS data in predicting organic matter and clay content in this library by dividing it into smaller sub-libraries based on their vis-NIR spectra and to compare these results to two nonlinear calibration techniques (BT and SVM) applied to the whole library. The general predictive models for clay performed well ($\mathbb{R}^2 > 0.79$), reflecting the influence of the direct spectral responses of this property in the NIRS range. Predictions of OM were reasonably good, especially with clustering, and in view of the very low variation in this parameter. Results showed that the division of the large library into smaller subsets based on the variation in the mean-normalized spectra was the best alternative for using vis-NIR spectra to quantify soil attributes in tropical soils by Partial Least Square regressions. This divided the global data set into clusters that were more uniform in mineralogy, regardless of geographical origin, and improved predictive performance. Another alternative would be to use boosted regression trees for the whole library. It was also possible to identify regions of the vis-NIR spectrum that showed absorption features due to water, iron oxides and clay minerals that their variation might be responsible for the cluster divisions.

Keywords: Diffuse reflectance spectroscopy; Soil organic matter; Clay; PLS regression; Support vector machine learning; Boosted regression trees

2.1 Introduction

The efficient use of soils in agriculture requires a good understanding of their chemical, physical, mineralogical and biological characteristics. Soil texture and organic matter (OM) are two important properties of soils. Clay content directly affects the porosity, plasticity and erodibility of soils (WISCHMEIER; SMITH, 1978) and has, together with OM, a strong influence on soil structure (BRONICK; LAL, 2005). Both soil properties also affect soil fertility by their capacity for binding plant nutrients (CEC) and water, and OM plays an important role in the mineralization of nitrogen to phytoavailable forms (HOPKINS, 1995).

The accuracy of spatial maps of soil attributes is positively correlated with the density of soil observations. However, methods used to determine texture (GEE et al., 1986) and organic matter content (RAIJ et al., 2001) in conventional soil laboratories in Brazil and elsewhere are expensive and time-consuming. Moreover, such analyses can generate waste rich in Na and Cr, respectively, which may pose hazards to the environment. There is thus a need for more efficient methods to reduce the number of soil chemical analyses and generate

high-resolution soil property maps over large areas at reasonable costs. Visible and nearinfrared (vis-NIR) diffuse reflectance spectroscopy (400 - 2500 nm) has received increasing attention over the last two decades as a promising technique for soil analysis (e.g. UDELHOVEN et al., 2003; NANNI, DEMATTÊ, 2006; WETTERLIND et al., 2008; BELLINASO et al., 2010; DEMATTÊ et al., 2010).

The absorption of vis-NIR light occurs due to overtones and combinations of fundamental molecular absorptions in the mid-infrared region and is associated with soil moisture, organic materials, and mineralogy. As clay particles consist mainly of clay minerals, vis–NIR spectra can be assumed to be of value for predicting clay content (STENBERG et al., 2010). OM can be related directly to the absorption of vis-NIR spectra through a number of functional groups such as the carboxyl, hydroxyl and amine groups (CLARK et al., 1990; MADEJOVA; KOMADEL, 2005). However, the degree to which vis-NIR spectra data is capable of predicting OM content reported in the literature is highly variable (STENBERG et al., 2010).

Dunn et al. (2002) have pointed out that for spectroscopic techniques to be commercially practical for analyzing soils over large areas, there must be a wide range of spectroscopic data from different soil types with varying organic and inorganic components. This was further corroborated by Viscarra Rossel and Behrens (2010). Thus, a large number of samples are required to cover the relevant variation and the cost for building predictive models has to be considered. According to Sankey et al. (2008), global to regional calibrations are more cost-effective, but for many applications they may not provide sufficient accuracy. Those authors studied soil samples collected at three temperate sites (Montana, USA) and obtained improved predictions for some sites using the global library spiked with local samples compared with using only local samples. However, Wetterlind and Stenberg (2010) found that for a range of soil properties at farms in Sweden local calibrations with only 25 calibration samples outperformed both the national library (396 samples) and a subset of the national library consisting of the 50 samples most similar to each farm, and often resulted in equally good results compared with national and national subset models spiked with local samples, mainly through a decrease in bias and the root mean squared error of prediction.

According to Undelhoven et al. (2003), OM (approximated as1.72 times soil organic carbon) predictions can be improved by stratifying samples according to geological conditions and deriving individual PLSR calibrations for each region. Using large data sets representative of Swedish agricultural soils Stenberg et al. (2002) and Stenberg (2010) did not find any accurate soil organic carbon (SOC) calibration model, but these results were

substantially improved when sandy soils were removed from the data set. Similar results were observed by Sørensen and Dalsgaard (2005), who studied soils from throughout Denmark. They found that NIR calibration models of total carbon presented higher prediction errors for samples with low clay content (below 26%).

It is often suggested that libraries containing smaller soil variation at the field scale would result in better OM predictions than more general ones collected over larger geographic areas (e.g. KUANG; MOUAZEN, 2011). However, Stenberg et al. (2010), reviewing published predictions, found that variation in the texture or SOC variables themselves accounted for a majority of the variation in model accuracy for texture and SOC, respectively, and that the size of the geographic area had a small influence. Thus, attempts to improve the prediction accuracy of a large global/national spectral library may benefit from dividing the library into smaller sub-libraries with more similar soils, regardless of the geographical origin of the samples.

Because clay minerals and SOC tend to have the largest influence on soil vis-NIR spectra (STENBERG et al., 2010), dividing a global library into smaller models based on the variation in the spectra is one potential strategy for improving vis-NIR calibrations.

It is known that the soil vis-NIR spectra are largely non-specific, consisting of weak, broad, and overlapping absorption bands. For this reason, information needs to be mathematically extracted from the spectra in order to correlate them with soil properties, and multivariate statistics (MARTENS et al., 1989; MINASNY, 2008) are often used to calibrate soil prediction models.

Partial least square regression (PLSR) is one of the most commonly used techniques to analyze this type of data. Vasques et al. (2008) compared different techniques, such as stepwise multiple linear regression, principal component regression, regression trees, committee trees, and PLSR to analyze spectral information related to organic carbon and concluded that PLSR performed better than the other methods. Interest in using non-linear data-mining techniques is increasing, since relationships between soil characteristics are rarely linear in nature. Viscarra Rossel and Behrens (2010) compared PLSR and different data-mining algorithms for modeling SOC, pH, and clay content. They found that the support vector machine (SVM) technique using all vis-NIR wavelengths produced better models than PLSR and multivariate adaptive regression splines (MARS).When dealing with a highly heterogeneous sample set in which measured parameters may vary considerably, the precision of linear regression techniques tends to decrease due to the non-linear nature of the relationship between spectral data and the dependent variable. Brown (2007) suggest the use

of boosted regression trees, and Kovačević et al. (2009) the use of support vector machines as a solution for handling the calibration of large heterogeneous sample populations.

Although the soil electromagnetic spectrum has the potential to improve chemical analyses and soil mapping, vis-NIR spectroscopy has been rarely used to study soils of South America, in particular those in Brazil. There remains much to explore in this area. When it comes to spectroradiometry, we know far less about soils in the tropics than about soils in the temperate regions, and this is mainly due to lack of research (HARTEMINK, 2002).

This study aims to (i) explore the possibility of enhancing predictions of OM and clay content in a large Brazilian soil spectral library by dividing it into smaller sub-libraries based on their vis-NIR spectra. In the process, we also tested the effect of three different pre-treatments of the spectra; continuum removal, first derivative, and mean normalization before dividing the library; (ii) compare the predictive performance of the sub-models with global models using PLSR and two multivariate data-mining techniques: boosted regression trees (BT) and support vector machines (SVM).

Given the non-linear and contingent relationships between VNIR reflectance and soil composition (CLARK, 1999), it was expected that BT and SVM would perform better than PLSR, since they can incorporate complex, non-linear relationships and interactions whereas PLSR is built upon linear, continuous relationships between predictors and the target variable of interest.

2.2 Materials and Methods 2.2.1 Spectral library

For this study we used 7172 samples in the soil spectral library of the Remote Sensing Laboratory at the Soils Department, University of São. In total, chemical and spectral analyses were carried out for 5750 auger samples collected from boreholes and for 1422 samples collected from 233 soil profiles, at depths of 0-20, 40-60, or 80-100 cm, representing four Brazilian states (Goiás, Minas Gerais, Mato Grosso do Sul, and São Paulo). The soils in this spectral library are diverse and represent several orders of the World Reference for Soil Resources (WRB, 2006), including Ferrasols, Nitisols, Acrisols, Planosols, Gleysols, Acrisols, Arenosol, and Cambisols.

The samples were air-dried and ground to a particle size of <2 mm before being submitted to chemical and spectral analyses. Sand (2-0.05mm), silt (0.05-0.002 mm) and clay (<0.002 mm) contents were determined by the densimeter-sedimentation method, using 0.1 M calcium hexametaphosphate and 0.1 M sodium hydroxide as dispersing agents (GEE et al.,

1986). Organic matter (OM) content was determined by a colorimetric method (RAIJ et al., 2001).

2.2.2 vis-NIR measurements

The spectral reflectance of soils was measured in the vis-NIR (350-2500 nm) range, with a spectral resolution of 3 nm (from 350 to 1000 nm) and 10nm (from 1000 to 2500 nm), using a FieldSpec Pro FR spectroradiometer (Analytical Spectral Devices, Boulder, Colorado; Hatchell,1999). The spectrum acquisition software interpolated reflectance data to a sampling interval of 1 nm. Approximately 15 cm³ of each soil sample was placed in a Petri dish. A fiber-optic cable connected to the vis-NIR sensor was placed vertically at 8 cm from the sample, where we measured the reflected light in an area of approximately 15 cm² in the centre of the sample. The light source was a 50W halogen bulb with the beam non-collimated to the target plan, positioned at 35 cm from the sample at a zenith angle of 30°. As a reference standard, a white plate covered with barium sulphate (BaSO₄) was used. Each spectrum was averaged from 100 readings during 10 seconds. All spectral measurements were carried out in a dark room to avoid interference from stray light. Before further analyses, soil spectra were reduced by averaging 3 successive wavelengths. For further analyses we excluded the noisiest parts at the edges of the spectrum and only considered the spectral range from 366 nm to 2484 nm.

2.2.3 Model development

Prior to any model development the global spectral library was randomly divided into a calibration set (CS) with 5169 samples and a validation set (VS) with 2003 samples, keeping the layers of the same soil profile together to ensure independence between CS and VS (Figure 1). For subsequent analyses we removed samples with OM content above 6%, since there were very few of these. In total, 8 and 5 samples were removed from the CS and VS, respectively.



Figure 1 - Descriptive statistics, histograms and outlier box-plots for clay and organic matter content in the calibration (a) and validation (b) data sets. The mean (solid line), the median (rhombus), the 25th and 75th percentiles (box) and outliers (dots) are indicated. The red bracket indicates the standard deviation

The general approach in model development was that two major lines of calibration procedures were performed and compared. One involved straight forward on the calibration set as a whole (global models), and one involved calibrations that were performed cluster by cluster after the calibration set had been divided into spectrally similar clusters (clustered models). The first derivative using a 2nd order polynomial Savitzky-Golay smoothing over 11 points was applied as spectral pre-processing for all calibrations. This led to improved results for both clay and OM as compared to a range of other pre-treatments tested in our preliminary evaluation.

Global models were calibrated on the full, undivided calibration set (CS; n=5161). Three different calibration techniques were tested: PLSR, SVM, and BT. The PLSR technique is widely used, showing a good capacity for estimating attributes based on the spectral behavior of the soil (VASQUES et al., 2008). It was performed in Unscrambler v.10.1software on the calibration set using the orthogonalized PLSR algorithm for one Y-variable (PLS-1) and full cross-validation. The number of partial least-square (PLS) factors was chosen to minimize the root mean square error (RMSE) in the cross validation.

SVM is a relatively new nonlinear technique, compared with PLS, that is employed in classification and multivariate calibration problems (THISSEN *et al.*, 2003). In this technique, model complexity is limited by the learning algorithm itself, which prevents overfitting. In this study the Kernel radial basis function was used. Kernel transformation of the data avoids the use of complex functions and is computationally feasible (BALLABIO, 2009). It was performed with Statistica 64 software (2011).

BT is a multiple predictions based on re-sampling and weighing that belongs to the group of ensemble techniques (Friedman, 2001). BT has the ability to include a large number of weak relationships in a predictive model and it is insensitive to outliers in the calibration dataset. Moreover, BT has a relative immunity to overfitting (FREUND; SCHAPIRE, 1997, 2000; FRIEDMAN et al., 2000; RIDGEWAY, 2008). A committee of 400 trees was used to calibrate the soil carbon and clay equations using the calibration set, with a maximum number of sample redraws of tree. An optimal number of three nodes for clay and organic matter were identified by minimizing the least-square error. BT analyses were performed with Statistica 64 software (2011).

For the clustered models three different transformations prior to clustering were evaluated. The raw reflectance data were transformed to 1) the 1st derivative Savitzky-Golay (2nd order with 11 smoothing points; The Unscrambler v 10.1), 2) mean normalized (dividing each spectrum by its mean; The Unscrambler v 10.1), and 3) continuum removal (CR) calculated by a convex hull (ENVI 4.5, 2008; CLARK; ROUSH, 1984). The main purpose of the transformations was to see if they would divide the data differently and to assess what influence this would have on predictive performance for OM and clay. The procedures for calibrating and validating clustered data sets are summarized in Figure 2 as follows.



Figure 2 - Overview of steps taken during the pre-processing and analyses. First the calibration and validation datasets were defined. 1) The spectra from the calibration set were clustered with cluster analysis by their spectral features using three different transformations prior to the division. Subsequently, PLS calibrations were used to produce predictive models for OM and clay in each cluster. 2) To be able to allocate unknown samples (the validation set) to one of the spectrally defined clusters, the spectral features defining the clusters were identified by discriminant analysis models (DAM). 3) The validation set was clustered by the DAM's in step 2. For validation of the PLSR models in step 1, the validation samples clustered through step 2 and 3 were predicted and validation statistics compared

The three differently transformed data sets were submitted to a k-means clustering algorithm described by Wold (1982), with the statistical software Statistica 64 (Stat Soft. Inc.). This analysis starts with k random clusters, and then moves objects between those clusters in order to minimize the intra-group variability and to maximize the distances between groups. The software iteratively moves objects in and out of clusters, minimizing the square of the within-cluster sum of distances to get the most significant ANOVA results between clusters. For CR and 1^{st} derivative transformations, four clusters were found to be optimal and for normalized data the optimum number of classes was five. PLSR models were calibrated to test prediction performance depending on the different transformations.

2.2.4 Validation

All predictive models of OM and clay content, both the global ones by PLSR, BT and SVM and the clustered models, were validated using the predefined validation set (VS; n = 1998).

For the clustered models, the validation sample first had to be assigned to one of the clusters. Thus, the success of this assignment step was included in the validation of calibrations. Discriminant analysis (Wold, 1982) models, one for each transformation, were developed to define the spectral features that separate the clusters. The Euclidian metric distance method in Statistica 64 (Stat Soft.Inc.) was used to separate the pre-defined classes. For computational reasons the analyses were performed on dimensionally compressed data. Thus, score vectors from the 10 first principle components of a PCA based on the calibration set were used.Scores for the validation samples were calculated by projecting the transformed spectral data on the PCA based on the calibration set. Each validation sample was then assigned to one of the clusters for each transformation by the corresponding discriminant analysis model (Figure 2).

Finally, the coefficients of determination (R^2) , the root mean square error (RMSE), and the ratio of performance to deviation (RPD) were used to compare the results, calculated using the following equations:

$$RMSE = \sqrt{\frac{1}{n}} \sum_{i=1}^{n} (yi - yi^{\circ})^2$$

and

RPD = SD/RMSE

where n is the number of samples and SD is the standard deviation of laboratorymeasured values for the property in question.

2.3 Results and discussion

2.3.1 Global calibrations: prediction accuracy obtained with PLS, BT and SVM techniques

The validation results of the global predictions produced using the PLS, BT and SVM methods are summarized in Figure 3. Different regression methods provided different levels of predictive accuracy for OM and clay content. In general, we observed a tendency towards better results when using the boosted regression trees technique than SVM and PLSR
(Figure 3), but the differences were small. These results corroborate Brown et al. (2006), who compared BT and PLS techniques for analyzing soil properties with vis-NIR and found BT to be a superior modeling approach. Those authors used 4184 compositionally diverse, well-characterized, and largely independent soil samples. In our study we also used a large number of samples (more than 7000) and a heterogeneous data set with soil properties measured in the topsoil and subsoil in different soil orders. According to Friedman and Meulman (2003), the BT technique tends to be resistant to the effects of outliers, handling missing values and correlated variables. It also allows the inclusion of a potentially large number of irrelevant predictors (JALABERT et al., 2010).

However, Viscarra Rossel and Behrens (2010) and Vasques et al. (2008) observed that BT and regression trees models produced the worst results among many multivariate techniques, including PLSR and SVM, tested to analyze total carbon, organic carbon, and clay. Those studies used 1104 samples from four regions in Australia (50% of them surface soils) and 554 samples collected to a depth of 180 cm in north-central Florida, respectively. The contrasting results reported by these authors may be due to the very diverse origin of the data sets.

SVM also provided slightly better RMSE and RPD statistics than PLSR (Figure 3). Sá et al. (2010) also used the SVM technique to quantify total carbon in Brazilian soils and obtained an error of 0.11 % total carbon. They used 250 samples (0.4 - 3.1 % of total carbon) and a spectral interval of 1100 to 2498 nm.



Figure 3 - Validation scatter plot of laboratory-measured data versus vis-NIR predictions obtained from (a) partial least square regression, (b) boosted tree regression and (c) support vector machine for organic matter (OM) and clay content

2.3.2 Clustered calibrations: PLS model performance 2.3.2.1Clustering

The spectral library data were divided into spectrally defined clusters with different numbers of samples according to the transformation employed (CR, 1st derivative, and mean normalized) (Table 1). This division can be attributed to the variation of clay content in the dataset, given that soil mineralogy is one of the principal factors influencing soil reflectance (HARTMANN, APPEL, 2006) and that the type and concentration of soil minerals are strongly correlated with soil texture through the amount of clay minerals. In the discriminant analysis used to assign validation samples to the right clusters, the average and standard deviation values of OM and clay were similar in the validation and calibration sets for all the transformations (Table 1). Thus, the key requirement for empirical modeling, that validation samples are similar to the calibration samples (DARDENNE et al., 2000), was fulfilled.

Т	Classes	Ν	Minimum	Maximum	Mean	SD	Ν	Minimum	Maximum	Mean	SD				
						ОМ	, %								
			Cal	libration se	et		Validation set								
				k-means		discriminant analysis									
Ν	1	1251	0.10	5.30	1.09	0.76	512	0.20	5.30	1.08	0.75				
	2	715	0.20	5.40	2.07	1.10	238	0.20	4.80	2.09	1.07				
	3	955	0.20	5.60	1.82	0.91	347	0.30	4.30	1.81	0.85				
	4	450	0.20	3.30	1.29	0.71	175	0.20	3.30	1.26	0.70				
	5	1790	0.30	5.40	1.43	0.82	726	0.20	6.40	1.32	0.75				
D	1	2438	0.20	5.40	1.31	0.79	802	0.20	5.30	1.33	0.75				
	2	953	0.10	5.40	1.48	1.03	687	0.20	4.80	1.37	0.99				
	3	481	0.20	3.30	1.21	0.65	195	0.20	3.60	1.28	0.75				
	4	1289	0.20	5.60	1.84	0.93	314	0.30	4.20	1.88	0.86				
CR	1	745	0.20	5.30	1.80	0.90	289	0.40	4.20	1.80	0.82				
	2	740	0.20	5.40	1.70	1.00	312	0.20	4.80	1.62	1.00				
	3	2086	0.10	5.20	1.26	0.81	794	0.20	4.80	1.21	0.77				
	4	1590	0.20	5.60	1.48	0.89	603	0.20	5.30	1.42	0.86				
						Clay	y, %								
				k-means				discriminant analysis							
Ν	1	1251	6.00	92.00	29.20	18.27	512	8.00	89.00	29.77	18.89				
	2	715	6.90	96.00	64.77	23.32	238	8.00	94.00	64.29	24.75				
	3	955	0.20	99.00	62.44	17.75	347	4.00	92.00	63.49	16.23				
	4	450	12.00	92.00	53.04	17.27	175	12.00	86.00	49.55	15.79				
	5	1790	1.00	85.00	21.93	16.28	726	1.00	82.00	21.87	16.14				
D	1	2438	4.00	92.00	27.93	22.27	802	6.00	89.00	28.00	21.46				
	2	953	6.80	96.00	45.18	27.87	687	1.00	94.00	39.45	27.51				
	3	481	8.00	92.00	48.80	18.06	195	10.60	84.00	46.24	17.22				
	4	1289	0.20	99.00	56.46	21.22	314	9.80	87.00	58.84	18.89				
CR	1	745	0.20	91.00	59.50	18.97	289	14.00	89.00	59.39	17.44				
	2	740	8.00	94.00	54.13	20.38	312	4.00	93.00	50.20	21.38				
	3	2086	6.00	99.00	39.28	26.12	794	1.00	94.00	36.72	25.50				
	4	1590	4.00	96.00	25.86	21.05	603	6.00	92.00	25.05	20.84				

Table 1 - Calibration and validation sample statistics of data sets of the groups divided by cluster *k*-means and discriminant analysis respectively.

N, D and CR means normalization, first derivative and continuum removal transformations, respectively.

2.3.2.2 Clustered predictions

The validation statistics calculated based on the combined prediction results (CPR) of all validation samples in all clusters by the respective pre-transformations (CPR-N, CPR-D and CPR-CR, respectively) (Table 2) showed that transforming the data using continuum

removal and especially mean normalization prior to cluster analysis provided more accurate models than transforming the data by applying the 1st derivative.

Preprocessing	Cluster	Number		Clay	•		OM				
1 0		of samples	R^2	RMSEv	RPD	R^2	RMSEv	RPD			
	1	512	0.75	9.63	1.96	0.54	0.51	1.47			
Normalized	2	238	0.83	10.43	2.37	0.76	0.53	2.02			
	3	347	0.40	11.13	1.46	0.53	0.47	1.81			
	4	175	0.68	9.15	1.73	0.40	0.55	1.29			
	5	726	0.77	7.80	2.07	0.58	0.27	2.85			
CPR - N			0.87	9.28	2.74	0.60	0.42	2.07			
1st derivative	1	802	0.61	13.34	1.66	0.40	0.56	1.35			
	2	687	0.79	12.65	2.18	0.62	0.53	1.78			
	3	195	0.57	11.62	1.19	0.30	0.61	1.24			
	4	314	0.52	12.75	1.45	0.27	0.76	1.14			
CPR - D			0.76	12.84	1.98	0.30	0.59	1.47			
CR	1	289	0.53	12.22	1.43	0.60	0.53	1.54			
	2	312	0.61	13.89	1.54	0.60	0.65	1.55			
	3	794	0.85	9.90	4.46	0.60	0.30	2.61			
	4	603	0.76	10.30	2.02	0.59	0.38	2.25			
CPR - CR			0.81	10.98	2.31	0.56	0.41	2.12			
PLS	all	1988	0.79	11.16	2.27	0.52	0.60	1.45			
ВТ	all	1988	0.83	10.80	2.35	0.61	0.54	1.60			
SVM	all	1988	0.81	11.00	2.30	0.55	0.62	1.40			

Table 2 - Summary statistics of validation results of calibrations for clay (%) and OM (%) using an independent validation dataset

The number of samples was based on discriminant analyses. *PLS, BT and SVM* refer to nonclustered models obtained by Partial Least Squares regression, Boosted Regression Trees, and Support Vector Machines, respectively; CPR - N,CPR - D, andCPR - CR refer to combined prediction results(CPR) with mean normalization (N), 1st derivative (D),and continuum removal (CR) as pre-transformation treatments, respectively.

Predictive accuracy differed among and within the clustering methods (Table 2). Comparing the validation results obtained from the global library and from combined cluster predictions, the data that was transformed by normalization before the clustering analysis resulted in improved validation results (Table 2).We observed a larger improvement in accuracy of models for OM than for clay with clustered models, with a reduction of the RMSE of 30 % and 17% for OM and clay, respectively.

When normalization was used as a pre-processing treatment, the global spectral library was divided into 5 clusters. The independent validation results for clusters 2 and 5 presented the highest values of RPD and R^2 , followed by clusters 1, 4, and 3, respectively for clay and 3, 1, and 4 for OM. The combined prediction results with mean normalization (CPR-N) are shown in Figure 4. In the CR approach we observed differences between the independent validation model results, especially for cluster 3, which presented RPD values of 4.46 for clay and 2.61 for OM (Table 2).



Figure 4 - Validation scatter plot of laboratory measured data versus vis-NIR predictions obtained from partial least square regression (CPR- N)

The results of the RMSE (Table 2) reveal higher values of model errors when the 1st derivative was applied before the cluster analysis, with mean values of RMSE of 12.84 for clay and 0.59 for OM. According to Brown et al. (2005), the 1st derivative analysis can introduce instability and noise to soil reflectance data because of changing spectral contributions of soil minerals (ROUSH, 1984; KOKALY, CLARK, 1999). This may have reduced the accuracy of the discriminant analysis of our data.

Models	Cla	ay	OM				
	RMSEcv	RMSEv	RMSEcv	RMSEv			
CPR - N	8.84	9.28	0.51	0.42			
CPR - D	10.97	12.84	0.57	0.59			
CPR - CR	10.16	10.98	0.51	0.41			
PLS	11.32	11.16	0.62	0.60			
BT	9.32	10.80	0.51	0.54			
SVM	14.56	11.00	0.64	0.62			

Table 3 - Prediction results of cross-validation (RMSEcv) and independent validation (RMSEv) of clay (%) and OM (%)

PLS, BT and SVM refer to non-clustered models obtained by Partial Least Squares regression, Boosted Regression Trees, and Support Vector Machines, respectively; CPR - N,CPR - D, andCPR - CR refer to combined prediction results (CPR) with mean normalization (N), 1st derivative (D), and continuum removal (CR) as pre-transformation treatments, respectively.

The success of assigning the validation samples to the right cluster by discriminant analyses on normalized data can be seen in Figure 5, which shows the linear discriminate analyses projection of the 5 clusters. The relevance of using normalization transformation is in accordance with other authorswho found this pre-processing to improve soil propertycalibrations. For example, Kuśnierek (2011), in a study of Polish soils, observed that this transformation was the best of several for SOC modeling.



Figure 5 - Projection of linear discriminant analysis clusters, obtained with normalized transformation, on the corresponding K-means cluster. The letters a, b, c, d, and e refer to cluster numbers 1, 2, 3, 4, and 5, respectively

In our study, the additional step of assigning validation samples to the right class in the prediction process did not add substantially to the overall prediction error. We observed that cross validation (which does not involve sample-to-cluster assignment) and independent validation (which does) results did not differ substantially more for the clustered models as compared to the global models (Table 3). If the assignment of validation samples to clusters added substantially to the prediction error, a larger difference for the clustered models would be expected.

Based on Stenberg et al. (2010), we compared our results to the standard deviations and RMSE or R^2 of most large-scale published data sets with all three values available (Figure 6). Since the relationship between SD and RMSE is so strong, it is more relevant to compare results with other studies in this context rather than simply comparing RMSE's, R^2 values, or RPD's. We observe that our R^2 values are slightly lower than expected from previously published data, but less so for BT and normalized clustering. RMSE's were, on the other hand, more or less as expected, but while global PLS and SVM were found slightly above the regression line normalized clustering was found slightly below the line, which should indicate a successful result.

Predictions of clay were equal, or slightly better, than what could be expected from the standard deviation of 25% clay in the global library, according to the strong correlation between standard deviations and RMSE's found in a compilation of published data by Stenberg et al. (2010), corresponding to the one for OM in Figure 6.



Figure 6 - Correlations between the standard deviation and RMSE (a) and R² (b). Published data on organic matter predictions with vis-NIR spectroscopy extracted from Malley *et al.*, 2000; Chang *et al.*, 2001; Chang & Laird, 2002; Dunn *et al.*, 2002; Fystro, 2002; Martin *et al.*, 2002; Moron &Cozzolino, 2002; Stenberg *et al.*, 2002; Islam *et al.*, 2003; Udelhoven *et al.*, 2003; Chang *et al.*, 2005; Sorensen &Dalsgaard, 2005; Todorova *et al.*, 2009; Stenberg, 2010; ViscarraRossel& Behrens, 2010; Nocita *et al.*, 2011; Vohland *et al.*, 2011; Cambule *et al.*, 2012; Goge *et al.*, 2012; Tekin *et al.*, 2012 (o); PLS results data: global model (●); BT regression results: global model (▲); SVM results: global model (■) and PLS results data: normalized cluster models (▼). Adapted from Stenberg et al. (2010)

2.3.2.3 Soil spectra

Bands around 1100, 1600, 1700, 2000, and 2300 nm have been identified as being particularly important for SOC and total N calibration (MALLEY et al., 2000; MARTIN et al., 2002; DALAL, HENRY, 1999). Although we observed different spectral features in these ranges, by removing the continuum from the average reflectance spectra of the classes, they were not enhanced according to the OM content, as observed by Stenberg (2010). This is probably explained by the very low concentrations and narrow range of OM values in the library we worked with (Table 1) and by the fact that the dominant features in the spectra are often related to soil mineralogy (BEN-DOR, BANIN, 1995; STENBERG et al., 2010).

The mean spectral curves of samples of classes that were transformed by mean normalization prior to the cluster analysis were analyzed in detail by their continuum removed spectra (Figure 7) since these classes presented the most stable clustering and the best regression model results (Table 3). We observed that soil mineralogy has the greatest influence on spectra clustering and that spectral variation related to mineralogy makes more uniform data sets and consequently more robust soil prediction models.

The 1400 and 1900 nm bands are associated with water vibrations connected to bonds of lattice layers as hydrated cations (structural), combined with water adsorbed on the particle surfaces. In all classes we observed absorptions duo to charge transfers near 400 - 780 nm which are indicative of the presence of iron oxides (SHERMAN, WAITE, 1985). In turn, bands near 489 and 530 are attributed to absorptions edges of intense charge transfer absorptions that occur in the UV (SHERMAN, WAITE, 1985). The lower reflectance observed around 510-560 nm (Figure 7b) suggests that soils belonging to classes 1, 3, and 5present higher hematite contents, followed by the soils of classes 2 and 4, respectively (DEMATTÊ, GARCIA, 1999). Scheinost et al. (1998) reported that the most intense absorption band for hematite occurred at 521 to 565 nm, clearly separated from the more yellowish Fe oxides (479 to 499 nm and 930 nm).In fact, the mean spectral reflectance of classes 2 and 4 showed a shift to the right at 930 nm which may indicate a greater presence of goethite than hematite (Figure 7a) in those classes. Although these classes and class number 3 have similar average levels of clay (Table 1), their characteristic patterns of kaolinite are different.

Regarding the clay minerals in the soil, it is known that kaolinite (1:1) and 2:1 minerals show characteristic patterns between 1400 and 2200 nm due to the vibrations of molecules of OH of their structures (HUNT; SALISBURY, 1970). Their shapes are different, however, which is attributed to the existence of a shoulder (Figure 7c) in the formation of the absorption band related to a1.1 mineral, a fact that does not occur when there is predominance of a 2:1 mineral in the soil (DEMATTÊ et al., 1998). This shoulder is smoother for clusters numbers 3, 5, and 1 (Figure 7c). Hunt et al. (1973) argued that the intensity of the kaolinite trait at 2200 nm is associated with the dioctahedral layers of the mineral structure. Although the absorption near 2345 nm may represent illite or mixtures of smectite and illite (POST, NOBLE, 1993), we observed only a slight difference in reflectance between classes 2 and 4 and others at this peak.



Figure 7 - The continuum-removed spectra average of classes obtained by k-means clustering analyses when the global data was submitted to mean normalization

2.4 Conclusions

The general predictive models for clay were good, which reflects the influence of the direct spectral responses of this property in the NIR range. OM predictions were reasonably good, especially with clustering and in view of the very low variation in OM levels in the data set.

The division of the large library into smaller subsets based on variation in the meannormalized spectra was the best alternative for using vis-NIR spectra to quantify soil attributes in tropical soils by Partial Least Square regressions. It divided the global data set into more mineralogically uniform clusters, regardless of geographical origin, and improved predictive performance. The additional step of assigning the validation samples to the right class in the prediction process (clustered models) did not add substantially to the overall prediction error. Another alternative would be to use Boosted regression trees for the whole library. Comparing the results of this study and previously published ones indicates that the selection of the best performing pre-processing method is dataset-dependent. It was also possible to identify regions of the vis-NIR spectrum that showed absorption features due to water, iron oxides, and clay minerals that their variation might be responsible for the cluster divisions.

References

BALLABIO, D.; TODESCHINI, R. Multivariate classification for qualitative analysis in infrared spectroscopy for food quality: Analysis And Control. London: Elsevier, 2009. p. 83–104.

BEN-DOR, E.; BANIN, A. Near-infrared analysis as a rapid method to simultaneously evaluate several soil properties, **Soil Science Society of American Journal**, Madison, v. 59, p. 364-372, 1995.

BELLINASO H.; DEMATTÊ J.A.M.; ARAÚJO S.R.A. Soil spectral library and its use in soil classification. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 34, p. 861-870, 2010.

BRONICK, C.J., LAL, R. Soil structure and management: a review. **Geoderma**, Amsterdan, v 124, n.1/2, p.3-22, 2005

BROWN, D.; SHEPHERD, K.D.; EALSH, M.G.; MAYS, M.D. REINSCH, G. Global soil characterization with VNIR diffuse reflectance spectroscopy. **Geoderma**, Amsterdan, v. 132, p. 273-290, 2006.

BROWN, D.J.;BRICKLEMYER, R.S.;MILLER, P.R. Validation requirements for diffuse reflectance soil characterization models with a case study of vis–NIR soil C prediction in Montana. **Geoderma**, Amsterdan, v. 129, p.251–267, 2005.

BROWN, D.J. Using a global vis–NIR soil-spectral library for local soil characterization and landscape modeling in a 2nd-order Uganda watershed. **Geoderma**, Amsterdan, v.140, 444–453, 2007.

CAMBULE, A.H.;ROSSITER, D.G.;STOORVOGEL, J.J. &SMALING, E.M.A. Building a near infrared spectral library for soil organic carbon estimation in the Limpopo National Park, Mozambique. **Geoderma**, Amsterdan, v 183, p.41-48, 2012.

CHANG, C.W.; LAIRD, D.A. Near-infrared reflectance spectroscopic analysis of soil C and N. **Soil Science**, Philadelphia, v. 167, n. 2, p. 110-116, 2002.

CHANG, C.W.; LAIRD, D.A.; MAUSBACH, M.J.; HURBURGH, C.R Near-infrared reflectance spectroscopy-principal components regression analyses of soil properties. **Soil Science Society of American Journal**, Madison, v. 65, p. 480-900, 2001.

CHANG, G.W., LAIRD, D.A.; HURBURGH, G.R. Influence of soil moisture on nearinfrared reflectance spectroscopic measurement of soil properties. **Soil Science**, Baltimore, v 170, 244-255, 2005

CLARK, R.N. Spectroscopy of rocks and minerals and principles of spectroscopy. In: RENCZ, A.N. (Ed.). **Remote Sensing for the Earth Sciences**. Canada: John Wiley, 1999. chap. 1, p. 3-58.

CLARK, R.N.; ROUSH, T.L. Reflectance spectroscopy: quantitative analysis techniques for remote sensing applications. **Journal of Geophysical Research**, Washington, v. 89, p. 6329–6340, 1984.

CLARK, R.N.; KING, T.V.V.; KLEJWA, M.; SWAYZE, G.; VERGO, N. High resolutionreflectance spectroscopy of minerals. **Journal of Geophysical Research**, Washington, v. 95, p. 12653-12680, 1990.

DALAL, R.C.; HENRY, R. J. Simultaneous determination of moisture, organic carbon and total nitrogen by near infrared reflectance spectrophotometry. **Soil Science Society of America Journal**, Madison, v. 50, p.120-123, 1986.

DARDENNE, P.; SINNAEVE, G. ;BAETEN, V. Multivariate calibration and chemometrics for near infrared spectroscopy: which method?.**Journal of Near Infrared Spectroscopy**, New York, v 8, n.4, p. 229–237, 2000.

DEMATTÊ, J.A.M.; GARCIA, G.J. Alteration of soil properties through a weathering sequence as evaluated by spectral reflectance. **Soil Science of America Journal**, Madison, v. 63, n. 2, p.327-342, Mar./Apr. 1999.

DEMATTE, JAM. ;NANNI, M.R.; SILVA, A.P.; MELOFILHO, J.F., SANTOS, W.C.; CAMPOS, R.C. Soil density evaluated by spectral reflectance as an evidence of compaction effects. **International Journal of Remote Sensing** (Print), v.31, p. 403-422, 2010.

DUNN, B.W.; BEECHER, H.G.; BATTEN, G.D.; CIAVARELLA, S. The potencial of nearinfrared reflectance spectroscopy for soil analysis – a case study from the Riverine Plain of south-eastern Australia. **Australian Journal of Experimental Agriculture**, Melbourne, v.42, p.607-614, 2002.

ENVI. Environment for Visualizing Images.Guia do ENVI 3.5 emPortuguês. Disponívelem: http://www.envi.com.br. Acesso em: 2012.

FREUND, Y.; SCHAPIRE, R. E. A decision-theoretic generalization of on-line learning and an application to boosting.**J. Comput. System Sci**. 55 119 139, 1997.

FRIEDMAN, J.H.; MEULMAN, J.J. 2003. Multiple additive regression trees with application in epidemiology. **Statistics in Medicine**, New York, v.22,p.1365–1381, 2003.

FYSTRO, G. The prediction of C and N content and their potential mineralisation in heterogeneous soil samples using Vis-NIR spectroscopy and comparative methods. **Plant and Soil**, Dordrecht, v. 246, p.139-149, 2002.

FRIEDMAN, J.H. Greedy function approximation: a gradient boosting machine. **The Annals of Statistics**, Beachwood, v. 29, p. 1189-1232, 2001.

GEE, G.W.;BAUDER, J.W. Particle size analysis. IN: KLUTE, A. (Ed.). Methods of SoilAnalysis: pt 1. Physical and Mineralogical Methods. **Soil Science Society of America**, Madison, WI, p. 383–411, 1996.

GOGE, F.; JOFFRE, R.; JOLIVET, C.;ROSS, I.; RANJARD, L. Optimization criteria in sample selection step of local regression for quantitative analysis of large soil NIRS database. **Chemometrics and Intelligent Laboratory Systems,** Amsterdam, v.110, p.168-176, 2012.

HARTMANN, H.P.; APPEL, T. Calibration of near infrared spectra for measuring decomposing cellulose and green manure in soils. Soil Biology & Biochemistry, Madison,v.38, p. 887–897, 2006.

HARTEMINK, A.E. Soil science in tropical and temperate regions – Some differences and similarities. Advances in Agronomy 77: 269-292, 2002.

HARTEMINK, A.E.; MCBRATNEY, A. A soil science renaissance. Geoderma, Amsterdam, v. 148, p. 123-129, 2008.

HUNT, G.R.; SALISBURY, J.W. Visible and near-infrared spectra of minerals and rocks: I silicate minerals. **Modern Geology**, London, v. 1, p. 283-300, 1970.

ISLAM, K.; SINGH, B.; McBRATNEY, A. Simultaneuous estimation of several properties by ultra-violet, visible, and near-infrared reflectance spectroscopy. **Australian Journal of Soil Research**, Sidney, v. 41, p. 1101-1114, 2003.

JALABERT, S.S.M. ;MARTIN, M.P.; RENAUD, J.P.; BOULONNE, L.; JOLIVET, C.; MONTANARELLA, L.; ARROUAYS, D. Estimating forest soil bulk density using boosted regression modelling. **Soil Use and Management**, London, v. 26, p. 516-528, 2010.

KOKALY, R.F.; CLARK, R.N. Spectroscopic determination of leaf biochemistry using banddepth analysis of absorption features and stepwise multiple linear regression. **Remote Sensing of Environment,** New York, v 67,p. 267–287, 1999.

KUANG, B.; MOUAZEN, A.M. Calibration of a visible and near infrared spectroscopy for soil analysis at field scales across three European farms. **European Journal of Soil Sciences**, v. 62, 629–636, 2011.

KUŚNIEREK, K. Pre-processing of soil visible and near infrared spectra taken in laboratory and field conditions to improve the within-field soil organic carbon multivariate calibration. The Second Global Workshop on Proximal Soil Sensing – Montreal 2011.

MADEJOVA, J.; KOMADEL, P. Baseline studies of the clay minerals society source clays: infrared methods. **Clays Clay Minerals**, New York, v. 49, 410–432, 2001.

MALLEY, D.F.; MARTIN, P.D.; MCCLINTOCK, L.M.; YESMIN, L.; EILERS, R.G.; HALUSCHAK, P. . Feasibility of analysing archived Canadian prairie agricultural soils by near infrared reflectance spectroscopy. In: DAVIES, A.M.C.; GIANGIACOMO, R. (Ed) 'Near Infrared Spectroscopy: In: INTERNATIONAL CONFERENCE, 9., 2000. **Proceedings...** Chichester, UK :NIR Publications,2000. p 253

MARTENS, H.; NAES, T. Multivariate Calibration. Chichester, UK:John Wiley, 1989. 419p.

MARTIN, P.D.; MALLEY, D.F.; MANNING, G.; FULLER, L. Determination of soil organic carbon and nitrogen at the field level using near-infrared spectroscopy. **Canadian Journal of Soil Science**, Montreal, v.82, p.413–422, 2002.

MINASNY, B.; TRANTER, G.; MCBRATNEY, A.B.; BROUGH, D.M.; MURPHY, B.W. Regional transferability of mid-infrared diffuse reflectance spectroscopy prediction for soil chemical properties. **Geoderma**, Amsterdam,v.153, p. 155-162, 2009.

MORON, A.; COZZOLINO, D. Application of near infrared reflectance spectroscopy for the analysis of organic C, total N and pH in soils of Uruguay. **Journal of Near Infrared Spectroscopy**, New York, v. 10, 215-221, 2010.

NANNI, M.R.; DEMATTÊ, J.A.M. Spectral reflectance methodology in comparison to soil analysis. **Soil Science Society of American Journal**, Madison, v. 70, p. 393-407, 2006.

NOCITA, M.; KOOISTRA, L.; BACHMANN, M.; MUELLER, A.; POWELL, M.; WEEL, S. Predictions of soil surface and topsoil organic carbon content through the use of laboratory and field spectroscopy in the Albany Thicket Biome of Eastern Cape Province of South Africa.**Geoderma**, Amsterdam, v 167/168, p.295-302, 2011.

POST, J. L.; NOBLE, P. N. The near-infrared combination band frequencies of dioctahedralsmectites, micas, and illites. **Clays and Clay Minerals**, New York, v. 41, p.639–644, 1993.

RIDGEWAY, G. 2007. \Generalized Boosted Models: A Guide to the gbm Package." R package vignette, URL http://CRAN.R-project.org/package=gbm.

SÁ,S.O.;ALTHMANN,D.;FIGUEIREDO,K.L.;BERNOUX,M.;POPPI,R.J.;CERRI, C.C. NIRS-LS-SVM to estimate carbon content of agricultural land in Brazilian Cerrado soils. IOPConf. : Series: **Earth and Environmental Science**, New York, 6, p. 242-237, 2009.

SANKEY, J.B.; BROWN, D.J.; BERNARD, M.L.; LAWRENCE, R.L. Comparing local vs. global visible and near-infrared (VisNIR) diffuse reflectance spectroscopy (DRS) calibrations for the prediction of soil clay, organic C and inorganic C. **Geoderma**, Amsterdam, v. 148, p. 149-158, 2008.

SHERMAN, D.M.; WAITE, T.D. Electronic spectra of Fe⁺³ oxides and oxide hydroxides in the near IR to near UV. **American Mineralogist**, Chantilly, v. 70, p. 1296-1269, 1985.

SORENSEN, L.K.; DALSGAARD, S. Determination of clay and other soil properties by near infrared spectroscopy. **Soil Science Society of American Journal**, Madison, v. 69, p. 159-167, 2005.

StatSoft, Inc. (2011). STATISTICA (data analysis software system), version 10.www.statsoft.com.

STENBERG, B.; BORJESSON; T.; JONSSON, A. Near infrared reflectance spectroscopy - a rapid method for predictive field mapping of soil-N mineralisation? DIAS Report, **Plant Production**, London, p. 103-111, 2002.

STENBERG, B. Effects of soil sample pretreatments and standardised rewetting as interacted with sand classes on Vis-NIR predictions of clay and soil organic carbon. **Geoderma**, Amsterdam, v 158, p.15-22, 2010.

STENBERG, B.; VISCARRA ROSSEL, R.A.; MOUAZEN, A.M.; WETTERLIND, J. 2010.Visible and near infrared spectroscopy in soil science. **Advances in Agronomy**, Amsterdam, v.107, n. 107, p. 163-215, 2010.

THISSEN, U.; VAN BRAKEL, R.; DE WEIJER, A.P.; MELSSEN, W.J.; BUYDENS, L.M. C. **Chemometrics Inteligent Laboratory System,** Amsterdan, v. 69, p. 35–49, 2003.

TEKIN, Y.; TUMSAVAS, Z.; MOUAZEN, A.M. Effect of Moisture Content on Prediction of Organic Carbon and pH Using Visible and Near-Infrared Spectroscopy. **Soil Science Society of America Journal**, Madison, v. 76, p.188-198, 2012.

TODOROVA, M.; ATANASSOVA, S.; ILIEVA, R. Determination of soil organic carbon using near-infrared spectroscopy. **Agricultural Science and Technology**, New York, v. 1,p. 45-50, 2009.

UDELHOVEN, T.; EMMERLING, C.; JARMER, T. Quantitative analysis of soil chemical properties with diffuse reflectance spectrometry and partial least-square regression: A feasibility study. **Plant Soil**, Dordrecht, v. 251, p.319–329, 2003.

VASQUES, G.M.; GRUNWALD, S.; SICKMAN, J.O. Modeling of soil organic carbon fractions using visible-near-infrared spectroscopy. **Soil Science Society of American Journal**, Madison, v. 73, p. 176-184, 2009.

VISCARRA ROSSEL, R.A.; BEHRENS, T. Using data mining to model and interpret soil diffuse reflectance spectra. **Geoderma**, Amsterdam, v. 158, p. 46-54, 2010.

VOHLAND, M.; BESOLD, J.; HILL, J.; FRUEND, H.-C. Comparing different multivariate calibration methods for the determination of soil organic carbon pools with visible to near infrared spectroscopy. **Geoderma**, Amsterdam, v. 166, v.198-205, 2011.

WETTERLIND, J.; STENBERG, B.; SÖDERSTRÖM, M. The use of near infrared (NIR) spectroscopy to improve soil mapping at the farm scale. **Precision Agriculture**, Berlin, v. 9, p. 57-69, 2008.

WETTERLIND, J.; STENBERG, B.; SÖDERSTRÖ, M. The use of near infrared (NIR) spectroscopy to improve soil mapping at the farm scale. **Geoderma**, Amsterdam, v. 156, p. 152-160, 2010.

WISCHMEIER, W.H.; SMITH, D.D. **Predicting rainfall erosion losses**: a guide to conservation planning. Washington: Department of Agriculture, 1978. 58p. (Agriculture Handbook, 537),

WOLD, S.; ANTTI, H.; LINDGREN, F.; O["] HMAN, J. Orthogonal signal correction of nearinfrared spectra. **ChemometricsInteligent Laboratory System**, Amsterdan ,v. 44, p.175– 785, 1998. IUSS WORKING GROUP WRB. **World reference base for soil resources** 2006. 2nd ed. Rome:FAO, 2006.(World Soil Resources Report, 103)

3 CHARACTERIZATION OF POTENTIAL AMAZONIAN DARK EARTH AREAS WITH PROXIMAL SENSING TECHNIQUES

Abstract

In the Brazilian Amazon region there are soils known as Terra Preta de Índio or Amazonian Dark Earths (ADE), which are rich in carbon (C) and plant nutrients. A better understanding of ADE areas is important for choosing appropriate management strategies to maintain the fertility of ADE under current agricultural regimes. We investigated if rapid spectroscopy data collection could be used to assess the spatial distribution of properties of this kind of soil, in order to reduce costs, and explored the possibility of predicting soil properties based on their spectral (400-25000 nm) characteristics using Partial Least Square (PLS) regressions. We also tested whether the PLS models generated by soil data from one geographical area could be applied to soil data from another. The study was carried out in the Santarém-Belterra region of Pará state, Brazil, in two sites. In total, more than 300 soil samples were collected in these two locations, each of which had some soils that could be classified as ADE. As a reference, 225 of the samples were analyzed by traditional methods in the laboratory (e.g., pH, P, K, Ca, CEC, and soil organic carbon (SOC)). General properties typical of ADE (high SOC, Ca, and P) were found in portions of the study areas. Characterizing the spectral curves allowed us to distinguish between different layers and soils. Models of soil properties using the mid-IR (4000-400 cm⁻¹) sensor data outperformed those using vis-NIR (400-2500 nm). Comparing the interpolation results revealed that the predictions of the PLS regression (mid-IR and vis-NIR) of CEC and SOC were able to adequately reproduce the spatial pattern of the properties evaluated (r > 0.81). The mid-IR method worked particularly well. In conclusion, proximal soil sensing can be useful for assessing the spatial distribution of ADE soils and quantifying some of the most important soil properties. The methodology we used has the potential to facilitate the study of areas where ADE may potentially occur.

3.1 Introduction

In general, the agricultural soils in the Brazilian Amazon region are strongly weathered and thus tend to be acidic and have low cation exchange capacity (CEC). According to Falcão et al. (2003) 75% of these soils are classified as Ferralsols and consist of old, deeply weathered kaolinitic clays with low pH and low amounts of nutrients. The low fertility level becomes a limiting factor for productivity and economy.

However, in this same region soils higher in carbon (C) with elevated contents of plant nutrients are found. This group includes soils known as *terra preta de índio* or Amazonian dark earths (ADE), which are found in circumscribed distributions in a wide variety of environmental contexts.

ADE occurs as fertile patches from less than a hectare (ha) up to, unusually, 300 hundred ha (WOOD, 1999; MCCAAN, 1999; SOMBROEK, 2002, KERN, 2003). ADE are formed as a result of land use strategies of pre-Columbian complex societies from 2500 to

Keywords: Diffuse reflectance spectroscopy; Soil organic matter; PLS regression; Terra Preta de Índio.

500 years B.P. and were abandoned on a large scale as part of the demographic and economic collapse of the region following European contact (SMITH, 1980; WOODS; DENEVAN, 2010). Given the persistence of ADE through time, they provide important and complex archaeological datasets for understanding long-term human-environmental interactions and the historical ecology of the Amazon rain forest (GLASER et al., 2004; LEHMANN et al. 2010). Suggested procedures for the formation of ADE include particular methods of clearing, usually referred to as "slash and char", in which pyrolysis (a burning method with limited supply of oxygen) is the dominating type of burning, possibly combined with the addition of various kinds of organic waste (e.g. STEINER et al. 2004). The resulting soils contain much higher amounts of C, especially a form denominated as *biochar* (BURNS; RITZ, 2012), than other soils in the Amazon region and contribute thereby to carbon sequestration.

To soil scientists the ADE topsoil comprises an anthropogenic A horizon, that may fit the requisites of a diagnostic horizon related to a soil taxonomy system, like a *fimic A* horizon (FAO, 2006), plagic or hortic horizon (WRB, 1988) or an anthropic A horizon (EMBRAPA, 2006). Thus, according to the preferred soil classification system, these soils are classified as Latossolos, Argissolos, Cambissolos and others (EMBRAPA, 2006); or may classify as Fimic Anthrosols (FAO, 2006) or as Plaggic or Hortic Anthrosols (WRB, 1988). In 2002, at the First International TPA workshop in Manaus, a new archeo-pedological classification legend specific for ADE and soils influenced by human activities was proposed aimed to improve interdisciplinarity of soil scientists, anthropologists, biologists and geologists engaged with ADE environments (e.g. ANDRADE, 1986; WOODS; McCANN, 1999). In this system a reference horizon comprises the upper part (A and AB horizons) of the soil profile and has the following properties: a thickness of 20 cm or more; presence of artifacts at any amount, and/or Mehlich-1 extractable P (OLSEN; SOMMERS, 1982) in the fine earth fraction of at least 65 mg kg⁻¹; charcoal in the fine earth fraction; organic C content determined by the Walkley and Black method (EMBRAPA, 2009) of 10 g kg⁻¹ or more in the fine earth (KAMPF et al., 2003).

Although ADEs are not homogeneous when it comes to fertility and productive potential and varies with respect to their depth and extension as well as their physical and chemical characteristics (LEHMANN et al., 2003), some important properties related to the degree of fertility are common in most of them: high soil organic carbon (SOC), P, Ca and micronutrients contents, besides being remarkably resistant to leaching compared to the adjacent soils. Better knowledge of ADE areas in the region evaluated in this study - the greater Santarém-Belterra region at the confluence of the Tapajós River with the Amazon headwaters- is important for many reasons (see e.g. LEHMANN; JOSEPH, 2009; VERHEIJEN et al., 2010; CORNELL UNIVERSITY, 2012). One of them refers to the fact that large areas in this region that were forested or under subsistence agriculture have now been cleared for conventional large-scale monocrop agriculture. The impact of this on fertility and structure stability of ADE is not clear. The characterization of soils in this region is important for choosing appropriate management strategies to keep the fertility of ADE in current agricultural regimes.

In order to characterize these soils it is crucial to perform soil chemical analyses. These analyses are expensive and time-consuming. In recent years, proximal soil sensing techniques have, by many authors, been studied as a tool to improve the quantitative assessment of the management problems (e.g. SHEPHERD; WALSH, 2002; DUNN et al., 2002). Some authors found good correlation between soil spectral reflectance in the visible NIR region (350-2500 nm) and soil chemical and physical properties (e.g. REEVES III et al., 2002; SHEPHERD; WALSH, 2002; DEMATTÊ et al., 2004; STENBERG et al., 2010). Some of them used successfully the NIR region for quantitative analysis of carbon (REEVES et al., 1999; EHSANI et al., 1999; CHANG et al., 2001; FYSTRO, 2002; MCCARTY et al., 2002; SHEPHERD, WALSH, 2002; VISCARRA ROSSEL et al., 2006). However, there are still only few studies that used spectral ranges of the mid-infrared (mid-IR) (4000 to 400 cm⁻¹ or 2500 to 25000 nm) to evaluate soil properties (MCCARTY; REEVES, 2006; VISCARRA ROSSEL et al., 2006), even though mid-IR diffuse reflectance spectroscopy exhibits powerful signatures that can be used to derive many physical, chemical and biological properties.

The reflectance spectroscopy is based on the detection of electromagnetic radiation reflected from the soil without having direct contact with the sensors. There is no sample destruction, no use of hazardous chemicals, minimal sample preparation is required and the measurements can be performed on-the-go in situ. Despite of there was no studies about the patterns of ADEs the reflectance spectroscopy can assist on ADE identification.

Thus, aiming to facilitate the study of areas where ADE can be potentially found, we investigated if rapid spectroscopy data collection could be used to assess the spatial distribution of properties of this kind of soil, in order reduce costs. Specifically, this work's aims were to: (i) characterize these soils chemically and spectroscopically (visNIR and mid-IR) and compare them with other studies carried out in this region; (ii) identify parameters (e.g. depth of the band, and reflectance intensity) of spectral variation associated to soil

attributes content; (iii) explore the possibility to predict soil properties based on their spectral characteristics. In doing the latter, we also tested whether the PLS models generated by soil data from one geographical area could be applied to soil data from another. Successful results from this study would support the hypothesis that mapping of ADE areas can be facilitated by the use of spectroscopy techniques even when it is occurring in small patches. This process could improve and facilitate archaeological work, supporting the identification of locations where to focus sampling and excavations. The extent of these patches of soils with high fertility surface horizons is of local and regional importance, and has been considered as an indication of former sustainable land use (SMITH, 1980; GLASER et al., 2000).

3.2 Material and Methods3.2.1 Description of studied region

This study was conducted in the north of Brazil, in the Belterra region, located 40 km southwest from Santarém, in the state of Pará (Figure 1). The studied area belongs to the substate region of Baixo Amazonas, with a rainfall and an average annual temperature of 1920 mm and 25-28 °C, respectively, and with an average relative air humidity of 86%. Geologically, the study area is located at the Barreiras Formation (sediments) (BRASIL, 1983), which is now named *Alter do Chão Formation* (FEARNSIDE; LEAL FILHO, 2001). The mineral matrix of soil in the area is mainly strongly weathered; often showing high contents of kaolinite and quartz, and therefore possesses few weatherable minerals which could potentially release nutrients (KERN, 1996).



Figure 1 - Map of the southern part of the Brazilian Amazon. The Santarém-Belterra study area is marked with a red box (adapted from SOARES et al., 2011)

3.2.2 Studied areas 3.2.2.1 Bom Futuro 2

An area called Bom Futuro two (BF2) in the Belterra district was chosen for the main field study (Figure 2). The area of 27 ha is delimited by the coordinates UTM approximately 732000 to 732700 metres E and 96977800 to 9698400 metres N, fuse 21, *datum* WGS 1984. The soil study was conducted as part of a larger project which also included archaeological excavations. The location of BF2 was chosen because of its potential interest for the archaeologists.

Soil sampling was made along a system of transects at BF2 (Figure 2). The soil samples (0-20 cm) were taken with an auger at every 40^{th} meter and the depth and color of the A-horizon was noted. At each sampling site, we obtained a composite sample of three cores obtained with a soil auger in a triangle with a side length of approximately 1 m. In total, 179 samples were taken at BF2 transects.

At excavation 1 (Exc. 1) (Figure 2) three soil profiles were studied in detail (eastern part of the studied area): Profile 1 was made where the soil was affected by seasonal waterlogging and was depleted in Fe; the Profile 2 was located in the upper more well drained

part with a reddish soil profile, whereas Profile 3 was in an intermediate position where there was a thin plinthic layer in the subsoil. At excavation 2 (Exc. 2 in Figure 2), three profiles were also described according to the Brazilian Soil Classification System (SiBCS) (EMBRAPA, 2006).



Figure 2 - Overview of the soil sampling locations and position of the soil samples (red dots) of Bom Futuro 2 area. (Exc. 1 and Exc. 2 indicate approximate locations of the soil profiles)

3.2.2.2 Bom Futuro 6

Another area of approximately 3.5 ha called Bom Futuro six (BF6) located approximately 1.5 km southwest from BF2 was also studied. In this area, along the baseline systems of transects, soils were sampled at every 20th m and scanned by sensors FieldSpec and Nicolet 6700 Fourier Transform Infrared (FT-IR) (Figure 3).

In this area 10 profiles covering different potentially anthropogenic soil types were also sampled at three horizont layers and analyzed chemically and by sensors (approximately an area of 0.8 ha currently under slash-and-burn cultivation with crops like banana, cassava and corn). These soils were well documented with photos and the Munsell color components



hue, value and chroma were obtained using a colorimeter MINOLTA. In total 69 samples were taken at BF6.

Figure 3 - Overview of the soil sampling locations and position of the soil samples (red dotswith the extended transects in the adjacent forest area) and the soil profiles at Bom Futuro 6 area (dotted area = 0.8 ha)

3.2.3 Laboratory analysis

The soil samples were air-dried and sieved to pass through a 2 mm mesh sieve before they were submitted to chemical and spectral analyses.

3.2.3.1 Chemical analyses

The soil samples were analyzed for pH in a soil:water solution ratio of 1:2.5; OC (organic carbon) content was determined by wet oxidation with K-dichromate by a modified Walkley& Black method (EMBRAPA, 2009); total C by dry combustion using a LECO CN-2000 instrument (LECO Corp., St. Joseph); extractable P by Mehlich 1; calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}), and aluminium (Al^{3+}) by extraction with 1M KCl (EMBRAPA, 2009) and analysis with atomic absorption spectrophotometry (AAS); extractable acidity ($H^+ + Al^{3+}$) by extraction with 1N Ca (CH₃COOH) pH 7. Contents of sand

(2-0.05mm), silt (0.05-0.002 mm) and clay (<0.002 mm) were determined by the densimeter - sedimentation method, using calcium hexametaphosphate 0.1M and sodium hydroxide 0.1 M as dispersing agents (GEE et al., 1986). Cation exchange capacity (CEC at pH7), sum of bases (SB) and base saturation (V) were calculated from the analyses of base cations and exchange acidity.

3.2.3.2 Spectroscopy measurements

The spectral reflectance of soils was measured in the vis-NIR (350-2500 nm) range, with a spectral resolution of 3 nm (from 350 to 1000 nm) and 10 nm (from 1000 to 2500 nm), using a FieldSpec Pro FR spectroradiometer (Analytical Spectral Devices, Boulder, Colorado; Hatchell,1999). The spectrum acquisition software interpolated reflectance data to a sampling interval of 1 nm. Approximately 15 cm³ of each soil sample was placed in a petri dish. A fiber-optic cable connected to the vis-NIR sensor was placed vertically at 8 cm from the sample, and the reflected light was measured in an area of approximately 15 cm² in the centre of the sample. The light source was a 50W halogen bulb with the beam non-collimated to the target plan, positioned at 35 cm from the sample at a zenith angle of 30°. As a reference standard, a white plate covered with barium sulphate (BaSO₄) was used (STEFFEN et al., 1996). Each spectrum was averaged from 100 readings during 10 seconds.

In the mid-IR range measurements were made with a Nicolet 6700 Fourier Transform Infrared (FT-IR) equipped with an accessory to acquire diffuse reflectance (Smart Diffuse Reflectance). Approximately 1 cm³ of each soil sample (100 mesh) was used, and placed in the proper recipient of the sensor. The internal light source is the HeNe laser with a calibration standard for each wavelength (2,500 to 25,000 nm). The spectra were obtained with a spectral resolution of 1.2 nm and with 64 scans per second. Before each measurement a reference background spectrum was obtained to calibrate the sensor.

3.2.4 Data analyses

The scheme of the spectroscopy procedures carried out in this study is showed in figure 4 and detailed in the steps below. After the selection of the samples to be analyzed chemically at BF2, the calibration and validation data sets of BF2 were chosen randomly. The PLS calibrations of soil properties were tested on the validation data set. These models were also applied to spectral data of BF6 samples (unknown samples from a different geographical

area). Some samples (N = 20) at BF6 were selected to be sent to the chemical laboratory to validate these predictions.



properties using vis-NIR and mid-IR spectroscopy

3.2.4.1 Selecting samples

We selected 150 soil samples from BF2 (N total = 179) to be analyzed chemically at soil laboratory. It was done based on the *fuzzy clustering* analysis (ADAMS, 1995) and the results are shown in figure 5. For this analysis we used the data from the two spectroradiometers (FieldSpec and Nicolet 6700 Fourier Transform Infrared) and the depth of layer A from field notes. The aim was to have the sensors values well represented with this selection. Thus the *fuzzy clustering* was applied to the first four principal components scores of these data. The *fuzzy clustering* provides the basis for analysis of systems characterized by a high degree of uncertainty, nonlinearly and complexity (JAGER, 1995; PEDRYCZ, GOMIDE, 1998). A major advantage of the fuzzy modeling method is the use of qualitative parameters to represent relationships being modeled, instead of using the quantitative variables of traditional methods (TORBERT et al., 2008).

Thus, the BF2 data set was randomly divided into a calibration set (CS) with 50 samples and validation set (VS) with 100 samples. This division promoted independence between CS and VS (Table 1).



Figure 5 - Fuzzy clustering results of Bom Futuro 2 study area. 150 samples selected; 4 fuzzy classes (red, yellow, dark green, green); samples removed based on highest confusion index (blue dots)

Descriptive	EC	OC	pН	pН	Р	K	Ca	Mg	Al	CEC	H+A1	BS
statistics	uS cm ⁻¹	g kg ⁻¹	H ₂ O	KCl	mg kg ⁻¹ .		m	mol _c kg	-1			%
	Bom Futuro 2 (N = 150)											
Mean	87	23.0	5.0	4.3	10.2	1.2	32.0	9.8	8.7	102.0	59.0	39.2
StDev	27	4.7	0.5	0.5	15.0	0.6	25.6	5.6	7.5	26.0	15.7	19.2
Minimum	35	10.4	4.0	3.6	2.0	0.5	2.0	1.0	2.0	48.2	26.0	4.0
Median	84	22.6	4.9	4.2	5.0	1.0	26.0	9.0	5.0	96.0	59.0	39.0
Maximum	203	38.3	6.1	5.5	117.0	3.1	128.0	36.0	29.0	197.3	102.0	87.0
	Bom Futuro 2, validation data set $(N = 100)$											
Mean	91	23.4	5.0	4.3	10.9	1.2	33.8	10.3	8.5	104.0	58.7	40.6
StDev	29	4.7	0.5	0.5	16.6	0.6	26.9	5.9	7.4	24.00	16.1	19.8
Minimum	34	12.8	4.2	3.7	2.0	0.5	3.0	2.0	2.0	57.5	26.0	10.0
Median	86	22.6	4.9	4.2	5.0	1.0	29.0	10.0	5.0	98.5	60.0	41.0
Maximum	203	38.3	6.1	5.5	117.0	3.1	128.0	36.0	26.0	197.3	102.0	87.0
				Bom	Futuro 2,	calibra	tion dat	a set (N	N = 50)			
Mean	80	22.2	4.9	4.2	8.6	1.1	27.7	8.6	9.2	97.3	59.8	36.2
StDev	21	4.7	0.4	0.4	10.6	0.5	22.0	4.6	7.9	24.8	14.7	18.7
Minimum	43	10.4	4.0	3.6	2.0	0.6	2.0	1.0	2.0	48.2	32.0	10.0
Median	77	21.5	4.9	4.1	5.0	1.0	24.0	8.0	7.0	91.5	58.0	35.0
Maximum	203	35.4	5.9	5.1	110.0	2.8	116.0	32.0	29.0	182.5	91.0	87.0

Table 1 - Descriptive statistics for soil attributes at Bom Futuro 2 area: global, calibration and validation data sets

In BF6 all samples collected (N = 69) were analyzed spectrally by vis-NIR and mid-IR sensors. Part of the samples from transects (N = 20) were purposely selected (to cover the entire area), to be analyzed chemically in order to validate the BF6 soil properties predicted by models (based on BF2 models).

3.2.4.2 Statistical analyses

Summary statistics and correlation analysis were performed using Jump software version 8.0 (JMP 7.0.1).

For qualitative analysis of the spectra data we calculated the band depth of particular absorption features at each depth of the ten BF6 profiles by subtracting the continuum removed reflectance (Envi, 2004) at a particular wavelength from 1 (one) (VISCARRA ROSSEL et al, 2009). A continuum removal technique has been used to isolate particular absorption features in diffuse reflectance spectra (VISCARRA ROSSEL et al., 2009). In soil science, it has been used mostly in hyperspectral remote sensing applications (e.g. GOMEZ et al., 2008). In addition, the soil color of these samples was determined using a colorimeter in the Munsell color system. For that, 50 g of each soil sample was placed in a Petri dish

overlain by a quartz plate. The colorimeter used was the Konica Minolta CR-300 (Konica Minolta Holdings Inc., Tokyo, Japan). We also made a descriptive analysis of the spectral curves of the BF2 profiles based on Bellinaso et al. (2010) and Rizzo (2011).

The quantitative spectroscopy analyses were performed in Unscrambler10.1 (CAMO SOFTWARE AS, Oslo, Norway). Before spectroscopy multivariate analyses the soil vis-NIR spectra were reduced to 400-2450 nm to eliminate the noise at both edges of each spectrum. The mid-IR spectra were transformed from reflectance to absorbance.

A principal components analysis (PCA) of spectral data using a leave-one-out crossvalidation was carried out in order to summarize the main spectral variation of data. The scores in each principal component summarize the relationships among the samples and the loadings summarize the relations among the spectral values in the wavelengths (variables), and these are a means to interpret the score patterns. PCA results in a reduction of data that aims to explain most of the variance in the data while reducing the number of variables to a few uncorrelated components (SHARMA, 1996; ANDERSON, 2003). Spectral outliers were not observed through the Mahalanobis distance. The loadings obtained with the PCA were used to identify the main spectral variation (absorption and reflection features) in the spectra.

The calibration models of soil attributes (OC, P, CEC, EC, Ca, Mg, K, Al, H+Al and pH-H₂O, pH-KCl and BS) of BF2 were validated using the predefined validation set (VS). The predicted model obtained from BF2 samples considered to have potential to be used, were also applied to the new unknown samples data set (BF6). The calibration technique used was partial least square regression (PLSR), using the orthogonalized PLSR algorithm for one Y-variable (PLS-1) and full cross-validation. The number of PLS factors was chosen to minimize the root mean square error (RMSE) in the cross validation. A calibration model that uses fewer factors is more likely to yield accurate predictions for newer samples (MADARI et al. 2006). If the samples are very diverse, calibration is likely to use more factors. The PLSR technique is widely used, showing good performance to estimate attributes based on the spectral behavior of the soil (e.g. VASQUES et al., 2008).

We used the coefficients of determination (R^2) , the root mean square error (RMSE) and the ratio of performance to deviation (RPD) to compare the results, calculated using the following equations:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(\gamma i - \gamma yi)^2}$$
 and $RPD = SD/RMSE$

where n is the number of samples and SD is the standard deviation of laboratory-measured values for the property in question.

3.3 Results and Discussion3.3.1 Bom Futuro 23.3.1.1Chemical properties

The occurrence of charcoal was observed in BF2 area, especially around at excavation 2. According to field notes, adjacent soils to excavation 2 sometimes had visible charcoal too, but only in the topsoil. The regular occurrence of charcoal in ADEs (SOMBROEK 1966; SOMBROEK et al. 1993) and their highly aromatic humic substances (ZECH et al. 1990) indicate that residues of incomplete combustion (black carbon), derived mainly from cooking fires, may contribute to the SOM of ADEs. It has been proposed that polyphenols and condensates (e.g. of lignin-degradation products) contribute to the major part of the aromatic compounds in SOM (STEVENSON, 1994).

A correlation matrix of the analyzed soil properties of the BF2 samples is shown in Table 2. The correlation between CEC and SOC was high (r = 0.91) and may indicate that the soil organic fraction is an important contributor to the potential fertility of soils in this area. SOC occurs especially by the presence of charcoal in ADE. According to SOMBROEK, (1966) P is mainly present as inorganic phosphate in ADE and may not correlate with SOM. In soil samples of the BF2 area no correlation was found between P on one hand and EC, SOC and BS on the other. Some soils in the BF2 area exhibit ADE characteristics and Ca and SOC are closely related (r = 0.71), in contrast with P (r = 0.10 and 0.30).

The spatial distribution of measured SOC, CEC and P contents in the BF2 area (N = 150 samples) obtained by point kriging interpolation using the software Vesper (MINASNY et al. 2005) is shown on Figure 6. These maps visualize the positive correlation between CEC and SOC. We observed SOC content higher than 10 g kg⁻¹ fine earth throughout the BF2 area (Figure 6) and high contents of phosphorus (> 65 mg kg⁻¹) extracted by Mehlich-1 in some points, which are characteristics of dark earths according to Archeo-pedological classification system (KAMPF et al., 2003). The high C content in soils with anthropogenic A horizons were observed by Sombroek (1966), Ranzani et al. (1970), Smith (1980), Éden et al. (1984), Kern and Kämpf (1989), and Pabst (1991) in the Amazon region, and was attributed to organic matter stabilization by complex-formation with Ca²⁺, and enrichment in stable C structures (black C). In the BF2 area the SOC content and soil fertility properties found at

excavation 2 are comparable to those reported by Madari et al. (2003) that studied 56 profiles of ADEs (mean SOC = 30 g kg^{-1}).

	EC	SOC	pHH ₂ 0	pHKCl	Р	K	Ca	Mg	Al	H+Al	SB	CEC	BS	m
EC	1													
SOC	0.63 **	1												
pHH ₂ 0	0.30	0.42 **	1											
pHKCl	0.38 *	0.43 **	0.96 **	1										
P	0.05	0.10	0.39	0.40 *	1									
K	0.19	0.16	0.55 **	0.56 **	0.50 **	1								
Ca	0.55 **	0.71 **	0.86 **	0.89 **	0.30 *	0.43 **	1							
Mg	0.63 **	0.62 **	0.72 **	0.72 **	0.17	0.30 **	0.78 **	1						
Al	-0.23	-0.31 *	-0.85 **	-0.81 **	-0.33 *	-0.33 **	-0.42 **	-0.70 **	1					
H+Al	-0.09	0.13	-0.72 **	-0.74 **	-0.30 *	-0.30 **	-0.47 **	-0.51 **	0.68 **	1				
SB	0.58 **	0.71 **	0.86 **	0.90 **	0.30 *	0.30 **	0.44 **	0.99 **	0.72 **	-0.51 **	1			
CEC	0.62 **	0.91 **	0.57 **	0.60 **	0.16	0.16	0.23 **	0.85 **	-0.43 **	0.01	0.85 **	1		
BS	0.41 **	0.47 *	0.96 **	0.97 **	0.37	0.56 *	0.90 **	0.77 **	-0.83 **	-0.74 **	0.91 **	0.60 **	1	
m	-0.29	-0.40 *	-0.86 **	-0.82 **	-0.33 *	-0.44 **	-0.73 **	-0.70 **	0.98 **	0.61 **	-0.75 **	-0.50 **	-0.90 **	* 1

Table 2 - Correlation matrix for relationships between soil properties evaluated at Bom Futuro 2

** (p< 0.01); * (p< 0.05) - Student's t-test



Figure 6 - Kriging interpolation to derive spatial distribution of measured soil properties contents by chemical analyses (N = 150) at BF2 area

3.3.1.2 Profiles characterization

The profile descriptions of excavations 1 and 2 are provided below. Some soil analytical characteristics considered important for analyzing profiles are shown in Table 4.

We did not observe soils with an anthropogenic A horizon in the eastern part of the BF2 area (excavation 1) (Table 5). Profile 1 was classified as Gleissolo (GX) Háplico Tb Distrófico típico (EMBRAPA, 2006). Hydromorphy in these soils is expressed as a strong gleization due to the effect of the fluctuating groundwater. We observed very clayey soil that was generally whitish in color (Tabatinga) due to Fe depletion under reducing conditions; abundant precipitates in the C horizon; and a mosaic of redox depletions and accumulations with only a slight difference in color from the whitish matrix soil. Profile 2 (excavation 1), located in the upper, better-drained portion of the study area, had a reddish soil profile and was classified as Latossolo Amarelo (LA) Distrófico plíntico. Profile 3 (excavation 1) was a Latossolo Amarelo (LA) Distrófico típico with a deep reddish-yellow soil profile and very gradual boundaries between horizons (Table 5).

At the excavation 2 area, however (Figure 2), the three profiles studied were classified as Latossolo Amarelo (LA) Distrófico antrópico. These soils are well developed and significantly affected by weathering processes, with an accumulation of resistant clay minerals or iron and aluminum oxides or hydroxides (EMBRAPA, 2006). The surface horizon, characterized as anthropogenic A, was more than 50 cm thick, with dark colors and a well-developed structure. We also observed pieces of charcoal and ashes in between aggregates, pieces of ceramics and earthworm channels, and channels in peds. Roots were most abundant in the topsoil but present throughout the profiles. Soil texture analysis showed values of clay between 670 and 890 g kg⁻¹ and sand between 38 and 156 g kg⁻¹. The silt/clay ratio was low (mean of 0.16), reinforcing the high degree of soil weathering.
ID	Sand	Silt	Clay	SOC	Р	Κ	Ca	Mg	Al	H+Al	SB	CEC	BS	m	$\rm pHH_2O$	pH KCl	Matix	Value	Chroma
		g kg ⁻¹		. g kg ⁻¹	mg kg⁻¹			mmol _c l	ي					.%					
									Excavatio	on 1									
P1A	79	114	808	20	66	2.3	22	6	10	69	30.7	99.7	31	25	5.3	4.5	2.5Y	6	1
P1B	40	79	881	3	5	0.5	4	2	9	34	6.5	40.2	16	58	4.5	4	2.5Y	6	3
P1C_upper	62	160	778	0	7	0.6	3	2	8	28	5.8	34.1	17	57	4.5	4.1			
P1C	87	31	882	1	7	0.6	2	2	8	27	5.1	32.5	16	60	4.6	4.2	10YR	8	3
P2A	140	133	727	20	38	6.7	38	12	<2	61	56.2	117.3	48	2	5.6	4.6	2.5Y	6	1
P2AB	67	131	802	7	4	0.4	6	3	11	42	8.9	50.6	18	56	4.6	4.1	10YR	6	5
P2B	71	55	874	1	7	0.3	<2	2	5	32	3.5	35.4	10	58	4.6	4.2	10YR	6	5
P2B1	64	62	874	2	5	0.3	5	2	10	36	7.6	43.9	17	57	4.8	4.1	10YR	6	5
P2C	139	31	829	1	13	0.7	3	3	5	30	6.2	36.3	17	46	4.5	4.3			
P3A	168	78	754	17	67	2.1	28	6	6	73	36.1	108.8	33	14	5.2	4.2	2.5Y	6	1
P3BA	77	19	904	5	5	0.8	5	2	14	44	8.1	52.4	15	64	4.5	3.9	10YR	6	6
P3B1	67	26	907	2	5	0.7	3	1	13	39	5.3	44.3	12	71	4.3	3.9	10YR	7	8
P3C	73	75	852	1	5	0.6	3	1	11	42	5.1	46.7	11	68	4.4	4.1	5YR	6	6
									Excavatio	on 2									
P4Ah1	137	162	702	56	49	1.8	121	24	2	85	147.1	232.2	63	1	5.8	5.1	10YR	1	1
P4Ah2	45	193	762	23	8	0.9	52	12	2	46	64.7	110.7	58	2	6	5.2	10YR	5	2
P4Ah3	67	82	850	10	108	0.4	17	6	10	79	24	102.8	23	29	5	4.1	2.5Y	5	2
P4B	43	81	876	3	14	0.2	11	3	7	38	14.3	52.4	27	33	4.8	4.3	10YR	6	6
P5Ah1	128	162	710	37	22	2.7	40	14	5	125	56.8	181.7	31	8	5.1	4.4	10YR	6	3
P5Ah22	100	121	780	11	75	0.4	12	6	13	80	17.7	97.4	18	42	4.8	3.9	10YR	2	2
P5Ah23	40	140	820	11	141	0.4	8	5	14	85	13.5	98.5	14	51	4.9	3.9	10YR	7	2
P5Ah24	50	110	840	13	31	0.5	22	7	7	68	29.3	97.5	30	20	5.1	4.1			
P5Ah31	38	140	850	12	12	0.6	41	10	2	51	52.1	103.5	50	3	5.8	4.9			
P5BA	38	81	890	6	64	0.3	8	4	7	43	12.7	55.2	23	36	4.8	4.1	10YR	6	4
P6Ah1	156	165	679	57	348	1.7	144	11	2	52	156.6	209.0	75	0	6.4	5.9	10YR	2	1
P6Ah21	97	101	802	27	209	1	91	15	2	66	106.7	172.2	62	1	6	5.3	2.5Y	4	1
P6Ah22	99	150	751	27	354	0.6	85	13	3	103	98.3	201.0	49	3	5.7	4.8			
P6BA	70	74	855	3	149	0.3	26	5	2	37	31.1	68.3	46	6	5.4	4.6	10YR	6	4

Table 4 – Chemistry, texture, and colors of soil samples related to profiles studied in excavations 1 and 2 at the Bom Futuro 2 area

Horizon (cm)	Color	Texture	Structure	Moist consistency	Sticky	Plasticity wet	Transition
· · ·			Gleissolo Háplico Tb Distro	ófico típico (excav	ation 1)		
			medium	frichlo	stielar	slightly	abrupt
A 0-17	2.5Y 6/1	clayey	subangular blocky	madie	SUCKY	plastic	wavy
			moderate medium	friable	sticky	slightly	gradual
B 17-80	2.5Y 6/3	/3 clayey angular blocky		maore	SUCKY	plastic	wavy
			weak very fine		- 4 - 1-	slightly	
C 80-185+	80-185+ 10YR 8/3 clayey angular blocky			SUCKY	plastic		
			Latossolo Amarelo Distrófi	co plíntico (excav	ation 1)		
			medium frichla sticlar	slightly	abrupt		
A 0-20	2.5Y 6/1	clayey	subangular blocky	madie	SUCKY	plastic	wavy
			moderate fine/medium	(slightly)	- 4 - 1	slightly	gradual
AB 20-50	10YR 6/5	clayey	fine (sub)angular blocky	hard	sucky	plastic	smooth
			weak/moderate very fine	frichlo	slightly	slightly	gradual (abrupt when
B 50-122	10YR 6/5	clayey	subangular blocky	madie	sticky	plastic	plinthite) wavy
C 122-174	+ 10YR 6/5	clayey	moderate fine/medium	firmer	slightly	slightly	
			subangular blocky	11111	sticky	plastic	
			Latossolo Amarelo Distróf	ico Típico (excava	ntion 1)		
			moderate very fine/medium	slightly hard	sticky	slightly	abrupt
A 0-25	2.5Y 6/1	clayey	subangular blocky		sticky	plastic	wavy
			moderate fine/medium	friable/	slightly	slightly	gradual
BA 25-69	10YR 6/6	clayey	fine subangular blocky	hard	sticky	plastic	smooth
			weak fine	very friable	slightly	nlastic	diffuse
B1 69-145	10 YR 7/8	clayey	subangular blocky		sticky	Prastic	smooth
C 145+	5YR 6/6	clayey	weak very fine/fine	friable	slightly	plastic	
			subangular blocky		sticky	r	

Table 5 – Soil morphological attributes of profiles of excavations 1 at the Bom Futuro 2 area

3.3.1.3 Qualitative and exploratory vis-NIR analysis of the BF2 profiles

Graphs for selected profiles (1, 2, 3 and 4) were generated from the spectral data (Figures 7 and 8), such that each graph contained the spectral curves of the horizons of the respective profile. Comparisons between the information from the spectral curves of the profile (intensity, shape, slope, presence of features and behavioral variation among curves from the same profile) were carried out based on Bellinaso et al. (2010) and Rizzo (2011).

The spectral signature of the anthropogenic Latossolo Vermelho Amarelo Distrófico (P4 in Table 4) is shown in Figure 7a. Mean soil reflectance intensity was approximately 0.3, with the highest values seen for subsurface samples. This may reflect the high levels of organic matter in the Ao layer (96 g kg⁻¹). Demattê, Ephiphanio, and Formaggio (2003) observed that the removal of OM increased the reflectance of soils. In this context it is worth noting that the reflectance intensities of the A horizons of the other soils (P1, P2, and P3) were higher than that of the anthropogenic Latossolo Vermelho Amarelo Distrófico (P 4). The sloping pattern from 400 to 1300 nm also differed between this soil and the others. Coleman and Mongomery (1987) argued that OM 'masks' the features of the curve, and we observed this between the different horizons of this profile (Figure 7a). Al-Abbas et al. (1972) have suggested that the effect of reduced soil reflectance with increased OM content may also be associated with clay content, since there must be a strong correlation between clay content and OM. In the subsurface horizons of the profiles classified as Latossolos (Figure 7a, 7c and 7d) we observed absorption features between 750 and 950 nm that are characteristic of the presence of oxides (HUNT; SALIBURY, 1970; MADEIRA NETTO et al., 1995). The Gleissolo (Figure 7b) showed features typical of hydromorphic horizons, such as the convexity between 400 and 450 nm and the absence of a concavity of iron oxides in the 750-950 nm region, in accord with the data of Epiphanio et al. (1992). In this soil we also observed a change in the slope of the curve near 800 nm (for the subsurface horizons), almost forming a peak (Figure 7b). Similar results have been reported by Bellinaso, Demattê, and Araújo (2010).

In the mid-IR range the differences between the layers of the profiles were not very clear as for vis-NIR data. The mean soil reflectance intensity of Gleissolo (Figure 8b) was slightly higher than the Latossolos (Figure 8a, 8c and 8d). The lowest values of reflectance were observed for layer Ao of the Latossolo Amarelo Distrófico antrópico. For the others soils (Figure 8b, 8c, 8d), horizons B or BA and A presented lowest reflectance values than the

subsurface horizons. The degree and the direction of the spectra slope were similar for all profiles.



Figure 7 - Spectral vis-NIR signature of the horizons composing the profiles studied at Bom Futuro 2. (a) Latossolo Amarelo Distrófico antrópico, (b) Gleissolo Háplico Tb Distrófico típico, (c) Latossolo Amarelo Distrófico plíntico, (d) Latossolo Amarelo Distrófico Típico



Figure 8 - Spectral mid-IR signature of the horizons composing the profiles studied at Bom Futuro 2. (a) Latossolo Amarelo Distrófico antrópico, (b) Gleissolo Háplico Tb Distrófico típico, (c) Latossolo Amarelo Distrófico plíntico, (d) Latossolo Amarelo Distrófico Típico.

3.3.2 Bom Futuro six: pits and forest transect 3.3.2.1 Chemical properties

Samples of the BF6 field (profiles) presented higher levels of fertility than soils in general in the Belterra-Santarem region (as reported by e.g.: SOMBROEK, 1966; FALCÃO, 2001; MOREIRA; MALAVOLTA, 2002). The soil chemical analyses results for layers A of the BF6 profiles (Table 6) demonstrated similar results as those found by other authors for anthropogenic soil sites in the Brazilian Amazon (e.g. ÉDEN et al., 1984; PABST, 1991; LIMA, 2001;). In the cited studies, the surrounding soils were acid with pH (H₂O) values between 4.0 and 5.0, which is in comparison with the conditions at the BF6 field. In the BF6 study area the average soil pH values at profiles were high (Table 6) and may reveal a direct effect of burning and the production of pyrogenic charcoal and ashes, neutralizing the effects of Al³⁺ (2.3 to 3.2 mmol_c kg⁻¹, values considered low) which is precipitated as Al (OH)₃ in pH values greater than 5.5 (HAVLIN et al., 2005).

		Layers		ANOVA
Property	А	В	С	Prob > F
SOC $(g kg^{-1})$	42.1 a	18.9 b	9.3 c	< 0.001*
Total Carbon (%)	4.5 a	1.9 b	1.0 c	< 0.001*
EC (uS cm^{-1})	321.6 a	104.1 b	81.6 b	< 0.001*
pH (H ₂ 0)	6.6 a	5.9 a	6.0 a	<0.048*
pH (KCl)	6.1 a	5.3 b	5.1 b	0.0064*
$P (mg kg^{-1})$	94.0 a	44.5 ab	19.4 b	0.0110*
K (mmol _c kg ⁻¹)	4.6 a	2.1 b	1.3 b	0.0015*
Ca (mmol _c kg ⁻¹)	141.6 a	59.4 b	24.0 c	< 0.001*
$Mg \ (mmol_c \ kg^{-1})$	22.3 a	11.7 b	7.3 c	< 0.001*
Al (mmol _c kg ⁻¹)	2.3 a	3.2 a	2.7 a	0.7418
$H + Al (mmol_c kg^{-1})$	31.6 a	34.9 a	28.6 a	0.2829
CEC (mmol _c kg ⁻¹)	195.4 a	104.3 b	56.9 c	< 0.001*
BS (%)	83.6 a	68.4 ab	55.3 c	0.0045*

Table 6 - Average values of soil chemical attributes of the 10 mini profiles in the BF6 area in three depths (layers A, B and C)

Means followed by same letters in rows (for the same attribute) do not differ by Tukey test at 1 and 5% significance level.

Parameters such as CEC and base saturation (BS) of the BF6 field are similar as those at BF2 and higher than in adjacent forest soils (0-20 cm) (average of 20 forest samples: $CEC = 124.78 \text{ mmol}_c \text{ kg}^{-1}$, BS = 63 %, pH-H₂O = 5.5, Al³⁺ = 4.6 mmol_c kg⁻¹, P = 32 mg kg⁻¹). It can be attributed to the large quantity of organic material in the BF6 field (SOC up to 55 g kg⁻¹). According to Liang et al. (2006) the high density of charges present on carbon, especially in soils with high amounts of pyrogenic charcoal, is also responsible for the higher CEC values (CUNHA et al., 2009). Figure 10a shows the CEC of BF6 samples of layers A, B and C at profiles as influenced by organic contents in comparison to adjacent forest soils (BF6 forest). We observed that CEC values of the majority of the BF6 field samples lie above the

CEC/SOC found in the forest soils (BF6 forest) (Figure 10a). The mineralogy of this area (3.5 ha) seems to be the same. Some profiles have ADE characterizes and according to Lehmann et al. (2003) SOC in ADE usually is more effective in increasing CEC than it is in non-ADE soil. These authors also observed that it is not necessarily true for P.

When it comes to plant available P, we observed a relationship with organic carbon, especially in soils with SOC concentrations higher than 25 mg kg⁻¹ (Figure 10b). These results are contradictory to those observed in the eastern part of BF2 area (Figure 6), which represents a more mixed soil population than BF6.



Figure 10 - Cation exchange capacity (CEC) and phosphorus (P) of mini profiles samples (BF6 field) (dots), influenced by organic carbon contents in comparison to adjacent forest soils (BF6 forest)

The profiles photos and its SOC contents are shown in figure 11. The horizons in a given profile have colors that are similar in hue, but vary with respect to chroma and value. The darker soil colors of layers A, the high fertility characterizes and the presence of ceramic fragments of the mini pits soil samples (compared to soils in the adjacent forest transect) might indicate an area under human prolonged occupation. The color value and chroma of the profiles samples (N = 30) were negatively correlated to SOC contents (-0.83 and -0.80, respectively), corroborating the results observed by Fontes and Carvalho Junior (2005) and Demattê et al. (2011). The negative correlation indicates that for increasing values of the value and chroma parameters, the SOC content decreases.



Figure 11 - Soil organic carbon (g kg⁻¹) distribution in the different depths at BF6 mini pit numbers 1(a), 2 (b), 3 (c), 4 (d), 5 (e) and 6 (f) (continues)



82



Figure 11 - Soil organic carbon (g kg⁻¹) distribution in the different depths at BF6 mini pit numbers 7 (g), 8 (h), 9 (i) and 10 (j)

The soil chemical properties of BF6 mini profiles vary spatially within the area and with depths (Figure 12). In general, the values of SOC, pH-KCl, EC, BS and CEC decreased with depth. There was no statistically difference between the averages of Al³⁺concentrations of layers A, B and C in these soils, but these values are considered low (Table 6).

Sombroek (1966), while studying ADE profiles in the region around Belterra encountered elevated levels of P in both the topsoil and the subsoil. Glaser (1999) found values of inorganic phosphorus of 912 mg kg⁻¹P₂O₅ in samples of top soils (0-10 cm) of cultivated and fertilized fields in Belterra. In the current study we encountered values of available P in layers A higher than 65 mg kg⁻¹, except at pits 4, 5 and 6 (Figure 12). Although ADE soils have been showing high amounts of P also in subsurface A horizons (PABST,

1985; LIMA, 2001) it was not observed in our study area (BF6), except for pits 1, 6 and 8 that also presented concentrations of extractable P higher than 65 mg kg⁻¹(Figure 12).



Figure 12 - Soil properties at different depths in BF6 profiles

3.3.2.2 Qualitative and exploratory vis-NIR and mid-IR analysis of BF6 area

The variations of soil chemical attributes with depth observed in the BF6 profiles samples (Table 6 and figure 12) caused corresponding changes in their soil spectral curves. Layers A, B and C from all profiles (BF6) presented different spectral behavior as shown by principal component analysis (Figure 13). The PC1 of vis-NIR spectra explained 84% of the data variation and PC2, 15%. For the mid-IR range these numbers were 68 and 24 %, respectively. It indicates that the main differences between PCs of data (mid-IR and vis-NIR) are related to their albedo (reflectance intensity). It can be influenced by texture, organic matter and mineralogy of samples (DALMOLIN, 2002; DALMOLIN et al., 2005). According to Smith (1999) there is more spectral information in the mid-IR range (4000 to 400 cm⁻¹).



Figure 13 - Score plot results from PCA of spectra on soil from BF6 profiles; (a) visNIR and (b) mid-IR data. Layers A, B and C

Table 6 shows these spectral variations when it comes to SOC and CEC. According to a literature review by Stenberg et al. (2010), bands around 1100, 1600, 1700 to 1800, 2000, and 2200 to 2400 nm have been identified as being particularly important for SOC calibrations. In the mid-IR range, these peaks are 2900 cm⁻¹, 2930 cm⁻¹, 2850 cm⁻¹, 1750 - 1449 cm⁻¹ and 1157 cm⁻¹ (KANG, XING, 2005; MADARI et al., 2006; REEVES, 2010; TERRA , 2012). Although the absorptions in the visible region (400-780 nm) are assigned to hematite and goethite (STENBERG et al., 2010), SOC can also have a broad absorption band in this region of the electromagnetic spectrum which are dominated by chromospheres and the

darkness of organic matter. These wavelength ranges were studied in detail by subtracting their continuum removal (CR) reflectance from 1 in the different layers. Thus we measured the band depth at these specific ranges and found correlation between them and SOC and CEC values (Table 7). By removing the continuum from the average reflectance spectra of the layers; they were enhanced with regard to the SOC content, as was also observed by Stenberg (2010).

			vis-NII	R (nm)			
	SOC	CEC	1100	1600	1700-1800	2000	2200-2400
SOC	1						
CEC	0.95 **	1					
950-1100	-0.41 *	-0.40	1				
1600	-0.68 *	-0.42 *	0.11	1			
1700-1800	-0.76 **	-0.82 **	0.45 *	0.62 **	1		
2000	-0.41 **	0.62 **	0.35	-0.31	-0.47 **	1	
2200-2400	-0.86 **	-0.87 **	0.59 *	0.54 *	0.90 **	-0.31	1
			mid-IR	(cm ⁻¹)			
	SOC	CEC	2930	2900	2850 1	750-1449	1157
SOC	1						
CEC	0.95 **	1					
2930	0.63 **	0.54 **	1				
2900	0.50 **	0.40 *	0.98 **	1			
2850	0.68 **	0.57 **	0.98 **	0.94 **	1		
1750-1449	0.90 **	0.93 **	0.67 **	0.53 *	0.71 **	1	
1157	-0.82 **	-0.83 **	-0.41 *	-0.30	-0.45 *	-0.71 **	1

Table 7 - Correlation matrix for relationships between soil properties evaluated at Bom Futuro6 (profiles) and band depths at specific wavelengths

For vis-NIR data the negative (1100, 1600, 1700-1800, 2000 and 2200-2400) significantly correlations between SOC and depths were confirmed with the average values of CR reflectance of layers A, B and C at the BF6 mini pits area (Figure 14). Concerning the mid-IR data these correlations were positive at 2930, 2900, 2850 and 1750-1449 cm⁻¹ and negative at 1157 cm⁻¹.



Figure 14 - Continuum-removed (CR) reflectance spectra showing specific absorption features of mini pits samples (average of layers A, B and C) visNIR (a) and mid-IR (b)

We observed that the characteristic organic matter absorptions bands in the mid-IR range contain considerably more visually apparent information than the corresponding NIR spectra (Figure 15). It results in a large number of broad peaks and often masked by overlaps from fundamentals, combinations and overtones of other soil components. Thus, most of these peaks (in the mid-IR range) could not readily be identified by simple visual evaluation of spectra. Some soil components, such as silica, absorb very little in the vis-NIR in contrast

to mid-IR (REEVES et al., 2005). However, the mid-IR range still has also been found to be efficient in recognizing various forms of carbon in the soil (JANIK et al., 2007; ZIMMERMANN et al., 2007; BORNEMANN et al., 2008).We observed differences of peak intensities at 1499 cm⁻¹(Figure 15b) in accordance to Haberhauer et al., (1998) that found a peak intensity close to 1510 cm^{-1} significantly negatively correlated to the total C content and C:N ratio, whereas distinct peaks in the region of 1510 to 1230 cm⁻¹ may serves as a proxy for the evaluation of the forest litter in soils. Characteristic absorptions peaks at 2930–2850 cm⁻¹ can be related to the aliphatic C-H vibration (HABERHAUER et al., 1998; LEIFELD, 2006) and it was more pronounced on samples with high SOC content (Figure 16b). Carboxyl C, hydroxylic C-O-H or aromatic C-H, and C = C vibrations probably form the spectral peaks at wavenumbers less than 1500 cm⁻¹ (SOLOMON et al., 2005; BORNEMANN et al., 2010).

Generally the vis-NIR spectrum is flattened in higher SOC concentrations (Figure 15a), specially from 400-970 nm, as reported by Madeira Neto (1993). High SOC concentration can mask iron features of the spectral curves, such as absorptions features of goethite at 480 and 930 nm (BEN-DOR; BANIN, 1995; STENBERG et al., 2010) (Figure 15a) ("concavity alteration"). In the mid-IR range we also observed a reduction of the reflectance intensity of samples rich in SOC (Figure 15b). However the alteration occurs at the magnitude of reflectance, but it does not change the general spectrum's shape and format visually.



Figure 15 - Vis-NIR (a) and mid-infrared (b) spectrum of soil samples with lowest (6.96 g kg⁻¹) and highest (54.52 g kg⁻¹) soil organic carbon content at Bom Futuro 6 area (the diagrams to the right are enlargements of the encircled areas)

3.3.3 Modeling PLS regression models

The parameters of the calibration and validation predicted soil property models of the BF2 area are shown in Tables 8 and 9. The models using the mid-IR sensor data outperformed those using vis-NIR. According to Viscarra Rossel et al. (2006), mid-IR multivariate calibrations are more robust, because the fundamental molecular vibrations of soil components occur in the mid-IR, while only their overtones and combinations are detected in the vis-NIR.

The calibration models of SOC and CEC showed excellent correlations with R^2 > 0.90 and RPD > 3.0 with both vis-NIR and mid-IR data. Good model performance was also indicated by low cross-validated RMSEs. This makes sense because SOC (and clay minerals) are the fundamental constituents of the soil and have well-recognized absorption features in

both the vis-NIR and mid-IR regions. Furthermore, there are well-defined organic molecule absorption features in the mid-IR range (STENBERG et al., 2010), for which models showed lower error (Table 8).

All soil property models were tested with the validation data set (N = 100). The results for some attributes were somewhat poorer than expected, with $R^2 < 0.50$ and relatively high RMSE (Table 9). The validation models for EC, P, Al, and pH (H₂O and KCl) provided poor predictions with very low R^2 . In the case of K, other authors have also reported unreliable predictions (e.g. CHANG et al., 2001; MALLEY et al., 2002; SHEPHERD; WALSH, 2002; CHODAK et al., 2004). By contrast, results for SOC, CEC, Ca, H+Al and BS, especially with the mid-IR models, were considered useful for applying to other areas (CHANG et al., 2001).

Property	Sensor data	R^2	RMSE	RPD	PLS factors	Slope	Offset
<u> </u>	vis-NIR	0.90	1.52	3.02	8	0.86	2.42
SOC, $g kg^{-1}$							
	mid-IR	0.94	1.12	4.20	5	0.93	1.29
	vis-NIR	0.80	10.60	2.34	3	0.79	17.56
CEC, $mmol_c dm^{-3}$							
	mid-IR	0.88	8.45	2.93	5	0.88	11.31
	vis-NIR	0.65	10.25	2.15	7	0.79	7.18
Ca, $\text{mmol}_{c} \text{ dm}^{-3}$							
	mid-IR	0.87	8.06	2.73	5	0.92	2.06
	vis-NIR	0.65	1.93	2.38	14	0.75	0.47
Mg, $mmol_c dm^{-3}$							
	mid-IR	0.70	2.30	2.00	3	0.72	2.38
	vis-NIR	NA	0.52	0.96	1	0.00	1.18
K, mmol _c dm ⁻³							
	mid-IR	NA	0.53	0.94	1	0.00	1.15
	vis-NIR	0.32	6.64	1.19	8	0.54	3.21
Al. mmol _c dm ⁻³							
, - C -	mid-IR	0.80	2.45	3.22	7	0.91	0.72
	vis-NIR	0.11	19.89	1.03	1	0.11	70.90
EC, uS cm ⁻¹							
	mid-IR	0.39	16.99	1.22	1	0.53	38.15
	vis-NIR	0.05	6.37	0.01	1	0.14	6.12
P, mg kg ⁻¹							
	mid-IR	0.23	5.63	1.88	1	0.33	5.04
	vis-NIR	0.31	0.33	1.21	3	0.37	2.90
pH-H ₂ O		0.07	0.1-	a	-	0.07	0.50
	mid-IR	0.85	0.15	2.67	6	0.87	0.60
nH KCl	V1S-NIK	0.40	0.30	1.33	8	0.54	2.02
μη-κτι	mid_IR	0.85	0.15	2 67	7	0.80	0.43
	vis-NIR	0.30	12.60	1.17	2	0.44	33.13
H + AL mmol dm ⁻³		0.00	12.00	1,1/	-		22.12
ii +7 ii, mmor _c um	mid-IR	0.70	5.16	2.85	б	0.86	15.32
	vis-NIR	0.57	11.11	1.68	6	0.57	15.30
BS, %					-		
	mid-IR	0.93	4.90	3.82	7	0.96	1.30

Table 8 - Calibration results of partial least squares regressions (PLSR) cross-validation technique models on BF2 data set

Property	Sensor data	R^2	RMSE	RPD	Correlation	Slope	Offset
	vis-NIR	0.52	3.00	1.57	0.72	0.54	8.40
SOC, $g kg^{-1}$							
	mid-IR	0.50	2.90	1.62	0.74	0.54	7.29
	vis-NIR	0.53	17.20	1.40	0.72	0.52	40.56
CEC, mmol _c dm ⁻³							
	mid-IR	0.55	16.90	1.42	0.74	0.59	39.81
	vis-NIR	0.53	18.30	1.47	0.74	0.52	11.42
Ca, $\text{mmol}_{c} \text{ dm}^{-3}$							
	mid-IR	0.64	15.25	1.76	0.80	0.68	7.60
	vis-NIR	0.10	5.87	1.01	0.47	0.40	5.00
Mg, mmol _c dm ⁻³							
	mid-IR	0.49	4.06	1.45	0.60	0.35	5.65
	vis-NIR	0.10	0.59	1.02	0.09	0.07	2.14
K, mmol _c dm ⁻³							
	mid-IR	0.10	0.59	1.02	0.13	0.10	2.09
	vis-NIR	0.22	8.39	0.88	0.60	0.45	5.63
Al. mmol _{c dm⁻³}							
, - C -	mid-IR	0.46	5.62	1.32	0.72	0.69	2.16
	vis-NIR	NA	80.85	0.36	0.20	41.55	79.00
EC, uS cm ⁻¹							
	mid-IR	0.24	27.50	1.05	0.55	0.38	46.70
	vis-NIR	NA	16.34	1.02	0.15	0.03	7.00
P, mg kg ⁻¹							
	mid-IR	0.10	15.60	1.06	0.32	0.10	6.25
	vis-NIR	NA	1.10	0.45	0.12	0.12	7.50
pH-H ₂ O		0 0 7	0.00	0.60	0.00	0.1.6	4.10
	mid-IR	0.07	0.80	0.63	0.33	0.16	4.10
	V1S-INIK	0.10	0.91	0.55	0.32	0.12	4.05
рп-ксі	mid-IR	0.16	0.70	0.71	0.40	0.20	3 36
	vis-NIR	0.10	15.58	1.03	0.47	0.20	47.06
H + AL mmol dm ⁻³							
i i i i i i i i i i i i i i i i i i i	mid-IR	0.71	9,55	1.69	0.85	0.66	21.74
	vis-NIR	0.34	16.32	1.21	0.60	0.36	22.00
BS, %							
	mid-IR	0.66	11.83	1 67	0.81	0.70	10.00

Table 9 - Validation results of partial least squares regressions (PLSR) cross-validationtechnique models on independent validation data set (N = 100) of BF2 data set

Putting reflectance spectroscopy to practical use for soil monitoring demands a more or less accurate reproduction of the real spatial concentration pattern of chemical properties. In order to test the prediction power beyond the point data, semivariograms were modeled and point kriging interpolation was carried out using the software Vesper (MINASNY et al., 2005) for both observed and predicted concentrations of SOC, Ca, CEC, BS, and H+A1 (properties that presented $R^2 > 0.50$ in the validation models) in the BF2 samples (N = 100 samples). The interpolated data were imported to the software SMS Advanced from AgLeader Technology, and then classified using the natural breaks classification method (JENKS, 1967), that was designed to determine the best arrangement of values into different classes. The resulting maps are shown in Figures 16, 17, 18, 19, 20 and 21 and the corresponding parameters of the fitted variogram models are shown in Table 10 (from the Vesper software package).

Based on these semivariograms we estimated nugget (C_0) , sill $(C_0 + C_1)$, range (a) and the ratio nugget efect/sill (expressed as a percentage) parameters for the attributes under study. The selection of the fitted models was based on the visual inspection of the experimental semivariograms and on the low mean error. The semivariograms constructed for SOC, CEC, Ca, H+Al, and BS fit the spheric model, in agreement with various other studies which have shown that model to be better adapted to soil chemistry semivariograms studied from a spatial point of view (CAMBARDELLA et al., 1994; SALVIANO et al., 1998; OLIVEIRA et al., 1999). The semivariograms for SOC, CEC, Ca, H+Al, and BS (chemical and mid-IR data), based on the classification proposed by Cambardella et al. (1994) and due to the intrinsic characteristics of soils, showed a strong spatial dependence, since the values of nugget effect were lower than 25% of the sill values (Table 10). Salviano et al. (1998) also reported a strong spatial dependence for OM. Table 10 shows that the range obtained varied from 96 to 255 m, which correspond to the radii of the areas considered homogeneous for each variable under study. In this fashion, all neighboring sites located within a circle with those radii may be used to estimate values for any point between them (VIEIRA; LOMBARDI NETO, 1995).

and	root mean sq	uare error (KMSE)	for the	variables studied	with th	ne two s	ensors
Property	Data	Model	C_0	C ₁	[C ₀ /C ₀ +C ₁]x 100	а	RMSE	AIC
	chemical	Spherical	5.7	18.4	23.7	251.8	1.8	144.0
SOC, g kg ⁻¹	vis-NIR	Spherical	7.3	15.4	32.2	240.0	1.8	136.5
	mid-IR	Spherical	5.3	16.7	24.0	184.6	1.5	132.1
	chemical	Spherical	105.0	615.3	14.6	175.0	82.5	372.8
CEC, mmol _c dm ⁻³	vis-NIR	Spherical	137.3	421.2	24.6	230.6	a RMSE AI 251.8 1.8 144 240.0 1.8 13 184.6 1.5 13 175.0 82.5 37 230.6 38.5 31 175.4 52.3 34 229.5 32.7 30 223.3 48.3 32 96.0 19.2 28 106.0 11.6 24 201.4 28.9 29 188.0 21.4 29 199.0 23.5 28	315.5
	mid-IR	Spherical	137.8	395.6	25.1	175.4		345.4
	chemical	Spherical	2.1	997.1	0.2	255.9	93.4	366.0
Ca, mmol _c dm ⁻³	vis-NIR	Spherical	95.7	341.0	21.9	229.5	32.7	306.0
	mid-IR	Spherical	148.9	442.0	25.2	223.3	48.3	328.6
	chemical	Spherical	0.0	258.0	0.0	96.0	1.5 132. 82.5 372. 38.5 315. 52.3 345. 93.4 366. 32.7 306. 48.3 328. 19.2 285. 5.5 210. 11.6 245. 28.9 298.	285.4
H+Al, mmol _c dm ⁻³	vis-NIR	Spherical	34.3	34.9	49.5	190.0	5.5	210.0
	mid-IR	Spherical	0.0	165.0	0.0	106.0	11.6	245.5
	chemical	Spherical	104.4	359.1	22.5	201.4	28.9	298.8
BS, %	vis-NIR	Spherical	111.0	108.0	50.7	188.0	21.4	291.7
	mid-IR	Spherical	101.0	295.0	25.5	199.0	23.5	287.0

Table 10 - Parameters of semivariograms, nugget C₀, sill C₁, range of spatial dependence (a), and root mean square error (RMSE) for the variables studied with the two sensors



Figure 17- Kriged maps of SOC based on (a) observations in the validation dataset - chemical; (b) estimated SOC using the vis-NIR calibration model; and (c) estimated SOC using the mid-IR calibration model (N=100)



Figure 18 - Kriged maps of CEC based on (a) observations in the validation dataset; (b) estimated CEC using the vis-NIR calibration model; and (c) estimated CEC using the mid-IR calibration model (N=100)



Figure 19 - Kriged maps of Ca based on (a) observations in the validation dataset; (b) estimated Ca using the vis-NIR calibration model; and (c) estimated Ca using the mid-IR calibration model (N=100)



Figure 20 - Kriged maps of H+Al based on (a) observations in the validation dataset; (b) estimated H+Al using the vis-NIR calibration model; and (c) estimated H+Al using the mid-IR calibration model (N=100)



Figure 21 - Kriged maps of BS based on (a) observations in the validation dataset; (b) estimated BS using the vis-NIR calibration model; and (c) estimated BS using the mid-IR calibration model (N= 100).

A comparison of the interpolation results revealed that the predictions of the PLS regression (mid-IR and vis-NIR) adequately reproduced the spatial pattern for SOC, CEC and Ca. The pattern provided by the mid-IR estimates largely coincided with the pattern interpolated from the measured properties (r > 0.81) (Figures 17 to 21). In contrast to mid-IR, the predictions of the vis-NIR PLS regression models for Ca, H+Al, and BS were not capable of reproducing the spatial pattern precisely, although the correlation was statistically significant for the point samples (Table 9).

Figure 22 shows the disparities for SOC, CEC and Ca concentrations. In order to highlight differences between the patterns, the spatially interpolated estimates (vis-NIR and mid-IR) were subtracted from the values derived from measurements. Negative values indicate that the estimated value of the attribute is lower than the actual value, while positive values indicate that it is higher. In total, the disparities for SOC were very low. However, we observed that in the western portion of the BF area (close to excavation 2), where soils were classified as anthropogenic, differences exceeded 4 mg kg⁻¹ (Figure 22). We also noted a trend for both sensors to underpredict samples (SOC, Ca and CEC) with high levels of OM. Despite the fact that the dominant features in the spectra are often related to soil mineralogy (BEN-DOR, BANIN, 1995; DALMOLIN, 2002; DEMATTÊ; EPIPHANIO; FORMAGGIO, 2003; STENBERG et al., 2010), the organic matter also played an important role in determining their spectral signatures and may have masked the others absorptions features, when in very high concentrations (SOC > 24 g kg⁻¹).

Disparities for the CEC data were greater than those for SOC, and were mostly concentrated in regions of high SOC levels (Figure 22). In general, the optical properties of a soil are influenced by its organic matter content (JARMER et al., 2008). In fact, according to Baumgardner et al. (1995), this is especially true for SOC contents exceeding 20 g kg⁻¹, whereas SOC becomes less effective in masking the influence of other soil constituents such as iron or manganese on the spectral signature when it drops below 20 g kg⁻¹. In soils with very low organic carbon content, secondary iron oxides are the most important pigmenting agents (TORRENT et al., 1983).



Figure 22 - Differences of spatial distribution (interpolated by Kriging) of measured and estimated soil properties contents by (a) vis-NIR and (b) mid-IR data (continues)



Figure 22 - Differences of spatial distribution (interpolated by Kriging) of measured and estimated soil properties contents by (a) vis-NIR and (b) mid-IR data

In order to test the predictive power of the calibration models for SOC, CEC, Ca, H+Al, and BS, data from the other geographical area were used. The BF2 calibration models for these soil properties were used to generate predictions about samples from the BF6 area. The validation results of the BF6 predictive models constructed based on spectroscopy models of BF2 of selected variables are shown in Figure 23. Chemical analyses of the soil samples from the BF6 profiles (N=30) and the BF6 forest transect (N=22) were used to test the models.

Results of the SOC, CEC, and Ca predictions showed that both mid-IR and vis-NIR models had the ability to predict unknown samples from different areas. Models with mid-IR data performed better than those with vis-NIR data.



Figure 23- Scatterplot of the partial least square regression model (validation) for predicting the soil attributes of BF6 samples

3.4 Conclusions

General soil properties typical of ADE (high SOC, Ca, and P) were found in portions of the study areas. Characterizing the spectral curves (profiles at BF2) allowed us to distinguish between different layers and soils. Variation in soil chemical attributes with depth observed in the BF6 profile samples also caused corresponding changes in their soil spectral curves. Spectral depths were enhanced with regard to SOC content. In the mid-IR region a reduction of the reflectance intensity of SOC-rich samples did not change the general spectrum's shape and format visually, unlike in the vis-NIR region.

Models based on the mid-IR sensor data outperformed those based on the vis-NIR data. Comparison of the interpolation results revealed that the predictions of the PLS regression (mid-IR and vis-NIR) adequately reproduced the spatial pattern of the properties evaluated, especially SOC and CEC. However, we observed a trend in both sensors towards underpredicting samples with high OC content.

Mid-IR calibrations were more robust and handled sample diversity better than vis-NIR calibrations. Results of SOC, CEC, and Ca predictions showed that both mid-IR and vis-NIR models had the ability to predict the soil properties of unknown samples from a different geographical location. To conclude, the proximal soil sensing techniques and the methodology we used can be useful for assessing the spatial distribution of ADE soils and for quantifying key soil properties.

References

ANDERSON, T.W. 2003. An Introduction to Multivariate Statistical Analysis, 3rd ed.. (New York: John Wiley, 2003. .

ANDRADE, Á. Investigación arqueológica de los antrosolos de Araracuara (Amazonas). **Arqueología Colombiana**, Bogotá, v. 31,p. 1–101, 1986.

BRASIL. Ministério de Minas e Energia. Projeto Radambrasil,Folhas SF 23/24. Rio de Janeiro/Vitória, geologia, geomorfologia, pedologia, vegetação e uso potencial daterra. Rio de Janeiro, 1983. 775p. (Levantamento de Recursos Naturais, 32) FAO, 2006. Guidelines for soil profile description. Fourth edition. FAO, Rome.

BELLINASO, H.; DEMATTÊ, J.A.M.; ARAÚJO, S.R. Soil spectral library and its use in soil classification.**Revista Brasileira de Ciência do Solo**, Viçosa, v. 34, p. 861-870, 2010.

BEN-DOR, E.; BANIN, A. Near-infrared analysis as a rapid method to simultaneously evaluate several soil properties. **Soil Science Society of America Journal,** Madison, v. 59, p.364–372, 1995.

BORNEMANN, L.; WELP, G.; AMELUNG, W. Particulate Organic Matter at the Field Scale: Rapid Acquisition Using Mid-Infrared Spectroscopy, Amsterdam, v. 74 n 4, p. 1147-1156, 2010.

BOWERS, S.A.; HANKS, R.J. Reflection of radiant energy from soils. **Soil Science**, Baltimore, v. 100, p. 130-138, 1965.

BURNS, R. G.; RITZ, K. Introduction. Biochar: Virtual Special Issue. Soil Biology and Biochemistry Online: http://www.journals.elsevier.com/soil-biology. 2012.

CAMBARDELLA, C.A.; MOORMAN, T.B; NOVACK, J.M; PARKIN, T.B; KARLEN, D.L; TURCO R.F.; KNOPKA, A.E. Field-scale variability of soil proprieties in central Iowa soils. **Soil Science Society America Journal**, Madison, v.58, p.1240-1248, 1994.

CHANG, C.W.; LAIRD, D.A.; MAUSBACH, M.J.; HURBURGH, C.R. Near-infrared reflectance spectroscopy-principal components regression analyses of soil properties. **Soil Science Society of America Journal**, Madison, v.65, p. 480–490, 2001.

CHODAK, M. KHANNA, P. HORVARTH, B. BEESE, F. Near infrared spectroscopy for determination of total and exchangeable cations in geologically heterogeneous forest soils. **Journal of Near Infrared Spectroscopy**, New York, v.12, p.315-324, 2004.

COLEMAN, T.L.; MONTGOMERY, O.L. Soil moisture, organic matter and iron content effect on the spectral characteristics of selected Vertisols and Alfisols in Alabama. **Photogrammetric Engineering and Remote Sensing,** Falls Church, v. 53, p. 1659-1663, 1987.

DALMOLIN, R.S.D. **Matéria orgânica e características físicas, químicas, mineralógicas e espectrais de Latossolo de diferentes ambientes**. 2002. 151p. Tese (Doutorado em Ciência do Solo) – Universidade Federal do Rio Grande do Sul, Porto Alegre, 2002.

DALMOLIN, R.S.D.; GONÇALVES, C.N.; KLAMT, E. ; DICK, D.P. Relação entre os constituintes do solo e seu comportamento espectral. **Ciência Rural**, Santa Maria, v. 35, n. 2. p. 481-489, 2005.

DEMATTÊ, J.A.M.; EPIPHANIO, J.C.N.; FORMAGGIO, A.R. Influência da matéria orgânica e formas de ferro na reflect6ancia de solos tropicais. **Bragantia**, Campinas, v. 62, p. 451-464, 2003.

DEMATTÊ, J.A.M.; BORTOLETTO, M.A.M.; VASQUES, G.M.; RIZZO, R. Quantificação de matéria orgânica do solo através de modelos matemáticos utilizando colorimetria no sistema Munsell de cores (Quantification of soil organic matter using mathematical models based on colorimetry in the Munsell color system), **Bragantia**, Campinas, v.70 n3, 2011.

DUNN, B.W.; BEECHER, H.G.; BATTEN, G.D.; CIAVARELLA, S. The potencial of nearinfrared reflectance spectroscopy for soil analysis – a case study from the Riverine Plain of south-eastern Australia. **Australian Journal of Experimental Agriculture**, Melbourne, v.42, p.607-614, 2002.

ÉDEN, M.J.; BRAY, W.; HERRERA, L.; MCEWAN, C. Terra Preta Soils and their archaelogical context in the Caquetá Basin of Southeast Colombia. **American Antiquity**,New York, v.49,p.125-140, 1984.

EHSANI, M.R.; UPADHYAYA, S.K.; SLAUGHTER, D.; SHAFII, S.; PELLETIER, M. A NIR technique for rapid determination of soil mineral nitrogen. **Precision Agriculture**, New York, v. 1, p. 217–234, 1999.

EMBRAPA. **Sistema brasileiro de classificação de solos.** 2.ed. Rio de Janeiro: EMBRAPA Solos, 2006. 306p.

EPIPHANIO, J.C.N.; FORMAGGIO, A.R.; VALERIANO, M.; OLIVEIRA, J.B. **Comportamento espectral de solos do Estado de São Paulo**. São José dos Campos: INPE, 1992. 131p.

FALCÃO, N.P.S; COMERFORD, N.B.; LEHMANN, J. Determining Nutrient Bioavailability of Amaznian Dark Earth Soil - Methodological Challenges. In: LEHMANN, J.; KERN, D.C.; GLASER, B.; WOODS, W. (Org.). Amazon Dark Earth, origin, properties and management. Holanda, v. 1, p. 255-270, 2003.

FEARNSIDE, P.M.; LEAL-FILHO, N., 2001. Soil and development in Amazonia: lessons from the biological dynamics of forest fragments project. In: BIERREGAARD, R.O., GASCON, C., LOVEJOY, T.E., MESQUITA, R. (Ed.). Lessons from Amazonia: The Ecology and Conservation of a Fragmented Forest. New Haven, CT: Yale University Press, in press.

FYSTRO, G. The prediction of C and N content and their potential mineralisation in heterogeneous soil samples using Vis-NIR spectroscopy and comparative methods. **Plant and Soil,Dordrecht**, v. 246, 139-149, 2002.

FONTES, M.P.F.; CARVALHO JUNIOR, I.A. Color attributes and mineralogical characteristics, evaluated by radiometry, of highly weathered tropical soil. **Soil Science Society of America Journal**, Madison, v.69, p.1162-1172, 2005.

GLASER, B.; GUGGENBERGER, G.; ZECH, W. Identifying the pre-Columbian anthropogenic input on present soil properties of Amazonian DarkEarths (terra preta)In: GLASER, B. ;WOODS, W.I. (Ed.) Berlin: Amazonian DarkEarths: Explorations in Space, Time, Springer, 2004, p. 145–158

GLASER, B.; LEHMANN, J.; ZECH, W. Ameliorating physical and chemical properties of highly weathered soil in the tropic with charcoal - A review. **Biology and Fertility of Soils**, New York, v.35, p.219-230. 2002.

GEE, G.W.; BAUDER, J.W. Particle size analysis. In: Klute, A. (Ed.), Methods of SoilAnalysis: Part 1. Physical and Mineralogical Methods. **Soil Science Society of America**, Madison, WI, p. 383–411, 1996.

GOMEZ, C.; LAGACHERIE, P.; COULOUMA, G. Continuum removal versus PLSR method for clay and calcium carbonate content estimation from laboratory and airborne hyperspectral measurements. **Geoderma**, Amsterdam, v. 148, p. 141-148, 2008.

HABERHAUER, G.; RAFFERTY, B.; STREBL, F.; GERZBACK, M.H. Comparison of the forest soil litter derived from three different sites at various decompositional stages using FTIR spectroscopy. **Geoderma**, Amsterdam, v. 83,p.331-342, 1998.

HUNT, G.R.; SALISBURY, J.W. Visible and infrared spectra of minerals and rocks. **Modern Geology**, Lausanne, v. 2, p. 23-30, 1970.

M.J. HECKENBERGER, A. KUIKURO, U.T. KUIKURO, C.J. RUSSELL, M. SCHMIDT, C. FAUSTO, B. Franchetto Amazonia 1492: Pristine forest or cultural parkland Science, 301 2003. p. 1710–1713

JANIK, L.J. todos et al. The prediction of soil carbon fractions using mid-infrared-partial least square analysis. **Australian Journal of Soil Research**, Collingwood, v. 45, p. 73-81, 2007.

JENKS, G.F. The Data Model Concept in Statistical Mapping. International Yearbook of Cartography, Prague, v. 7, p 186–190, 1967.

KÄMPF, N.;WOODS, W.I.; SOMBROEK, W.G.;KERN, D.C.;CUNHA, T.J.F. Classification of Amazonian dark earths and other ancient anthropic soils. In:LEHMANN, J.;KERN, D.C.; GLASER, B.;WOODS, W.I. (Ed.) Amazonian dark earths. Origin, properties, management. Dordrecht:Kluwer, 2003. p. 77-102

KERN, D.C.; KÄMPF, N. Antigos assentamentos indígenas na formação de solos com terra preta arqueológica na região de Oriximiná-Pará. **Revista Brasileira de Ciência do Solo,** Viçosa, v. 13, p.219-225, 1989.

KERN, D. C. Geoquímica e pedogeoquímica de sítios arqueológicos com terra preta na florestanacional de Caxiuanã (Portel-PA). 1996. 124p. Tese (Doutorado na área Arqueologia) - . Centro de Geociências, Universidade Federal do Pará.

KERN, D.C.; RODRIGUES; SOMBROEK, W. Distribution of Amazonian Dark Earths in the Brazilian Amazon. In: LEHMANN, J. ;KERN, ;D.C.; GLASER, B. **Amazonian dark earths**: origin, properties, Management. The Netherlands: Kluwer Academic Publishers, 2003. p. 51-75.

JAGER R.Fuzzy Logic in Control.Delft TU Press, Delft,Belgium.In: PEDRYCZ W. ;GOMIDE F. An Introduction to Fuzzy Sets:Analysis and Design. Cambridge:MIT Press, 1995. p270.

JARMER, T.; VOHLAND, M.; LILIENTHAL, H.; SCHNUG, E. Estimation of some chemical properties of an agricultural soil by spectroradiometric measurements. **Pedosphere**, Amsterdam, v. 18, n. 2, p. 163-170, 2008.

LAGACHERIE, P.; McBRATNEY, A.B. Spatial soil information systems and spatial soil inference systems: perspectives for digital soil mapping. In: LAGACHERIE, P.; McBRATNEY, A.B.; VOLTZ, M. (Ed.). **Developments in soil science**, Amsterdam: Elsevier, 2006. v. 31, p. 1-15.

LEHMANN, J.; KERN, D.C.; GERMAN, L.A.; McCANN, J.; MARTINS, G.C.; MOREIRA, A. Soil fertility and production potential. In: LEHMANN, J., KERN, D.C., GLASER, B.; WOODS, W.I. (Ed.). Amazonian dark earths; origin, properties and management. Dordrecht: Kluwer Academic Publishers, 2003. p.105-124.
LEHMANN, J. Terra preta nova e where to from here? In: WOODS, W.I. ; WENCESLAU, G. TEIXEIRA, W.G. ; LEHMANN, J. ; STEINER, C. A. WINKLER-PRINS, Et al.(Ed.). **Amazonian dark earths**: Wim Sombroek's vision Berlin: Springer Science, 2009. p. 473 – 484.

LEIFELD, J. Application of diffuse reflectance FT-IR spectro- scopy and partial least-squares regression to predict NMR properties of soil organic matter. **European Journal of Soil Science**. 57, 846–857, 2006.

LIMA, H.N.; SCHAEFER, C.E.R.; MELLO, J.W.V.; GILKES, R.J. & KER, J.C. Pedogenesis and pre-Colombian land use of "Terra Preta Anthrosols" ("Indian black earth") of Western Amazonia. **Geoderma**, Amsterdam, v.110, p.1-17, 2001.

MADARI B, BENITES VM DE, CUNHA TJF, 2003, The effect of management of the fertility of Amazonian dark earth soil. In: LEHMANN J, ;KERN, D.C.; GLASER, B.; WOODS, W.I.(Ed.).**Amazonian dark earths**: Origin, properties, management. The Netherlands:Kluwer Academic Publishers, p.407-432.

MADARI, B.E.; REEVES, J.B.; MACHADO, P.L.O.; GUIMARAES, C.M.; TORRES, E.; MCCARTY, G.W. Mid- and near-infrared spectroscopic assessment of soil compositional parameters and structural indices in two Ferralsols. **Geoderma**, Amsterdam, v.136, p.245-259. 2006.

MADEIRA NETTO, J.S.; BÉDIDI, A.; CERVELLE, B.; FLAY, N. Spectral (MIR) Determination of Kaolinite and Gibbsite Contents in Lateritic Soils. **Comptes Rendus de l'Àcademie des Science,** Serie Ila, Paris, v. 321, p. 119-128, 1995.

McCARTY, G.W.; REEVES, J.B.; REEVES, V.B.; FOLLET, R.F.; KIMBLE, J.M. Midinfrared and near-infrared diffuse reflectance spectroscopy for soil carbon measurement. **Soil Science Society of American Journal**, Madison, v. 66, p. 640-646, 2002.

McCARTY, G.W.; REEVES III, J.B. Comparison of near infrared and mid infrared diffuse reflectance spectroscopy for field-scale measurement of soil fertility parameters. **Soil Science**, Philadelphia, v. 171, n. 2, p. 94-102, 2006.

MALLEY, D.F.; YESMIN, L.; EILERS, RG. Rapid Analysis of hog manure and manureamended soils using near-infrared spectroscopy. **Soil Science Society of America Journal**, Madison, v.66, 1677-1686, 2002.

MINASNY, B., MCBRATNEY, A.B., AND WHELAN, B.M. VESPER version 1.62. Australian Centre for Precision Agriculture, McMillan Building A05, The University of Sydney, NSW 2006. (http://www.usyd.edu.au/su/agric/acpa) 2005.

MOREIRA, A.; MALAVOLTA, E. Variação das propriedades químicas e físicas do solo e na matéria orgânica em agroecossistemas da Amazônia Ocidental (Amazonas). Piracicaba: CENA/USP, 2002. 79p

NEVES, E.G.; PETERSEN, J.B.; BARTONE, R.N.; HECKENBERGER, M.J. The timing of terra preta formation in the central Amazon: archaeological data from three sites. In;GLASER, B. ;WOODS, W.I. (Ed.). Explorations in Amazonian Dark Earths (in press). Heidelberg: Springer Verlag, 2003.

OLSEN, S.R. ; SOMMERS, L.E. Phosphorus In: PAGE, A.L. todos (Ed.) et al. Methods of Soil Analysis, Agronomy. 2nd ed. Madison, Wis:American Soil Science Society, 1982.pt.2 p. 419–422.

OLIVEIRA, J.J.; CHAVES, L.H.G.; QUEIROZ, J.E.; LUNA, J.G. DE. Variabilidade espacial de propriedades químicas em um solo salino-sódico. **Revista Brasileira de Ciência do Solo**, Viçosa, v.23, n.4, p.783-789, 1999.

PABST, E. Critérios de distinção entre Terra Preta e Latossolos na região de Belterra e os seus significados para a discussão pedogenética. **Boletim do Museu Paraense Emilio Goeldi,** Série Antropologia, Belém, v.7, p.5-19, 1991.

PEDRYCZ, W.; GOMIDE, F. 1998. An Introduction to Fuzzy Sets; Analysis and Design. MIT Press, Boston.

RANZANI, G.; KINJO, T. ;FREIRE, O. Ocorrências de "Plaggen Epipedon" no Brasil. **Notícia Geomorfica**, Belém, v. 10,p.55-62, 1970.

REEVES, J.B., III.; FRANCIS, B.A.; HAMILTON, S.K. Specular reflection and diffuse reflectance spectroscopy of soils. **Applied Spectroscopy**, New York, v. 59, p.39–46, 2005.

REEVES III, J.B. Near- versus mid-infrared diffuse reflectance spectroscopy for soil analysis emphasizing carbon and laboratory versus on-site analysis: where are we and what needs to be done? **Geoderma**, Amsterdam, v. 158, p. 3-14, 2010.

RIZZO, R. **Técnicas espectroscópicas e atributos do terreno mapeamento digital de solos**. 2011. 171p. Dissertação (Mestrado em Solos e Nutrição de Plantas) – Escola Superior de agricultura "Luiz de Queiroz", Universidade de São Paulo, Piracicaba, 2011.

SALVIANO, A.A.C.; VIEIRA, S.R.; SPAROVEK, G. Variabilidade espacial de atributos de solo e de *Crotalaria juncea* L. em área severamente erodida. **Revista Brasileira de Ciência do Solo**, Viçosa, v.22, n.1, p 115-122, 1998.

SHARMA, S.Applied Multivariate Techniques. Local; Wiley, 1996.P 198.

SHEPHERD, K.D.; WALSH, M.G. Development of reflectance spectral libraries for characterization of soil properties. **Soil Science Society of America Journal**, Madison, v. 66, p. 988–998, 2002.

SMITH, N.J.H. Anthrosols and human carrying capacity in Amazonian. Annals of the Association of American Geographers., New York, v. 70, p. 553-566, 1980.

SMITH, M.O.; JOHNSON, P.E.; ADAMS, J.B. Quantitative determination of mineral types and abundances from reflectance spectra using principal components analyses. Journal of Geophysical Research, Washington, v. 90, p. C797-C804, 1985.

SOLOMON, D., J. LEHMANN, J. KINYANGI, B.Q. LIANG, T. SCHAFER. Carbon K-edge NEXAFS and FTIR-ATR spectroscopic investigation of organic carbon speciation in soils. **Soil Science Society of America Journal,** Madison, v. 69,p.107–119, 2005.

SOMBROEK, W. Amazon soils: A Reconnaissance of the Soils of the Brazilian Amazon Region. Wageningen:Center for Agricultural Publications and Documentation.1966. 292p.

SOMBROEK, W.G.; RUIVO, M.L.; FEARNSIDE, P.M.; GLASER, B.; LEHMANN, J. Amazonian Dark Earths as carbon stores and sinks. In.: LEHMANN, J.; KERN, D.C.; GLASER, B.; WOODS, W.I. (Ed.). Amazonian dark earths: origin, properties, and management. Dordrecht: Kluwer Academic Publishers, 2003. p.125-139.

STEFFEN, C.A.; MORAES, E.C.; GAMA, F.F. Radiometria óptica espectral: Tutorial. In: SIMPÓSIO BRASILEIRO DE SENSORIAMENTO REMOTO, 8., 1996, Salvador. **Anais...** São José dos Campos:INPE/SELPER, 1996. v. 1, p. 1-17

STENBERG, B.; VISCARRA ROSSEL, R.A.; MOUAZEN, A.M.; WETTERLIND, J. Visible and near infrared spectroscopy in soil science. **Advances in Agronomy**, Amsterdam, v. 107, n. 107, p. 163-215, 2010

STEINER, C.; TEIXEIRA, W.G.; LEHMANN, J.; ZECH, W. Microbial response to charcoal amendments of highly weathered soils and Amazonian dark earths in Central Amazonia – preliminary results. In: GLASER, B.; WOODS, W.I. (Ed.). Amazonian dark earths: explorations in space and time. New York: Springer, 2004. p.195-212.

STEVENSON, F.J. Humus chemistry. New York: Wiley, 1994.p 253

TERRA, F.S. Espectroscopia de reflectância do visivel ao infravermelho médio aplicado aos estudos quantitativos e qualitativos de solos. Piracicaba, 2012. 198p. Tese (Doutorado na área de Irrigação e Drenagem) – Escola Superior de Agricultura "Luiz de Queiroz", Universidade de São Paulo, Piracicaba, 2012.

VASQUES, G.M.; GRUNWALD, S.; SICKMAN, J.O. Modeling of soil organic carbon fractions using visible-near-infrared spectroscopy. **Soil Science Society of America Journal**, Madison, v. 73, p. 176-184, 2008.

VERHEIJEN, F.G.A., S. JEFFERY, A.C. BASTOS, M. VAN DER VELDE AND I. DIAFAS. 2010. Biochar application to soils - A critical scientific review of effects on soil properties, processes and functions. Rep. EUR 24099 EN. Office for the Official Publications of the European Communities, Luxembourg

VIEIRA, S.R.; LOMBARDI NETO, F. Variabilidade espacial do potencial de erosão das chuvas do estado de São Paulo. **Bragantia**, Campinas, v. 54, p. 405-412, 1995.

VISCARRA ROSSEL, R.A.; LARK, R.M. improved analysis and modelling of soil diffuse reflectance spectra using wavelets. **European Journal of Soil Science**, London, v. 60, p. 453-464, 2009.

VISCARRA ROSSEL, R.A.; BEHRENS, T. Using data mining to model and interpret soil diffuse reflectance spectra. **Geoderma**, Amsterdam, v. 158, p. 46-54, 2010.

VISCARRA ROSSEL, R.A.; WALVOORT, D.J.J.; McBRATNEY, A.B.; JANIK, L.J.; SKJEMSTAD, J.O. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. **Geoderma**, Amsterdam, v.131, p.59–75, 2006.

WOODS, W.I.;MCCANN, J.M. The Anthropogenic Origin and Persistence of Amazonian Dark Earths." YEARBOOK OF THE CONFERENCE OF LATIN AMERICANIST GEOGRAPHERS, Bogotá, v.25, p. 7–14, 1999.

ZECH, W; HAUMAIER, L.; HEMPFLING, R. Ecological aspects of soil organic matter in tropical land use. In: McCarthy P, Clapp CE, Malcolm RL, Bloom PR (eds) Humic substances in soil and crop sciences: selected readings. American Society of Agronomy and Soil Science Society of America, Madison, Wis., pp 187–202, 1990.

ZIMMERMANN, M.; LEIFELD, J.; FUHRER, J. Quantifying soil organic carbon fraction by infrared-spectroscopy. **Soil Biology & Biochemistry**, New York, v. 39, p. 224-231, 2007.

4 SOIL ENVIRONMENTAL MONITORING: INVESTIGATING HEAVY METALS BY VIS-NIR AND MID-IR SPECTRAL REFLECTANCE

Abstract

Soil contamination is an ever-growing concern and demands efficient methods for diagnosis of areas under suspected contamination. Spectroscopy reflectance vis-NIR has shown to be a reliable and environmentally friendly method for rapid detection and monitoring of soil contaminants. Although pure metals do not absorb in the vis-NIR region, they can be detected because of co-variation with spectrally active components (Stenberg et al., 2010). Despite the use of vis-NIR range in the study of soils, it is still necessary to test the effectiveness of other wavelengths (mid-IR 4000 to 400 cm⁻¹) less studied in the characterization and quantification of heavy metals in soil. We aim with this study to (i) evaluate over time Cr, Pb and Zn in three soils contaminated by salts commonly used in the industry; (ii) identify parameters of spectral variation associated to heavy metals in soils (iii) evaluate through sequential extraction procedures, soils contaminated with tannery sludge (solid), after 90 days of application; (iv) investigate the feasibility to use soil spectral data and chemometrics methods to predict metals in soils. Results indicate that the metals adsorption to soil constituents caused expressive changes in soil spectral curves, showing spectral differentiation between highly contaminated soil and soils that are relatively contaminant-free. However, the reflectance spectroscopy cannot be used to predict Cr, Zn and Pb extracted by DTPA (pH 7.0) accurately. On the other hand, Cr pseudo-total content can be predicted by spectroscopy reflectance with both sensors data. Fe and Mn also can be predicted accurately by vis-NIR. The vis-NIR models outperformed the mid-IR. The organic matter played a more important role in determining the soil spectral signatures than the mineralogical characteristics of soils, especially in soil with high organic carbon contents.

Keywords: Soil contamination; Proximal sensing; PLS regressions; Tannery sludge; mid-IR; vis-NIR; Heavy metals.

4.1 Introduction

Environmental monitoring of heavy metals in soils has become increasingly important, especially in regions under industrial activities and intensive agriculture, due to the potential risks of metals diffuse into several steps of the food chain (PEREIRA et al., 2011). Fertilizers and atmospheric deposition are considered to be the greatest heavy metals pollution sources (KABATA-PENDIAS; MUKHERJEE, 2007). Moreover, these elements have been dispersed in the environment, often through improper disposal of mining, industrial and even agricultural wastes. Arsenic (As), bismuth (Bi), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb), cadmium (Cd) and zinc (Zn) are considered environmental contaminants (TILLER, 1989, GUILHERME, 1999). Cd, Cu, Zn and Pb have been the subject of many studies due to high toxicity and bioaccumulation potential (CHANG et al., 1984).

The bioavailability of the heavy metals depends on their concentration in the soil solution, which in turn depends on their release from soil colloids. Metals release or adsorption to soil colloids is mainly affected by soil solution pH, soil cation exchange capacity (CEC), organic matter (OM) content, clay content, redox potential and presence of other elements in the

soil system (ALLEONI et al., 2005; KABATA-PENDIAS; MUKHERJEE, 2007; SPOSITO, 2008).

In this research we studied Cr in soils in more detail. The concern of the concentration rates of Cr in the environment has increased in the last decades because the hexavalent chromium [Cr(VI)] form, which is considered to be relatively toxic to humans and carcinogenic (PAUSTENBACH et al., 2002, UNIDO, 2005), besides its presence in phosphate fertilizers, limestones, nitrogen fertilizers and sludges (KABATA-PENDIAS; PENDIAS, 2001). Tannery sludge is one of the most important anthropogenic sources of Cr used in agriculture. Due to its high nutrient content and its potential for correcting soil acidity, the use of tannery sludge in agricultural areas can be an alternative for its disposal and recycling (MARTINES, 2009; NAIDU et al., 1998). However, several chemicals are used during the tanning processing of hides and skins, such as sodium bisulphate, sodium chlorite, NaCl, H₂SO₄ and formic acid, which more than 70% are not absorbed and are released as waste (UNIDO, 2005). Cr stemming from these sludges showed to be relatively nonbioavailable to plants, although high application rates can enrich the soil with metals, exceeding the toxic range in soils (IMAMUL HUQ, 1998). According to Chaney (1980) and Sikora et al. (1980) most heavy metals in various kinds of sludges present low availability to plants, due to the fixation of metals mainly in forms of oxides. The metals associated with iron and aluminum oxides found in the clay fraction for example, occur typically by specific adsorption with the formation of covalent bonds of metals with OH⁻ or O₂ groups on the surface of these minerals (SHEPPARD, 1992). But the effect of the sludges can be different, and Cr can be mobilized in other soil conditions (variation of soil pH and redox potential) as, for example, complexes with organic molecules.

In this context, the levels of metals during the disposal of sludge on farmland should be evaluated. According to federal normative in Brazil, CONAMA 375, the maximum concentration allowed of Cr in the sludge is 1000 mg kg⁻¹ (BRASIL, 2006) and the accumulative value in soils is 154 kg ha⁻¹. However inappropriate disposals of wastes with high levels of Cr may occur. Many authors studied the use of this residue focusing on the N and crop productions (MARTINES, 2009; FERREIRA et al. 2003; ALCÂNTARA etal., 2007; OLIVEIRA et al., 2008; KRAY et al., 2008). However, few researches exist involving the study of tannery sludge and heavy metals in soils (e.g. GONDEK, FILIPEK-MAZUR, 2003; TUDUNWADA et al., 2007; LÓPEZ-LUNA et al., 2012).

The development of modern analytical techniques has facilitated fast and reliable analysis of heavy metals in the soil, allowing determining very low amounts of these elements in various matrices. In general, heavy metals analysis is conducted by atomic adsorption spectroscopy (AAS) or inductively coupled plasma emission spectroscopy (ICP) on extracts obtained by high-temperature acidic digestion of the soil sample. However, analyzing soil attributes and residues by conventional methods is often expensive and time consuming. In addition, these analyses result in chemical residues, which may be environmentally hazardous.

In recent years, proximal soil sensing techniques, particularly soil spectroscopy; have been studied by many authors thus improving the quantitative assessment of the management problems (SHEPHERD; WALSH, 2002; DUNN et al., 2002). Reflectance spectroscopy is based on the detection of electromagnetic radiation reflected from the soil without having a direct contact by sensors. Near infrared reflectance spectroscopy (NIRS) has been reported to provide inexpensive, fast and accurate determination of many soil properties (DEMATTÊ et al., 2004, COHEN et al., 2005; BROWN et al., 2006; JARMER et al., 2008; STENBERG et al., 2010). NIRS it is a non-destructive technique that requires minimal sample preparation and the measurements can be performed on the go in situ, besides no hazardous chemicals are used.

Some authors obtained good correlation between soil spectral reflectance and heavy metals concentration (e.g KOOISTRA et al., 2001; KEMPER, SOMMER, 2002; SIEBIELEC et al., 2004; CHOE et al., 2008; BRAY et al., 2009).Wu et al. (2005) used the vis-NIR to predict Hg in soils in China and observed that this element was correlated with absorption overtones of goethite and clay minerals. However, despite the relevance of the potential of this technique to evaluate soil attributes, little information is found in the literature about detailed studies of potentially toxic elements in tropical soils evaluated by the mid-IR region (4000 to 400 cm⁻¹).It warrants new studies, given that more spectral information is found in the mid-IR region (SMITH, 1999). Although many papers have been published on the quantification of metals in soils, their relation to spectroscopy characteristics are insufficiently known.

In this context, as soil contamination is an ever-growing concern, a reliable and environmentally friendly method is need for rapid detection and monitoring of soil contaminants at any stage for the diagnosis of areas under suspected contamination. We aim with this study to (i) evaluate over time Cr, Pb and Zn in three soils contaminated by salts commonly used in the industry; (ii) identify parameters of spectral variation (vis-NIR and mid-IR) associated to heavy metals in soils and explore their viability in the evaluation of contaminated soils; (iii) evaluate through sequential extraction procedures, soils contaminated with tannery sludge (solid), after 90 days of application; (iv) investigate the feasibility to use soil spectral data and chemometrics methods to predict metals in soils.

Although pure metals do not absorb in the vis-NIR and mid-IR regions of the spectroelectromagnetic they can be detected by their co-variation with spectrally active components in this range (STENBERG et al., 2010). Thus, this approach starts from the premise that the spectrally assigned position of minerals varies with chemical composition and

surface activity (BEN-DOR et al., 1999). The metals can be coupled with organic matter, associated with hydroxides, carbonates or oxides that can be detected in the vis-NIR region or adsorbed to the clay minerals. The mid-IR spectroscopy also detects both absorbance by organic bonds and mineral components (COLTHUP et al., 1990). The surface of minerals has functional groups capable of forming complexes with organic and inorganic ions (ZACH; WESTALL, 1999). The chemical groups comprising soil organic matter, such as -CH₂ and -CH₃ (alkyl), C-OH (carbohydrate), -COO- and -COOH (carboxyl), -NH and -CNO (amide), -C=O (carbonyyl), and aromatic -C=C- and -CH (VAN DER MEER, BEUTELSPACHER, 1976; JANIK, SKJEMSTAD, 1995; PARTIFF et al., 1997) are nearly all infrared active. Thus, based on the theory and adsorption mechanisms of metals in soils, the spectral signatures of minerals that bind heavy metals can be used for the indirect detection and to quantify metal contents using spectrometer data and multivariate analysis. Despite the occurrence of otherwise similar minerals in different samples, variations in spectral features (e.g., shifts in peak wavelength, depths bands) may occur according to the nature and quantity of highly enriched cations in the mineral. It is expected to find the higher concentrations of heavy metals especially bound to organic matter or in the residual and more stable fraction, less bioavailable (KABATA-PENDIAS, PEDIAS, 2001).

4.2 Material and Methods 4.2.1 Soil characterization

The sites chosen for soil sampling varied widely in texture and chemical characteristics, previously defined based on maps and historical data of the areas. Three soils classified as Ferralsols, Cambisols and Arenosols (FAO, 2006) were selected and collected from 0-20 cm, air-dried for 48 hours at 45°C and sieved to < 2mm for chemical and particle-size distribution analyses(detailed below), (Table 1). The contents of heavy metals present in these soils are within or below those found in not contaminated areas (ZULIANI, 2006; KABATA-PENDIAS; PENDIAS, 2001) (Table 2). Mineralogical analyses were carried out using X-ray diffraction (DIXON; SCHULZE, 2002), showing the presence of kaolinite (Ca), gibbsite (Gb), goethite (Gt) and hematite (Hm) in all groups of soils evaluated, as well as traces of vermiculite (V), illite (IL) and quartz (Qz) in the Cambisol (Figure 1). The soil analyses are detailed in the steps below.

Table 1 - Characteristics of the studied soils

Table I -	Chara	actern	sucs of	ule s	luaiea	sons								
Soil Type	pН	Al	H+AL	Ca	Mg	K	SB	CEC(pH7)	V	Р	OM	Clay	Silt	Sand
				1	nmole	dm ⁻³			%	mg dm ⁻³	3 g dm ⁻³	g	; kg ⁻¹	
С	5.6	0.8	25.0	28.0	12.0	6.2	46.2	71.2	64.9	4.4	29.3	221	91	688
F	4.0	13.2	80.0	11.0	6.0	1.3	18.3	98.3	18.6	3.9	28.1	631	102	267
Α	4.0	8.2	47.0	5.0	3.0	0.6	8.6	55.6	15.5	4.1	15.4	63	28	909
C, F and	C, F and A refer to Cambisol, Ferralsol and Arenosol.													

Table 2 -Pseudo-total and available contents of metals found in the soils prior to the experiment installation, extracted by DTPA (pH 7) and acidic digestion assisted by microwave, respectively

Soil Type	Cd	Zn	Cu	Cr	Ni	Pb				
]	DTPA - di	ethylenetr	iaminepenta	acetic acio	d				
			ng l	xg ⁻¹						
С	< 0.02*	0.94	0.54	<10.00*	0.12	0.66				
F	< 0.02*	0.30	1.38	<10.00*	0.11	2.29				
А	< 0.02*	2.00	0.58	<10.00*	0.11	0.60				
	Acid digestion (HNO ₃) by microwaves									
			ng l	xg ⁻¹						
С	<1.50*	27.67	8.46	31.57	8.19	<15.00*				
F	<1.50*	23.88	25.47	67.44	9.77	26.84				
А	<1.50*	11.91	4.92	< 10.00*	<5.00*	<15.00*				

* below the quantification limit of the atomic adsorption spectroscopy (AAS). C, F and A refer to Cambisol, Ferralsol and Arenosol.



Figure 1 - Dyphratograms (XRD patterns) of the clay fraction de-ironed (1) and ironed (2) of samples of Cambisol (a), Ferralsol (b) and Arenosol (c)

4.2.2 Incubation experiment

Two incubation experiments were performed to study heavy metals in soils using proximal sensing techniques. The aim of Experiment I was to analyze how the available forms of metals (Cr, Pb, and Zn) changed over time in three soils to which different metal concentrations had been added, and to identify during the incubation any associated parameters of spectral variation in the vis-NIR and mid-IR bands (Table 3).

In Experiment II soils were treated with tannery sludge derived from cattle hide processing and analyzed after 90 days of incubation. This period was determined based on the natural degradation of organic matter in areas where this sludge has been commonly applied (MARTINES, 2009).

4.2.2.1 Experiment I

The experiment was carried out in a randomized complete design with three replications and twelve treatments for each soil type. The treatments consisted of three concentrations of Cr, Pb, and Zn (Table 3), in addition to a control treatment to which no heavy metals were added. The concentrations of each element were based on the threshold levels reported by Cetesb (2005), and included rates above and below the alert threshold.

Each experimental unit consisted of a 5-dm³ pot filled with soil from the 0–20 cm layer of Cambisols, Ferralsols, and Arenosols. Heavy metals were applied in an aqueous solution based on analytical reagents and miliQ water (Table 3). Throughout the experiment, soil moisture was maintained at 70% of field capacity. On the second, third, and 60th days of incubation we carried out chemical analyses and sensor scans (vis-NIR and mid-IR) of soil samples to test for parameters of spectral variation that were associated with Cr, Pb, and Zn in soils.

Metals	Reagents	D1	D2	D3
		•••••	mg kg ⁻¹	
Cr	CrCl ₃ .6H ₂ O	40	75	150
Pb	$(CH_3COO)_2Pb.3H_2O$	17	72	180
Zn	$ZnSO_4.7H_2O$	60	300	450

Table 3 – Treatments, rates and salts used in the incubation experiment I

75, 72 and 300 mg kg⁻¹ correspond to prevention values (PV) for Cr, Pb and Zn respectively (Cetesb, 2005). PV is the concentration of a substance, above which may occur harmful changes to soil quality and groundwater. This value indicates the soil quality of supporting their primary function, protecting the ecological receptors and groundwater quality.

4.2.2.2 Experiment II

The three soil orders were incubated in 0.5-dm³ pots and treated with tannery sludge (Table 4) at concentrations of 150, 2000, 4000, and 6000 mg kg⁻¹ Cr. The tannery sludge was processed and air-dried before application. After 90 days of incubation, chemical analyses and spectroscopic scans (vis-NIR and mid-IR) were performed on the soils to assess the effects of Cr, Zn, and Pb concentrations on soil pH, nitrogen, phosphorus, potassium, magnesium, calcium, and H+Al, and sequential extraction procedures were carried out to quantify Cr, Pb, Zn, Fe, and Mn contents.

At this stage, Cr was also added to soils in the form of CrCl₃.6H₂O. The same soil chemistry analyses were carried out for these soils as for those treated with tannery sludge. The aim was to determine if the spectral signature of the soils differs when Cr is added in the form of a residue product and when it is added as the reagent CrCl₃.6H₂O. Soil moisture in both incubated samples was maintained close to 70% of maximum retention capacity. Sequential extraction methods allow one to selectively measure the distribution of metals in soils and sediments. While they have been criticized due to the possibility that metals might be readsorbed and redistributed during extraction, they make it possible to compare the proportions of metals bound to chemically similar fractions (CANDELARIA et al., 1997). These analyses allowed us to determine the proportions of Cr and other metals that were associated with each component of the solid phase of soils, and thus predict their phytoavailability; to detail the soil spectral curves evaluation.

experiment n			
pHCaCl ₂	11.81	$H + Al (mmolc dm^{-3})$	9
Organic carbon (g kg ⁻¹)	72.03	Chromium (mg kg ⁻¹)	41694
Total Nitrogen Kjeldahl (g kg ⁻¹)	8.19	Copper (mg kg ⁻¹)	< 4
Alumminum (mg kg ⁻¹)	3	Nickel (mg kg ⁻¹)	78.95
Calcium (mmolc dm ⁻³)	950	Lead (mg kg ⁻¹)	< 15
Magnesium (mmolc dm ⁻³)	38	Cadmium (mg kg ⁻¹)	<1.50
Potassium (mmolc dm ⁻³)	7	$\operatorname{Zinc}(\operatorname{mg} \operatorname{kg}^{-1})$	93.72
Sodium (mmolc dm ⁻³)	21.53	EC (dS/m)	14.8

Table 4 – Physical-chemical characterization of the tannery sludge used in the incubation experiment II

4.2.3 Laboratory analysis 4.2.3.1 Analytical methods

The soil was analyzed according to methods described by Raij et al. (2009) and Embrapa (2001), for chemical and physical characteristics: pH values were determined in CaCl₂ 0.01 mol L⁻¹ (in a ratio of 1:2.5 w/w); organic carbon (OC) content by wet oxidation (modified

from Walkley and Black, 1964); phosphorus (P), calcium (Ca²⁺), magnesium (Mg²⁺) and potassium (K⁺) by ion exchangeable resin (RAIJ et al., 2001); aluminum (Al³⁺) by KCl 1 mol L⁻¹; H + Al by SMP buffer (RAIJ et al., 2001). We also analyzed "pseudo-total" contents of Cd, Cr, Cu, Ni, Pb and Zn extracted from the soil matrix by microwave assisted acid digestion(SW 846 – method 3051) and their available contents extracted by DTPA pH 7.3 (ABREU et al., 2005). The DTPA extractor is recommended as official extractant of metals from soils in the São Paulo state, duo to the positive and high correlations between soil and plant metal concentrations in several field studies (ABREU et al., 2007).The determination of the metals were made by atomic absorption spectroscopy (AAS).

The sequential extraction performed on the samples in Experiment II included some portions of the method adapted by Silveira et al. (2006) for tropical soils. The procedure consisted of several sequential steps. In the first step, the exchangeable fraction was determined. The next steps determined reducible fractions, fractions bound to carbonate, organic fractions, oxidizable fractions, and residual minerals. The fractions were: (i) exchangeable (F1); (ii) bound to carbonates (F2); (iii) bound to organic matter (F3); (iv) bound to Fe, Al, and Mn oxides (F4); and (v) residual (F5). The exchangeable fraction (F1) was obtained after extraction with 15 mL 0.1 mol L⁻¹ CaCl₂. After F1, the fraction bound to carbonates (F2) was obtained using 30 mL 1 mol L⁻¹ NaOAC with the pH adjusted to 5.0. The fraction bound to organic matter was obtained using 5 mL 5% NaOCl, with the pH adjusted to 8.5. The fraction bound to oxides (F4) was obtained with 0.2 mol L^{-1} ammonium oxalate + 0.2 mol L^{-1} oxalic acid + 0.1 mol L^{-1} ascorbic acid, with the pH adjusted to 3 (SCHWERTMANN, 1964). The residual fraction (F5) was obtained after near-total microwave-assisted digestion with HNO³⁺ and HCl at a 3:1 ratio, following the 3051a or "reverse aqua regia" method (ESTADOS UNIDOS, 1996). Between each successive extraction, samples were washed with 5 mL of 0.1 mol L⁻¹ NaCl to remove any of the previous solution remaining in the tube, and thus reduce sample dispersion and limit metal readsorption (AHNSTROM; PARKER, 1999). All suspensions were centrifuged at 2500 rpm. Extracts of the F1, F2, and F3 fractions were acidified to 1% with HNO₃, and a drop of toluene was added to the F4 extracts in order to prevent the growth of microorganisms. Metal contents were determined by atomic absorption spectrometry. Percent recovery was obtained by summing the metal contents in the fractions, dividing that sum by the semi-total metal content, and multiplying the result by 100.

In the tannery sludge, the metals were analyzed by the 3051a method (USEPA, SW-846) and determined by AAS; Na and K were analyzed by Mehlich-1 and determined by flame photometer. For total N, we used the Kjeldahl method. pH was measured in water extract at 1:10 ratio (waste: water) (ANDRADE; ABREU, 2006).

Contents of sand, silt and clay were determined by the hydrometer method, using calcium hexametaphosphate 0.1M and sodium hydroxide 0.1 M as dispersing agents.

The X-ray diffraction was used for the analysis and identification of minerals in the clay fraction (DIXON; SCHULZE, 2002). The organic matter was removed (H₂O at 30 %), each sample of the clay fraction was divided into two sub-samples; one was treated with dithionitecitrate-bicarbonate (DCB) for the removal of iron oxides, and the other with NaOH 5 mol L⁻¹ (hot) for the removal of silicates and gibbsite aiming to obtain the concentration of these oxides. Oriented blades were prepared for all sub-samples. The sub-samples of the treatment with DCB were saturated by magnesium (Mg) and potassium (K), and those resulting from the treatment with K were irradiated at room temperature and after heated (3 hours) at 300° and 500° C. Those resulting from the treatment with Mg were solvated with glycerol and irradiated at room temperature. The dyphratograms (XRD patterns) were obtained with a graphite monochromator of Shimadzu - $6000^{\text{@}}$, at 40 kV of tension and 20 mA current, radiation of Cu-K α of pace 0.02° 2 θ at a speed of 1 pace s⁻¹ and interval of 3 to 70° 2 θ .

4.2.3.2 Spectral measurement

The spectral reflectance of the soils was measured in the laboratory using the FieldSpec Pro FR spectroradiometer (Analytical Spectral Devices, Boulder, Colorado; HATCHELL, 1999), for vis-NIR (350-2500 nm) range, with a spectral resolution of 3 nm (from 350 to 1000 nm) and 10 nm (from 1000 to 2500 nm); and using the Nicolet 6700 Fourier Transform Infrared (FT-IR) equipped with an accessory to acquire diffuse reflectance (Smart Diffuse Reflectance) that covers the 2500-25000 nm range (4000-400 cm⁻¹).

For the vis-NIR scans, the spectra acquisition software interpolated reflectance data to a sampling interval of 1 nm. Approximately 15 cm³ of each sample soil was placed in a Petri dish. A fibre optic connected to the vis-NIR sensor was placed vertically at 8 cm distant from the sample, where we measured the reflected light in an area of approximately 15 cm² in the centre of the sample. The light source was a 50W halogen bulb with the beam non-collimated to the target plan, positioned at 35 cm from the sample at a zenith angle of 30°. As a reference standard, a white plate covered with barium sulphate (BaSO₄) was used (STEFFEN et al., 1996). Each spectrum was given by the average of 100 scan sensor readings in 10 seconds. All spectral measurements were carried out in a dark room to avoid interference by stray light.

For measurements at the MIR range it was used approximately 1 cm^3 of each sample (100 mesh), placed in the proper recipient of the sensor. The internal light source is the HeNe laser with a calibration standard for each wavelength (2500 to 25000 nm). The spectra were obtained with spectral resolution of 1.2 nm and with 64 scans per second. Before each

measurement the reference spectrum of a background spectrum were obtained to calibrate the sensor.

4.2.4 Statistical analysis

Summary statistics and correlation analysis were performed using Jump software version 8.0 (SAS, 2008). Data of chemical analyses were subjected to ANOVA, by the F test (at a 99% and 95% confidence level) and the differences between means were determined using the *Tukey* test (p < 0.01). The correlations between the metals contents and other soil properties were done by Pearson coefficient.

The spectroscopy analyses were performed in the Unscrumbler v.10.1 (CAMO SOFTWARE AS, Oslo, Norway). Before spectroscopy multivariate analyses, the soil vis-NIR spectra were first reduced to 400-2450 nm to eliminate the noise at both edges of each spectrum. The vis-NIR spectra obtained were also continuum-removed (CR) to enhance the spectral absorption features (VISCARRA ROSSEL et al., 2009). For the mid-IR soil spectra we considered all ranges to further analysis. The spectra reflectance of mid-IR data were also transformed to absorbance for soil attributes calibrations. For that it was used the partial least square regression (PLSR), using the orthogonalized PLSR algorithm for one Y-variable (PLS-1) and full cross-validation. The number of PLS factors was chosen to minimize the root mean square error (RMSE) in the cross validation.

The Principal Component Analyses were applied to the spectral curves of soils, aiming to reduce the dimensionality of the data, to group similar spectra and to evaluate outliers (WORKMAN, 1992).

4.3 Results and discussion 4.3.1 Exploratory analysis of the spectral data

An exploratory analysis of the spectral data of the three soils is presented in Figures 2 and 3. In this type of analysis it is important to keep in mind the variation in reflectance intensity (albedo) of the spectra throughout the wavelength, but especially between 600-2500 nm and 2900-2500 cm⁻¹, 2000-1600 cm⁻¹, 1200-750 cm⁻¹, as well as changes in the amplitude and the shape of the absorption features related to the attributes of each soil, as demonstrated by Bowers and Hanks (1965); Stoner and Baumgardner (1981); Galvão, Vitorello and Paradella (1995); Formaggio et al. (1996); Ben-Dor, Irons and Epema (1999); Demattê (2002); Demattê et al. (2004a); Dalmolin et al. (2005); Ben-Dor, Heller and Chudnovsky (2008); Bellinaso, Demattê and Romeiro (2010) and Terra (2012). In the mid-IR region we observed a shift between 2000

and 1200 cm⁻¹ for Ferralsols. This range is characteristic of the presence of quartz and in Ferralsols samples the absorptions features are more smoothed.

Kaolinite shows characteristic features near 2200 nm, 1400 nm and 3600 cm⁻¹. Characteristic absorption features near 1400 nm were attributed to harmonic vibrations of O-H (stretching) near 2778 nm (3600 cm⁻¹), while those near 2200 nm are due to combinations involving OH⁻ stretching and the bonding curves between Al-OH (HLAVAY et al., 1977). Hunt et al. (1973) have argued that the intensity of the kaolinite feature at 2200 nm is associated with the dioctahedral layers of the mineral structure. The 1400 and 1900 nm bands are associated with water vibrations connected to bonds of lattice layers as hydrated cations (structural), combined with water adsorbed to the particle surfaces. We observed a feature near 2340-2445 nm in the Cambisols (Figure 2) that can be attributed to illite (POST; NOBLE, 1993), and confirmed in the dyphratograms (XRD patterns) (Figure 1).

In the mid-IR region the main absorption peaks observed were: 3695-3622, 3529-3394, 2924-2843, 2333-1362, 1157, 1111-1018, 791-752, 702, and 436 cm⁻¹. Absorption bands in mid-IR are generally caused by fundamental molecular vibrations (Tables 5 and 6). In the soil spectra, peaks at 3692–3620 cm⁻¹ and 1640 cm⁻¹ may be related to clay mineral attributes that seem to be related to Al-OH stretching of the clay minerals, as reported by Janik et al. (2007) and van Groenigen et al. (2003). The peaks near 2200 and 1900 cm⁻¹ were attributed to the presence of quartz, and were stronger in the Arenosols and Cambisols. Quartz peaks in soil samples may be suppressed or overlapped by peaks of other soil components, such as clay minerals or organic matter (STUMP et al., 2011). A hematite feature was observed in the Cambisols and Ferralsols, but was absent from the Arenosols (Figure 3c). These features have been corroborated by various other authors (e.g. NGYEN, JANIK, RAUPACH, 1991; CHRISTENSEN et al., 2000; MADEJOVA, KOMADEL, 2005; NAYAK, SINGH, 2007; TERRA, 2011).



Figure 2 - Mean spectral signature of the set of soil samples used in the experiment: (a) vis-NIR reflectance values (± SD), (b) vis-NIR reflectance values with continuous removal spectra (± SD), (c) vis-NIR reflectance values of each soil. Details on numbered features are given in Table 5



Figure 3 - Mean spectral signature of the set of soil samples used in the experiment: (a) mid-IR reflectance values (± SD) and (b) mid-IR reflectance values of each soil. Details on numbered features are given in Table 6

Spectral	Spectral	Band	Functional	Soil	Microscopic	Interaction	Type of
features	region	cm ⁻¹	group	constituent	interaction		propagation
number							
1	visivel	425		goethite		eletronic	
2	visivel	480	ion Fe ³⁺	goethite	atomic level	transition	
3	visivel	513		hematite			
4	visivel	650	ion Fe ³⁺	goethite	atomic level	transition	
				hematite			
5	NIR	903	ion Fe ³⁺	goethite (940 nm)	atomic level	eletronic	
				hematite (850 nm)		transition	
6	NIR	1000	ion Fe ³⁺	goethite	atomic level	elet. transition	
			(H-O-H)+(O-H)	water in soil			$2v_2 + v_3$ combination tone and overtone
				kaolinite		not	$2v_{1a}$ or 2_{v1} overtone
7	swir	1414		vermiculite 2:1 HE	molecular	fundamental	$2v_1$ overtone
			2(O-H)	smectite		vibration	$2v_1$ overtone
				mica (ilite)			$2v_1$ overtone
-				water in soil		not	
8	swir	1917	(H-O-H)+(O-H)	or	molecular	fundamental	$v_2 + v_3$ combination tone
				structural		vibration	
				kaolinite		not	
9	swir	2205	(O-H)+(Al-OH)	vermiculite 2:1 HE	molecular	fundamental	$v_{1b} + \delta$ combination tone
				smectite		vibration	
				mica (ilite)			
10	swir	2260	(O-H)+(Al-OH)	gibbsita		not	$v_{1b} + \delta$ combination tone
11	swir	2316	С-Н	organic compost (methil)		fundamental	$3v_4$ overtone
12	swir	2355	(O-H)+(Al-OH)	mica (ilite)	molecular	vibration	$v_{1b} + \delta$ combination tone
13	swir	2382	C-O	organic compost (carbohydrate)			$4v_5$ overtone
14	swir	2448	(O-H)+(Al-OH)	mica (ilite)			$v_{1b} + \delta$ combination tone

Table 5 - Absorptions features observed between 350 and 2500 nm (extracted from Terra, 2011)

Spectral	Spectral	Band	Functional	Soil	Microscopic	Type of
features number	region	cm ⁻¹	group	constituent	interaction	propagation
				kaolinite		
1	MIR	3695	O-H	smectite	molecular level	stretching
				mica (ilite)		-
				kaolinite		
2	MIR	3653	O-H	smectite	molecular level	stretching
				mica (ilite)		
				kaolinite		
3	MIR	3622	O-H	smectite	molecular level	stretching
				mica (ilite)		
				vermiculite 2:1 HE		
4	MIR	3529	O-Al-OH	kaolinite	molecular level	stretching
				gibbsite		
				vermiculite 2:1 HE		
5	MIR	3448	O-Al-OH	kaolinite	molecular level	stretching
				gibbsite		
				vermiculite 2:1 HE	molecular level	stretching
6	MIR	3394	(H-O-H)+(O-H)	kaolinite		
7	MIR	2924	C-H	organic compost (aliphatic)	molecular level	stretching
8	MIR	2843				
9	MIR	2341		CO_2		
10	MIR	2233				
11	MIR	2133				
12	MIR	1975				
13	MIR	1867	Si-O		molecular level	stretching
14	MIR	1790				
15	MIR	1678				
				kaolinite		
16	MIR	1628	O-H	smectitie	molecular level	distortion
				mica (ilite)		
				vermiculite 2:1 HE		
			Si-O	quartz		stretching
17		1527				
18	MIR	1497	Si-O	quartz	molecular level	stretching
19		1362				
			C-O	organic compounds (polysaccharide)		stretching
			C-OH	organic compost (aliphatic)	_	
20	TIR	1157		smectite	molecular level	
	O-Al-OH		mica (ilite)		distortion	
				vermiculite 2:1 HE		

Table 6 - Absorptions features observed between 4000 a 400 cm⁻¹ (continued on the next page)

Spectral	Spectral	Band	Functional	Soil	Soil Microscopic	
features number	region	cm ⁻¹	group	constituent	interaction	propagation
				kaolinite		stretching
				smectite		
21	TIR	1111	Si-O-Si	mica (ilite)	molecular level	
				vermiculite 2:1 HE		
			O-Al-OH	gibbsita		distortion
				kaolinite		
				smectite		
22	TIR	1018	Si-O-Si	mica (ilite)	molecular level	stretching
				vermiculite 2:1 HE		
				kaolinite		
				smectite		
23	TIR	926	Al-O-H	mica (ilite)	molecular level	distortion
				vermiculite 2:1 HE		
		-	Fe-O	hematite		
			Si-O	quatrz		stretching
		_		kaolinite		
24	TIR	814	Al-OH	vermiculite 2:1 HE	molecular level	distortion
				gibbsite		
				kaolinite		
25	TIR	791	Si-O	mica (ilite)	molecular level	stretching
				vermiculite 2:1 HE		
				kaolinite		
26	TIR	752	Si-O	mica (ilite)	molecular level	stretching
				vermiculite 2:1 HE		
				kaolinite		
				smectite		
27	MIR	702	Si-O	mica (ilite)	molecular level	stretching
				vermiculite 2:1 HE		
				kaolinite		
			Si-O-Si	smectite		
28	MIR	517		mica (ilite) molecular leve		distortion
				vermiculite 2:1 HE		
		-	Si-O	quartz		
29	MIR	436	Si-O	quartz	molecular level	distortion

Table 6 - Absorptions features observed between 4000 a 400 cm⁻¹ (conclusion)

4.3.2 Experiment I 4.3.2.1 Chemical data

Pseudo-total Cr, Pb, and Zn were significantly intercorrelated (Table 7), as a result of the shared soil components involved in the sorption of trace elements, except for Pb and Zn. We did not find a significant correlation between metal availability on one hand and clay and organic matter content on the other, except for Cr (N = 27) (Table 7). However, for total contents these correlations were observed. The dependence of clay content can be attributed to the greater sorption capacity of soils richer in clay as showed by Siebielec et al. (2004). In general, metals with coordination number equal to six bind more strongly to secondary minerals than elements with a coordination number above six, such as Pb (VIANA, 2011). This occurs during the soil weathering and formation process, when metals are imprisoned in the octahedral

positions of secondary minerals. They are more retaining with smaller coordination number. In our study Pb content, for example, was correlated with organic matter, suggesting that OM is a factor in Pb retention. However, according to Pandit et al. (2010), when this correlation is weak OM cannot be used to determine Pb contents because only a small amount is needed to retain Pb (PANDIT et al. 2010).

	and pseudo-tota	al metals conte	ents (N = 27)	
	Cr	Pb	Zn	Clay	ОМ
Cr	1.000				
Pb	0.236 *	1.000			
Zn	0.267 *	0.563 *	1.000		
Clay	-0.513 *	0.126	0.079	1.000	
ОМ	-0.214	-0.102	0.160	0.677 *	1.000
$Cr^{(l)}$	1.000				
<i>Pb</i> ⁽¹⁾	0.928 **	1.000			
$Zn^{(1)}$	0.623 **	0.287	1.000		
$Clay^{(1)}$	0.994 **	0.963 **	0.535 **	1.000	
<u>OM</u> ⁽¹⁾	0.739 **	0.435 **	0.987 **	0.662 **	1.000

Table 7 - Pearson correlation matrix for relationships between clay, organic matter and available and pseudo-total metals contents (N = 27)

⁽¹⁾pseudo-total content; (**) Significant at the 0.01 probability level; (*)Significant at the 0.05 probability level

The distribution of the available metals obtained by DTPA of Experiment I is illustrated in Figure 4. Since there are no reference levels in the literature for metals extracted by DTPA at a pH of 7.3, we used thresholds for Cr, Pb, and Zn concentrations based on the work of Abreu et al. (2005) and Raij et al. (1996). The thresholds used for Cr and Pb were 0.21 mg kg⁻¹ and 1.15 mg kg⁻¹, respectively, which correspond to the maximum content of those elements found at a variety of depths in Brazilian soils. The threshold for Zn was >130 mg kg⁻¹, which is the level at which toxicity occurs. Figure 4 shows the mean concentrations of easily available Cr, Pb, and Zn, which indicate that these soils were severely polluted.



Figura 4 – Descriptive statistics, histograms and outlier box-plots for available metals of soils contamined in Experiment I, extracted by DTPA (pH 7.3). The mean (solid line), the median (rhomb), the 25th and 75th percentiles (box), the 10th and 90th percentiles (whiskers) and outliers (dots) are indicated. The red bracket indicates the standard deviation. The blue line indicates the prevention values for metals extracted by concentrated nitric acid (pseudo-total) (CETESB, 2005)

Table 8 shows the available contents of heavy metals at different times during the incubation. We observed a decrease in the content of almost all metals over time, which suggests that metals were adsorbed to oxides, clay minerals, and/or soil organic matter. Available Pb content, for example, declined by more than 50% between the first and second measurements (Cambissol), for all three experimental concentrations (from 32.84 to 8.47; 84.57 to 25.8; 152.78 to 59.97 mg kg⁻¹). In fact, Pb bond strongly to organic matter and tend to be adsorbed faster than the other trace elements (ALLEONI et al., 2005). This adsorption regulates the concentration of ions and complexes in the soil solution, and plays an important role in its availability to the environment.

Doses	Metal	Incubation	Cambisols	Arenosols	Ferrasols
		time	Mean	Mean	Mean
			mg kg ⁻¹	$mg kg^{-1}$	$mg kg^{-1}$
D1	Cr	1	26.03 a	9.76 a	3.45 a
		2	11.43 b	7.09 b	3.52 a
		3	5.49 c	4.81 c	3.05 a
D1	Pb	1	32.84 a	29.8 a	42.5 a
		2	9.91 b	23.72 b	21.79 b
		3	8.47 b	23.35 b	32.28 b
D1	Zn	1	88.67 a	130.52 a	141.74 a
		2	87.18 a	96.16 b	139.1 a
_		3	75.7 a	45.84 c	85.09 b
D2	Cr	1	19.86 a	21.46 a	11.2 a
		2	16.08 b	11.89 b	11.34 a
_		3	12.19 c	13.35 b	9.06 b
D2	Pb	1	84.57 a	83.78 a	93.58 a
		2	33.16 b	65.67 b	57.44 c
		3	25.8 c	56.7 c	75.59 b
D2	Zn	1	194.32 a	95.09 a	90.07 c
		2	139.59 b	94.85 a	144.22 b
		3	131.01 b	144.32 a	201.46 a
D3	Cr	1	34.91 a	34.22 a	6.93 ab
		2	33.07 a	27.28 b	7.4 a
		3	8.85 b	20.8 c	5.73 b
D3	Pb	1	152.78 a	146.8 a	164.24 a
		2	67.05 b	137.75 a	155.73 a
		3	59.97 b	149.5 a	128.89 a
D3	Zn	1	317.97 a	280 a	171.58 b
		2	359.07 a	184.71 b	182.33 b
		3	116.44 b	179.83 b	358.23 a

Table 8 - Results of chemical analyses (DTPA) from samples of soils after 2, 30 and 60 days of incubation (Experiment 1). Mean of 3 repetitions

Médias seguidas por letras iguais nas colunas (para um mesmo elemento e dentro de uma mesa dose) não diferem entre si pelo teste de Tukey ao nível de 5% de significância. D1, D2 e D3 referem-se às doses definidas no experimento I.

4.3.2.2 Spectra data

PCA results of vis-NIR and mid-IR data are shown for all samples via PC-1 *vs* PC-2 score plot which describes the spectral variances of soil samples (Figure 5). PCA is used to identify spectrally unique or dissimilar observations that might be difficult to model (SHEPHERD; WALSH, 2002; ISLAM, 2003). The first two components capture 100% and 98 % of the total variance of the data for vis-NIR and mid-IR data, respectively (Figure 5). It can be attributing to the variation on the reflectance intensity and absorptions features of the spectra (ARAÚJO, 2008; TERRA, 2012). Score vectors provide the principal component (PC)

composition related to the soil sample, while the loading vectors provide this sample composition related to the variables (SENA et al., 2002). The eigenvectors graphs (loadings) indicate the positive and negative contributions of reflectance values for each Principal Component score (Figure 5). The PC-1 and PC-2 loadings of mid-IR showed the wavelengths at 2400 cm⁻¹ and from 1400 to 450 cm⁻¹ have greater importance on PC's, agreeing with Siebielec et al. (2004), since in this region there are absorptions features characteristics of organic compounds and clay minerals (Tables 5 and 6). The peak around 450-500 cm⁻¹ for example can be assigning to quartz, mica and vermiculite 2:1 HE (TERRA, 2012). The PC-1 and PC-2 loadings of vis-NIR indicated the bands around 900-1200 nm, 1900 nm and 2200 nm to be important on PC's.

Principal components analysis was also performed for the vis-NIR and mid-IR spectra of each soil separately, to test for grouping or separation of the different measurement periods and/or metals and/or metal concentrations. Although no clear grouping of spectral attributes was observed with regard to the specific metal in the samples, there was separation between samples of each soil according to period evaluated (different concentrations of metals). The Arenosols showed clearer separation, as illustrated in Figure 6. The first two PC's of the Arenosols showed a clear pattern of grouping in the mid-IR data (Figure 6b). In these soils, PC1 accounted for approximately 72% of variation in reflectance intensities of the spectral curves (TERRA, 2012) caused by the various treatments and cycles. The corresponding number for the vis-NIR data was 98%. Considering that PC1 mostly represents albedo (GALVÃO et al., 1995; SALDANHA et al., 2004) and is related to soil texture (DEMATTÊ, 2002), sandy soils whose mineralogy mostly consists of quartz and feldspar and which have high levels of SiO₂ show spectra with high reflectance intensities. That PC-2 accounted for 20% of mid-IR variation for Arenosols indicates that besides the intensity, changes also occurred in specific regions of the spectrum, with similar spectra grouped better than for the other two soils.

It is important to highlight that the metals adsorption to soil constituents caused expressive changes in soil spectral curves, considering that they were applied to soils through aqueous solution only once, before the incubation experiment; and that the levels of available metals in soils declined over the sampled periods. The mid-IR range can have more information than vis-NIR, since all chemical bonds within the molecule are active in this region, whereas in the vis-NIR region only some of the bonds are active (e.g. OH-, NH-) (SCHWARTZ et al., 2011).



Figure 5 - PCA results of spectra of soil samples PC-1-PC-2 score plot and loadings of the first four PC's of mid-IR (a) and vis-NIR (b)



Figure 6 - Principal components analysis of spectral data in the Arenosol. Vis-NIR (a) and mid-IR (b) data.

The effects of metals added in soils on the modification of qualitative spectral information are shown in Figures 7, 8 and 9 for Arenosols (a quartz-rich), Ferralsols (a clayrich) and Cambisols (quartz and an organic carbon-rich) samples, respectively. The spectra of the soil samples were mainly affected by the spectral characteristics of their main components. In general, metals are all negatively correlated with reflectance (WU et al., 2007). Our data showed spectral differentiation between highly contaminated soil and soils that are relatively contaminant-free, even in smaller concentrations, reflecting findings by Bray et al. (2009) and Kemper and Sommer (2002). For example, the Cr concentrations of 107 and 142 mg kg⁻¹ showed no significant differences in the spectra up to 1300 nm (Table 9b). However, above 1300 nm we observed differences in the reflectance intensity of the three concentrations of Cr (107, 142 and 217 mg kg⁻¹). For Cambisols these differences were observed with concentrations higher than 106 mg kg⁻¹ (Table 8). On the other hand, the Cr concentrations varying from 50 to 160 mg kg⁻¹ (Table 7) in Arenosols were not high enough to separate visually the spectra characteristics. In the mid-IR range, we observed differences in albedo according to Cr concentration especially up to 2000 cm⁻¹.

The vis-NIR spectra were visually featureless, showing only a reduction of the reflectance intensity with higher levels of metals and characteristics peaks of hydroxyl groups and water (1400 and 1900 nm) and kaolinite (2200 nm) for the same soil, in accordance with Kemper and Sommer (2002).

The mid-IR spectra showed a larger number of features (Figures 7, 8, and 9). In this sensor data we observed that the alterations occur at the magnitude of reflectance and also change the general spectrum's shape and format, as observed at 2800-2400 cm⁻¹ (Figure 7) and at 2000 cm⁻¹ (Figure 8). These regions are characteristics of organic compounds and quartz

(Table 6). In general, the mid-IR reflectance intensity was reduced with higher levels of heavy metals from 3600 to 2040 cm⁻¹. Mid-IR reflectance intensity between 3600 and 2040 cm⁻¹ was lower in soils with higher levels of heavy metals. At the band between 3621 and 2071 cm⁻¹ occurs interaction of fundamental vibration and propagation (Table 5). Reflectance differences in this region can possibly be attributed, among other factors, to the interaction of metals with minerals and organic compounds (2900-2700 cm⁻¹).

For Arenosols (Figure 7), the mean levels of available Cr (and adsorbed Cr, in parentheses) in this period were <10.0 (<10.0), 4.81 (45.19), 13.35 (71.65), and 20.80 (139.2) mg kg⁻¹ for the control and for experimental doses 1, 2, and 3, respectively. The corresponding values for Pb were 0.60 (<15.0), 23.35 (8.65), 56.7 (30.3), and 149.5 (45.5). The corresponding values for Zn were 2.0 (11.91), 45.84 (26.07), 144.32 (167.6), and 179.83 (282.08). For Cambisols (Figure 8), the mean levels of available Cr (and adsorbed Cr, in parentheses) in this period were <10.0 (21.6), 5.49 (66.1), 12.19 (94.3), and 8.85 (172.7) mg kg⁻¹ for the control and experimental doses 1, 2, and 3, respectively. The corresponding values for Zn were 0.94 (27.67), 75.7 (11.97), 131 (197), and 116 (361). For Ferralsols (Figure 9), the mean levels of available Cr (and adsorbed Cr, in parentheses) in this period were <10.0 (z1.19), and 116 (361). For Ferralsols (Figure 9), the mean levels of available Cr (and adsorbed Cr, in parentheses) in this period were <10.0 (57.44), 3.05 (104), 9.06 (133), and 5.73 (211) mg kg⁻¹ for the control and experimental doses 1, 2, and 3, respectively. The corresponding values for Pb were 0.94 (27.67). The corresponding values for Pb were 0.95 (133), and 5.73 (211) mg kg⁻¹ for the control and experimental doses 1, 2, and 3, respectively. The corresponding values for Pb were 2.29 (~24.55), 32.28 (11.56), 75.6 (23.25), and 128.89 (77.9). The corresponding values for Pb were 0.30 (23.5), 85 (0.5), 201 (122), and 358 (115).



Wavelenghts, cm⁻¹Wavelenghts, nmFigure 7 - Mid-Infrared (a) and vis near-infrared spectra reflectance of samples of Arenosols
(mean of 3 repetitions). Pseudo- total metal contents in mg kg⁻¹

0.1

0.0

4000 3600 3200 2800 2400 2000 1600 1200 800



Figure 8 - Mid-Infrared (a) and vis near-infrared spectra reflectance of samples of Cambisols (mean of 3 repetitions).Pseudo- total metal contents in mg kg⁻¹



Figure 9 - Mid-Infrared (a) and vis near-infrared spectra reflectance of samples of Ferralsols (mean of 3 repetitions).Pseudo- total metal contents in mg kg⁻¹

Predictions results of available metals using PLS regressions were not significant (Table 9) with low precision for both datasets (vis-NIR and mid-IR). These predictions could likely be improved if the models were calibrated with a highly variable set of soil samples. Our results stand in contrast to those of Malley and Willians (1997), who obtained accuracy results of Zn and Pb in sediments even in low concentrations, using the range 1100 to 2500 nm.

Kemper and Sommer also reported a correlation between predicted and measured Pb concentrations with an R^2 value of 0.95, but insignificant for Zn (0.24) analyzing soils. These authors used total metal content for their predictions, however, while we tried to quantify available content in comparison to DTPA extraction results.

Metal	Sensor data	R_c^2	RMSE _c	RPD _c	PLS factors	R_v^2	RMSE _v	RPD _v
	vis-NIR	0.23	8.04	1.12	4.00	0.20	9.14	1.02
$\operatorname{Cr} \operatorname{mg} \operatorname{kg}^{-1}$								
	mid-IR	0.20	7.23	1.25	3.00	0.25	8.56	1.09
	vis-NIR	0.23	44.56	1.16	5.00	0.23	53.09	0.88
Pb mg kg ⁻¹								
	mid-IR	0.36	41.37	1.25	5.00	0.38	52.50	0.89
	vis-NIR	0.58	62.20	1.48	7.00	0.20	69.06	0.85
Zn mg kg ⁻¹								
	mid-IR	0.49	59.65	1.54	5.00	0.22	70.23	0.84

Table 9 - Summary statistics of cross-validation and validation results of partial least square regression (PLSR) for metals

4.3.3 Experiment II 4.3.3.1 Effects of Cr application on soils

The H+Al contents in the samples of the three soils that were treated with tannery sludge (especially in those that received >2000 mg kg⁻¹ Cr) were lower than in those treated with chromium chloride (Tables 10, 11, and 12). In oxidizing conditions in soils, chromium chloride is oxidated to form Cr^{6+} , releasing H⁺ and increasing soil acidity. This explains the low pH values observed in the samples treated with the salt. While a decline in pH was observed with higher concentrations of CrCl₃.6H₂O, an increase in pH was observed with increasing amounts of tannery sludge. The soil solution is one of the factors that affect the release or adsorption of metals by soil colloids (ALLEONI et al., 2005). One of the sources of charge in soils is the edge charge of clay minerals. The quantity of positive or negative charge because of the excess H⁺ associated with the exposed Si-OH and Al-OH groups, but at higher pH levels some H⁺ are neutralized and negative charges increase (HAVLIN et al., 2005). Levels of Al³⁺ were higher in samples that were not treated with tannery sludge. This was due to the low pH, since at pH >5.5 Al³⁺ precipitates in the form of Al (OH)₃.

Ca, Mg, and Na contents were higher in soils treated with tannery sludge (Tables 10, 11, and 12), which contained high concentrations of these elements (Table 4). The high CEC values in samples treated with sludge were attributed to the sludge's high levels of organic matter and exchangeable cations, and high pH. While samples treated with chromium salt

showed high CEC values, the colloid charges were occupied by H+Al instead of exchangeable cations.

In the case of Na, the concentrations recorded in the Ferralsols treated with the highest doses of sludge corresponded to 31% of CEC, while in the control this value was <1% (Table 10). The corresponding values for Cambisols were 32.4 and 0.6%, and for Arenosols 26 and 4%. According to Havlin et al. (2005), under field conditions when a high percentage of the CEC is occupied by Na⁺, soil aggregates disperse, reducing natural aggregation and soil structure. In tropical soils that are rich in Fe and Al oxides, 40% Na⁺ saturation is required before significant dispersion occurs. Martines (2009) observed a decline in the productivity of a grain crop when 1200 kg ha⁻¹ N was added to the soil as tannery sludge (33.7 Mg ha⁻¹ of sludge, dry basis). In that study, productivity was limited by high concentrations of salts, especially sodium, in periods of dry weather.

Soil nitrogen content varied minimally with added tannery sludge. Treatment with sludge helped increase the V% (Tables 10, 11, 12).

Rates	Treatment	pН	Р	Na	Ca	Mg	Κ	CEC	H + Al	V	Ν
			mg dm ⁻³			mmol _c	dm ⁻³			%	g kg ⁻¹
Т	CrCl ₃ .6H ₂ O	4.1	2.4	0.5	13.6	5.8	1.2	106.9	85.7	20.0	1.6
	Sludge	3.9	3.0	0.4	11.0	6.0	1.2	113.6	95.0	16.4	1.6
D1	CrCl ₃ .6H ₂ O	4.0	2.0	0.6	11.3	6.0	1.2	109.1	90.0	17.6	1.5
	Sludge	4.5	2.0	6.4	24.0	20.0	1.3	127.7	76.0	41.0	1.8
D2	CrCl ₃ .6H ₂ O	3.0	2.0	0.6	12.0	6.0	1.3	280.2	260.3	7.0	1.6
	Sludge	6.2	2.6	76.2	168.0	98.0	1.3	364.0	20.0	94.0	1.8
D3	CrCl ₃ .6H ₂ O	2.6	2.0	0.6	13.3	6.0	1.2	550.2	529.0	3.9	1.6
	Sludge	6.9	2.0	138.1	207.6	147.7	1.0	509.8	15.3	97.0	2.2
D4	CrCl ₃ .6H ₂ O	2.5	2.0	0.6	12.7	7.0	1.3	675.3	653.0	3.2	1.6
	Sludge	7.1	2.0	195.6	277.3	147.0	1.0	633.0	12.0	98.0	2.2

Table 10 - Mean attributes of Ferralsols under different treatments

Rates	Treatment	pН	Р	Na	Ca	Mg	Κ	CEC	H + Al	V	Ν
			mg dm ⁻³			mmol _c	dm ⁻³			%	g kg ⁻¹
	CrCl ₃ .6H ₂ O	5.3	4.4	0.5	25.3	11.0	6.2	67.3	24.3	64.0	1.8
Т											
	Sludge	5.3	4.4	0.4	27.3	12.3	6.0	68.7	22.7	67.0	1.8
DI	CrCl ₃ .6H ₂ O	5.2	3.3	0.5	25.0	11.0	5.2	63.4	21.7	65.8	1.8
DI	Cludes	5 0	12	62	20 7	21.0	6.6	00.6	20.0	<u>00 0</u>	1.0
	Sludge	5.8	4.3	0.3	38.7	21.0	0.0	99.0	20.0	80.0	1.9
	CrCl. 6H.O	28	2.0	0.6	32.0	12.0	65	142.7	01 7	35.0	17
D2	CICI3.0II ₂ O	2.0	2.0	0.0	52.0	12.0	0.5	142.7	91.7	55.7	1.7
	Sludge	7.1	3.3	93.6	138.3	74.3	4.6	321.2	10.3	96.8	2.0
	0										
	CrCl ₃ .6H ₂ O	2.2	2.0	0.7	34.0	13.7	6.3	496.3	441.7	11.0	1.7
D3											
	Sludge	7.5	2.0	144.8	167.0	84.3	3.9	408.7	8.7	97.9	2.3
	CrCl ₃ .6H ₂ O	2.1	2.0	0.7	35.3	14.0	6.6	986.0	929.3	5.7	1.8
D4			• •						. –		
	Sludge	7.5	2.0	149.8	200.0	101.0	3.9	463.4	8.7	98.1	2.4

Table 11 - Mean attributes of Cambisols under different treatments

	Table 12 - N	<i>Iean</i> attributes	of Arenosols	under differe	ent treatments
--	--------------	------------------------	--------------	---------------	----------------

Rates	Treatment	pН	Р	Na	Ca	Mg	Κ	CEC	H + Al	V	Ν
			mg dm ⁻³						%	g kg ⁻¹	
	CrCl ₃ .6H ₂ O	4.2	3.0	2.6	5.0	2.7	0.6	57.8	47.0	18.7	1.0
Т											
	Sludge	4.2	2.7	2.5	4.3	2.3	0.6	58.3	48.7	16.6	1.0
D1	CrCl ₃ .6H ₂ O	3.9	2.0	2.3	3.7	3.0	0.6	65.6	56.0	14.7	1.0
<u> </u>	Sludge	5.1	3.3	6.4	15.3	14.0	0.5	66.2	29.7	55.2	0.9
D2	CrCl ₃ .6H ₂ O	2.3	2.0	2.2	5.7	3.7	0.6	372.1	360.0	3.3	0.9
D2	Sludge	6.8	4.0	66.2	132.7	84.0	0.6	294.8	11.3	96.2	1.1
D3	CrCl ₃ .6H ₂ O	2.1	2.0	4.5	6.0	5.0	0.6	694.1	678.0	2.3	0.9
	Sludge	7.0	2.0	106.3	275.0	151.7	0.6	544.3	10.7	98.0	1.1
D4	CrCl ₃ .6H ₂ O	2.0	2.0	4.9	5.7	3.0	0.5	908.0	894.0	1.6	0.9
	Sludge	7.4	2.3	162.0	319.7	129.7	0.7	621.7	9.7	98.4	1.4
4.3.3.2 Chemical sequential extraction for Metals **4.3.3.2.1**Cromium

All Ferralsol, Cambisol, and Arenosol samples, except for the control treatments, had higher pseudo-total Cr concentrations than the intervention reference values (150 mg kg⁻¹) (CETESB, 2005). Most Cr in the Ferralsol control was in the residual fraction (42%), followed by the fraction bound to organic matter (34%) (Table 13 and Figure 10). In these samples, the fractions that were least important for Cr were the exchangeable fraction (3%) and the carbonate-bound fraction (3%). As higher doses of $CrCl_{3.}6H_{2}O$ were added to soils and soil pH declined, Cr content in the exchangeable fraction increased (from 3 to 12%). An opposite effect was observed in the samples treated with tannery sludge, which increased pH to 7.1 (Table 10 and Figure 10). At higher pH, the negative charges of the colloid surfaces were no longer occupied by the H⁺ ion and could be occupied by other cations, including cationic metals (SPOSITO, 1989). CEC is related to a soil's capacity for adsorbing metals; the higher the CEC, the more adsorption sites are available on the soil colloids. It is important to emphasize that the exchangeable fraction is a more direct measure of the probability of eventual negative impacts on the environment (CAMARGO et al., 2000). The distribution of Cr (III) species as a function of pH has been studied by Ferro et al. (1994), who showed that at pH 4.5 60% of Cr occurred as $CrOH^{2+}$ and 40% as Cr^{3+} . At pH close to 7.0, the predominant form in soils was $Cr(OH)^{2+}$.

				Cr fraction	is mg kg ⁻¹		
Levels	Treatment	Exchangeable	Carbonates	Organic Matter	Oxides	Residual	Pseudo-total
	CrCl ₃ .6H ₂ O	2.1±0.1	2.3±0.4	23.5±2.4	11.4±0.3	28.8±2.3	68.2±0.7
Т							
	Sludge	2.2±0.3	2.3±0.3	23.5±2.4	11.6±0.3	29.5±2.7	69.1±1.0
	CrCl ₃ .6H ₂ O	6.7±0.1	37.5 ± 2.0	54.3±4.3	33.7±3.5	75.1±30.1	207.3±21.3
D1							
	Sludge	2.0±0.1	$7.0{\pm}1.6$	68.7±5.2	36.2±4.3	110.7±5.9	224.8±1.6
	CrCl ₃ .6H ₂ O	96.3±4.6	340.0±15.4	649.8±38.4	337.0±13.1	359.6±22.1	1993.0±31.5
D2							
	Sludge	1.9 ± 0.1	124.5±18.1	846.0±8.5	441.5±14.6	1244.0±387.4	2658.0±369.0
	CrCl ₃ .6H ₂ O	297.2±2.3	830.9±10.2	959.0±35.2	589.5±45.5	1403.8±24.4	4079.3±17.8
D3							
	Sludge	2.0 ± 0.1	347.1±32.3	1779.8±197.3	871.8±7.9	1102.4±178.9	4103.2±5.5
	CrCl ₃ .6H ₂ O	712.3±35.9	1347.9±37.3	1408.2±77.0	856.8±14.7	1741.5±69.2	6067.6±30.9
D4							
	Sludge	1.8 ± 0.1	484.7±56.7	2547.0±87.2	1311.6±65.6	1745.5±45.1	6090.9±38.8

Table 13 - Fractional distribution of Cr content from the sequential extraction of the treated Ferralsol



Figure 10 - Percent Cr distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Latossols

Most Cr in the control samples of Cambisols (52%) occurred in the organic fraction, followed by the oxide-bound fraction (21%) (Table 14 and Figure 11). As in the Ferralsols, the exchangeable fraction was the least important for Cr (4%). Adding tannery sludge caused an increase in soil pH, which led to a decline in Cr content in the exchangeable fraction and a small

increase in the organic matter- and oxide-bound fractions, especially at the highest doses (Table 11 and Figure 11).

		Cr fractions mg kg ⁻¹ ExchangeableCarbonatesOrganic MatterOxidesResidualPseudo-tc 1.2 ± 0.9 3.5 ± 0.5 16.8 ± 0.1 6.6 ± 0.4 4.0 ± 1.3 $32.0\pm1.$ 1.5 ± 0.3 3.0 ± 0.2 17.4 ± 1.2 6.8 ± 0.2 4.0 ± 1.0 $32.7\pm1.$ 7.4 ± 0.3 15.9 ± 0.9 90.0 ± 3.0 43.3 ± 0.5 33.8 ± 2.7 190.4 ± 4 6.0 ± 0.4 19.8 ± 0.3 116.8 ± 1.4 53.0 ± 0.5 30.5 ± 0.4 226.2 ± 2 125.9 ± 3.5 253.2 ± 39.3 772.8 ± 96.4 58.2 ± 1.0 847.4 ± 70.7 2057.0 ± 6 8.5 ± 0.4 173.9 ± 14.7 1278.2 ± 44.4 812.0 ± 2.8 33.1 ± 24.5 2306.0 ± 5 380.5 ± 35.6 524.1 ± 63.3 1319.0 ± 77.0 113.7 ± 11.6 1752.6 ± 154.9 4091.0 ± 9					
Levels	Treatment	Exchangeable	Carbonates	Organic Matter	Oxides	Residual	Pseudo-total
	CrCl ₃ .6H ₂ O	1.2±0.9	3.5±0.5	16.8±0.1	6.6 ± 0.4	4.0±1.3	32.0±1.3
Т							
	Sludge	1.5±0.3	3.0±0.2	$17.4{\pm}1.2$	6.8±0.2	4.0±1.0	32.7±1.7
	CrCl ₃ .6H ₂ O	7.4±0.3	15.9 ± 0.9	90.0±3.0	43.3±0.5	33.8 ± 2.7	190.4 ± 4.0
D1							
	Sludge	6.0±0.4	19.8±0.3	116.8±1.4	53.0±0.5	30.5±0.4	226.2±2.0
	CrCl ₃ .6H ₂ O	125.9±3.5	253.2±39.3	772.8±96.4	58.2 ± 1.0	847.4±70.7	2057.0±67.1
D2							
	Sludge	8.5±0.4	173.9±14.7	1278.2 ± 44.4	812.0±2.8	33.1±24.5	2306.0±53.0
	CrCl ₃ .6H ₂ O	380.5 ± 35.6	524.1±63.3	1319.0±77.0	113.7±11.6	1752.6 ± 154.9	4091.0±9.9
D3							
	Sludge	5.8 ± 0.8	457.5 ± 28.2	3042.7±42.7	1912.0±10.9	60.9±1.3	5479.0±20.4
	CrCl ₃ .6H ₂ O	1526.0 ± 40.4	1087.0 ± 109.5	2193.8 ± 50.4	215.0 ± 3.2	1831.6±78.4	6854.0 ± 28.8
D4							
	Sludge	3.0±0.8	391.8±21.2	3836.8±144.5	2307.5±2.8	189.4±172.4	6728.6±41.4

Table 14 - Fractional distribution of Cr content from the sequential extraction of the treated Cambisol



 \blacksquare F1 \blacksquare F2 \blacksquare F3 \blacksquare F4 \Box F5



Figure 11- Percent Cr distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Cambisols

Most Cr in the Arenosols (up to 54%) occurred in the residual fraction, as was the case in the Ferralsols (52%). The next most important fraction under acidic conditions was the exchangeable (up to 24%; Table 15 and Figure 12). In less acidic conditions, most Cr (up to 54%) was observed in the organic matter-bound fraction (Figure 12b).

				Cr fractio	ns mg kg ⁻¹		
Levels	Treatment	Exchangeable	Carbonates	Organic Matter	Oxides	Residual	Pseudo-total
	CrCl ₃ .6H ₂ O	1.7±0.2	$1.7{\pm}0.1$	2.3±0.05	1.6±0.1	5.5±1.1	12.8±1.3
Т							
	Sludge	1.7 ± 0.2	1.5±0.2	2.3 ± 0.07	1.6 ± 0.30	5.6 ± 0.5	12.8±0.5
	CrCl ₃ .6H ₂ O	21.4±0.6	20.3 ± 0.1	23.9±1.5	11.3±0.7	85.1±0.9	$162.0{\pm}1.8$
D1							
	Sludge	4.2 ± 0.1	11.5±1.0	52.5±1.7	19.5±0.5	76.9±2.4	164.7±2.9
	CrCl ₃ .6H ₂ O	526.8±16.3	269.4 ± 45.0	310.4±11.7	197.6 ± 5.8	1580.0±37.7	2883.8 ± 25.6
D2							
	Sludge	10.2 ± 0.7	246.0±37.6	740.9 ± 39.5	264.4±12.1	988.0±54.9	2249.0±56.0
	CrCl ₃ .6H ₂ O	1062.2 ± 42.0	410.3±9.0	465.6±21.3	340.7±19.9	2131.4±66.0	4410.8±75.1
D3							
	Sludge	7.2 ± 0.4	498.2 ± 4.3	2529.6±50.5	668.5 ± 21.1	1361.0±26.0	5064.6±34.6
	CrCl ₃ .6H ₂ O	1426.1±65.4	669.4 ± 22.9	654.0 ± 38.7	460.4 ± 28.9	2986.0±247.6	6195.4±165.2
D4							
	Sludge	3.0±0.5	657.4±12.3	3363.8±318.0	817.2±20.7	1280.5±299.1	6121.9±48.5

Table 15 - Fractional distribution of Cr content from the sequential extraction of the treated Arenosol



 \blacksquare F1 \blacksquare F2 \blacksquare F3 \blacksquare F4 \Box F5



Figure 12- Percent Cr distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Arenosol

4.3.3.2.2 Iron

Results from the sequential extraction of the Ferralsols, Cambisols, and Arenosols showed that Fe occurred primarily in the residual (F5) and oxide (F4) fractions (Figures 13, 14, and 15). Other forms of Fe were almost negligible. These results were similar to those reported by Wu et al. (2007), who found most Fe in the crystalline Fe oxide, residual, and amorphous Fe oxide fractions. Solubility of Fe oxides is extremely low at the most commonly occurring soil pH values, and is typically influenced by factors such as particle size, degree of crystallization, and the substitution of Fe for Al (SCHWERTMANN, 1991). Sastre et al. (2001) have also argued that wastes with a high concentration of iron oxides pose lower risks for environmental pollution than heavy metals, due to the capacity of such wastes for retaining metals.



Figure 13 - Percent Fe distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Ferralsol

(a)



Figure 14 - Percent Fe distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Cambisol



Figure 15 - Percent Fe distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Arenosol

4.3.3.2.3 Manganese

The distribution of Mn among different fractions in Ferralsols treated with different rates of $CrCl_3.6H_2O$ was nearly identical, with the highest proportions in the residual fraction (up to 75%) and the lowest in the carbonate and organic matter fractions (1%) (Figure 16a). In the soils treated with sludge we observed a reduction in the proportion of Mn in the extractable fraction (F1) from 15% (level 4 - $CrCl_3.6H_2O$) to 1% (level 4 - tannery sludge), and an increase in the proportion of Mn in the organic fraction (from 1 to 8% in level 4) (Figure 16b), with

increasing soil pH. Similar results have been reported by Nachtigall et al. (2009) for Mn and Zn. At pH >6, high amounts of Mn are adsorbed to organic matter, concentrations of exchangeable forms are low, and those of organic and oxide forms are high (BIBAK, 1994; SHUMAN, 1986). As pH declines, so does the number of OH sites on the surface of the organic matter and the oxides that can retain Mn.

In Cambisols, when mean soil pH was <2.8 (in the CrCl₃.6H₂O treatments) (Table 11), the highest proportion of Mn occurred in the exchangeable fraction (up to 68%), followed by F4 (oxides) and F5 (residual) (Figure 17a). When soil pH was high, the exchangeable contents declined and the fraction bound to organic matter increased (Figure 17b and Table 11). A similar pattern was observed in the Arenosol samples (Figure 18). Shuman (1985) has noted that in clayey soils, most Mn tends to be adsorbed to oxides, while in less clayey soils it is complexed by organic matter (SIMS, 1986; ZHANG et al., 1997). At more neutral pH levels, Mn can precipitate in hydroxylated forms (Mn(OH)n).



Figure16 - Percent Mn distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Ferralsol



Figure 17 - Percent Mn distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Cambisol



Figure 18 - Percent Mn distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Arenosol

4.3.3.2.4 Zinc

Zn in the organic fraction decreased with decreasing soil pH (Figures 19, 20 and 21), which is explained by the fact that lower pH increases exchangeable forms of Zn and decreases Zn content in the organic fraction (NASCIMENTO et al., 2002; SHUMAN, 1986; SIMS, 1986). Lower soil pH also leads to the solubilization of Zn hydroxides, increasing the exchangeable contents of the element (Figures 19, 20, and 21 and Tables 10, 11, and 12). Sims (1986) reported that the exchangeable forms of Mn and Zn predominated at pH of <5.2, while at higher pH

levels after liming forms bound to organic matter and oxides predominated. In our study, we observed increased levels of Zn bound to the organic fraction in soils treated with tannery sludge, which increased their pH. In weakly acidic conditions of that kind, Zn can be co-precipitated together with Fe and Al oxides (ROSS, 1994), form weakly soluble complexes with organic matter (ADRIANO, 1986), or be strongly retained by processes of specific adsorption (KALBASI; RACZ; LOEWENRUDGERS, 1978; CUNHA; CAMARGO; KINJO, 1994). At pH values closer to neutral, Zn can be adsorbed to Fe and Al oxides and/or be precipitated in hydroxylated forms (Zn(OH)n) (SIMS; PATRICK, 1978).



Figura 19 - Percent Zn distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Ferralsol.



Figura 20 - Percent Zn distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Cambisol



Figura 21 - Percent Zn distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Arenosol

4.3.3.2.5 Lead

In all Ferralsol samples total Pb contents exceeded Cetesb's soil quality reference value (VRQ; 17 mg kg⁻¹) but were below the prevention value (72 mg kg⁻¹). In the other soils these values were below the VRQ. In contrast to Nogueirol (2009), who studied waste-polluted soils and found that most Pb was associated with the residual fraction, in our study the residual was the least important fraction for the metal (Figures 22, 23, and 24). Pb mostly occurred in the

organic fraction (up to 63% of total Pb content) in the sludge-treated samples (Figures 22b and 23b). In the Arenosol samples, exchangeable Pb content (F1) declined with increasing soil pH (Table 13 and Figure 24b).

Soil samples treated with CrCl₃.6H₂O showed higher levels of exchangeable Pb, which accounted for 29% of all Pb at the highest salt dose (Figura 22a) in the Ferralsols and for 44% in the Cambisols (Figure 23a). These results can be attributed to variation in pH. Borges and Coutinho (2004) studied the effect of pH and the application of biossolids on the distribution of metals in a Latossolo Vermelho cultivated with maize, and found that higher pH decreased metal concentrations in the exchangeable fraction and increased them in the organic fraction, indicating that at higher soil pH Pb is more strongly retained by OM. In fact, higher levels of pH decreased metal availability via precipitation reactions and by increasing adsorption to variable-charged colloids (SHUMAN, 1998). Pb is considered to be one of the least mobile metals in soils, since it can be complexed by organic matter, adsorbed to silicated oxides and minerals, or precipitated as carbonate, hydroxide, or phosphate in high-pH conditions (McBRIDE, 1994). No variation between treatments was observed for the Arenosols.



Figura 22 - Percent Pb distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Ferralsol



Figura 23 - Percent Pb distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Cambisol



Figura 24 - Percent Pb distributed in the fractions from the sequential extraction of each treatment: L0 (control), L1 (150 mg kg⁻¹ Cr), L2 (150 mg kg⁻¹ Cr), L3 (2000 mg kg⁻¹ Cr), L3 (4000 mg kg⁻¹ Cr), L4 (6000 mg kg⁻¹ Cr), added as a salt (a) and sludge (b) to Arenosol

4.3.3.2 Spectral response of Cr in soils

Figures 25 to 30 show the spectral variation in the vis-NIR e mid-IR ranges as a function of pseudo-total Cr concentrations. For all soils, absorptions bands from 400-2450 nm were observed in the vis-NIR range (original reflectance curve). Similar to metals of Experiment 1, a reduction of the reflectance intensity with high levels of Cr was observed (Figures 25, 27 and 29). The spectra differences between two levels of Cr (from 207 to 4079 mg kg⁻¹) in Ferralsol (Figure 25a) and Arenosols (from 13 and 162 mg kg⁻¹) (Figure 29a) were very small.

We tried to enhance these weak absorptions features with the CR of spectra (Figure 25b, 27b and 29b). It can be seen that the most of the strong spectral absorption peaks for all soils studied were found at approximately 480-530, 800-900, 1400, 1900 and 2200 nm. The peaks at 1400, 1900, and 2200 nm are known to arise mainly from the OH of water molecules, whereas lattice OH in minerals and iron has a spectral assignment near 500 and 900 nm (BEN-DOR et al., 1999). We used the absorption depth of these bands to correlate to pseudo-total heavy metals concentrations (Table 16). In the mid-IR range many strong absorption peaks were observed. We selected the peaks at around 3690 - 3600 cm⁻¹, 2930-2840 cm⁻¹, 1640 cm⁻¹ and 1157 cm⁻¹ to make this correlation. Characteristics absorptions peaks at 2930–2850 cm⁻¹ can be related to the aliphatic C-H vibration (HABERHAUER et al., 1998; LEIFELD, 2006). Carboxyl C, hydroxylic C-O-H or aromatic C-H, and C = C vibrations probably form the spectral peaks at wavenumbers less than 1500 cm⁻¹ (RUMPEL et al., 2001; SOLOMON et al., 2005; BORNEMANN et al., 2010). The ranges 3690-3600 cm⁻¹ and 1640 cm⁻¹ are related with clay minerals (Table 6).

Similar peaks were observed for samples treated with tannery sludge. In the mid-IR range the variation of the intensity of reflectance between the different rates were similar to those obtained for CrCl₃.6H₂O contaminations (Figures 26, 28, 30). However, in the vis-NIR range the albedo for Ferralsol were higher in samples treated with tannery sludge than with CrCl₃.6H₂O (Figures 25a and 26a). Generally the vis-NIR spectrum was flattened in higher organic matter concentrations, as observed in samples treated with sludge (Figures 26a, 28a and 30a), in accordance with Madeira Neto (1993). We also observed more clearly the separation between the soil spectral curves according to Cr concentrations of samples with this treatment (Figures 26a and 28a).These differences were confirmed by the scores of the principal component analysis of these data (Figure 32).

Correlation analysis between the depths (1-CR) and Cr concentrations are confirmed with the graphs of the mean spectra (Figures 25 to 30). Cr concentration is negatively correlated with soil reflectance and the depths at around 500, 800-920 and 2200 suggests Cr sorption by clay size minerals assemblages as the mechanism by which to predict spectrally featureless Cr in soils.

	vis-NIR data									
	480-520	830-920	1400	1900-2000	2200	Cr	Pb	Zn	Fe	Mn
480-520	1.00									
830-920	0.95 **	1.00								
1400.00	-0.21	-0.13	1.00							
1900-2000	-0.53 **	-0.48 **	0.58 **	1.00						
2200.00	-0.07	-0.02	0.93 **	0.35	1.00					
Cr	-0.48 *	-0.50 *	0.46 *	0.51 *	* -0.52 *	1.00				
Pb	-0.74 **	-0.83 **	0.09	0.38	-0.09	-0.02	1.00			
Zn	0.08	-0.20	0.85 **	0.47 *	-0.83 **	* 0.14	0.31	1.00		
Fe	-0.74 **	-0.85 **	0.02	0.36	-0.02	0.75 **	0.52 *	0.35	1.00	
Mn	-0.19	-0.09	0.95 **	0.47 *	-0.94 **	* 0.40 *	-0.09	0.88	** -0.03	1.00
	mid-IR data									
	3690-3600	2930-2840	1640	1157	Cr	Pb	Zn	Fe	Mn	
3690-3600	1.00									
2930-2840	0.74	1.00								
1640	0.21	0.63 **	1.00							
1157	0.98	0.75 **	0.25	1.00						
Cr	0.45 *	0.62 **	0.75 **	-0.26	1.00					
Pb	0.27	0.44 *	0.43 *	-0.86 *	* -0.02	1.00				
Zn	0.91 **	0.56 **	0.05	-0.32	0.14	0.31	1.00			
Fe	0.36	0.52 **	-0.49 **	-0.37	0.75 **	* 0.52 *	0.35	1.00		
Mn	0.86 **	0.41 *	0.21	-0.80 *	* 0.40 *	-0.09	0.88 **	* -0.03	1.00	

Table 6 - Correlation matrix for relationships between heavy metals (pseudo-total contents/ mg kg⁻¹) contents evaluated at Experiment II and band depths (vis-NIR) and absorbance (mid-IR) at specific wavelengths





Figure 25 - Reflectance spectra of Ferralsols artificially contaminated with CrCl₃.6H₂O with different contamination levels of Cr concentrations (a); vis-NIR continuum removed spectra (b); spectral parameters vis-NIR (c); mid-IR reflectance (d); mid-IR absorbance (e); spectral parameter mid-IR (f)



Wavelength, cm⁻¹ Figure 26- Reflectance spectra of Ferralsols artificially contaminated with tannery sludge with different contamination levels of Cr concentrations (a); continuum removed spectra (b); spectral parameters vis-NIR (c); mid-IR reflectance (d); mid-IR absorbance (e); spectral parameter mid-IR (f).





Figure 27 - Reflectance spectra of Cambisols artificially contaminated with CrCl₃.6H₂O with different contamination levels of Cr concentrations (a); continuum removed spectra (b); spectral parameters vis-NIR (c); mid-IR reflectance (d); mid-IR absorbance (e); spectral parameter mid-IR (f). Variations in spectral absorption features showed an association with heavy metals



Figure 28 - Reflectance spectra of Cambisols artificially contaminated with tannery sludge with different contamination levels of Cr concentrations (a); continuum removed spectra (b); spectral parameters to be evaluated (c); mid-IR reflectance (d); mid-IR absorbance (e); spectral parameter mid-IR (f). Variations in spectral absorption features showed an association with heavy metals



Figure 29 - Reflectance spectra of Arenosols artificially contaminated with CrCl₃.6H₂O with different contamination levels of Cr concentrations (a); continuum removed spectra (b); spectral parameters to be evaluated (c); mid-IR reflectance (d); mid-IR absorbance (e); spectral parameter mid-IR (f).Variations in spectral absorption features showed an association with heavy metals

-1.0

400

⁻⁻13 mg kg⁻¹

4000 3600 3200 2800 2400 2000 1600 1200 800 400

Wavelength, cm⁻¹

3600

3200

Wavelength, cm⁻¹

0

-1

4000 3600 3200 2800 2400 2000 1600 1200 800

Wavelength, cm⁻¹



Figure 30 - Reflectance spectra of Arenosols artificially contaminated with tannery sludge with different contamination levels of Cr concentrations (a); vis-NIR continnum removed spectra (b); spectral parameters vis-NIR(c); mid-IR reflectance (d); mid-IR absorbance (e); spectral parameter mid-IR (f). Variations in spectral absorption features showed an association with heavy metals

4.3.3.3 Principal component analysis

As in Experiment 1, principal components analysis of the spectral data effectively distinguished between soils, confirming that the chemical and mineralogical profiles of the Ferralsols, Cambisols, and Arenosols resulted in different spectral signatures (Figure 31) after pollution, in agreement with Bellinaso et al. (2010). The PC-1 and PC-2 loadings of mid-IR showed that wavelengths at 3700-3500, 2400, 2000 and 1200 contributed more to the PC's, which agrees with Siebielec et al. (2004) and Janik et al. (2009). PC-1 accounted for 86% of the spectral variation in the full data set and was characterized by peaks corresponding to kaolinite (3695-3620 cm⁻¹) and quartz (negative peaks below 2100 cm⁻¹). The PC-1 and PC-2 loadings of vis-NIR indicated that bands around 700-900 nm and 1900 nm made a significant contribution to the PC's. The CR results emphasized the importance of these bands on the PC's (Figure 31). Absorptions in the visible region were associated with iron-containing minerals (JANIK et al., 2009).

Most soils polluted with tannery sludge showed different spectral signatures in the vis-NIR region when compared to those treated with CrCl₃.6H₂O, as shown by a scatterplot of PCA results (Figure 32a). However, this was not the case for the mid-IR data (Figure 32b). According to Reeves et al. (2005), much of the information in the mid-IR soil spectra is derived from a combination of organic and inorganic materials, while information in the vis-NIR spectra is largely based on CH, OH, and NH groups found in organics (REEVES et al., 2005). The results of our study show that while the mineralogical characteristics of soils has a strong influence on soil reflectance (DALMOLIN, 2002; DEMATTÊ; EPIPHANIO; FORMAGGIO, 2003), the organic matter play a more important role in determining their spectral signatures and can mask the clay minerals absorptions for example, especially in SOC high concentrations. Here, it should be clarified that it does not mean that mineralogical characteristics does not have any effect on the relationship between soil spectra and heavy metals.



Figure 31- PCA results of spectra of soil samples PC-1-PC-2 score plot and loadings of the first two PC's of continnum-removal of vis-NIR data (a), vis-NIR reflectance (b) and mid-IR reflectance (c)



Figure 32 - PCA results of spectra of soil samples PC-1-PC-2 score plot and loadings of the first two PC's of vis-NIR data (a) and mid-IR reflectance (b)

4.3.3.4 Vis-NIR and mid-IR spectroscopy calibrations

Prior to any model development the role data (sludge and CrCl₃.6H₂O treatments) set was randomly divided into a calibration set (CS) with 63 samples and a validation set (VS) with 27 samples, including all soil types and metals levels to ensure independence between CS and VS. Table 17 presents a descriptive analysis of the two data sets. We observed high values of standard deviation, especially for pseudo-total metals contents of Cr and Fe. These elements are present in very high concentrations.

Calibrations produced for Cr, Fe, Mn, Zn and Pb for each fraction (sequential extraction) using vis-NIR and mid-IR spectroscopy were shown on figures 33, 34, 35, 36 and 37. We observed that the calibration performance with vis-NIR data performed slightly better than those with mid-IR, except for Cr. This fact disagrees with some researches comparing mid-IR and NIRS on the same samples that have demonstrated that mid-IR generally outperforms NIR in the analysis of soils (e.g. SIEBIELEC et al., 2004) but in these studies almost efforts have concentrated on C and N fractions. However, there are others reports in literature which state that NIR performs better than MIR (e.g. VAN GROENIGEN et al., 2003).

Properties	Min	Max	Mean	SD	М	lin	Max	Mean	SD
	(Calibration	data set				Validation	data set	
рН	2.1	7.4	4.7	1.8	2	.0	7.7	4.7	1.9
P, mg kg ⁻¹	2.0	12.0	3.5	2.9	2	.0	12.0	3.4	2.9
Ca, $\text{mmol}_{c} \text{dm}^{-3}$	4.0	306.0	72.0	90.0	3	.0	333.0	76.1	99.0
Mg, $mmol_c dm^{-3}$	2.0	158.0	42.3	53.4	2	.0	158.0	39.1	50.2
K, $\text{mmol}_{c} \text{ dm}^{-3}$	0.5	18.3	3.4	4.4	0	.5	6.7	2.5	2.2
Na, $\text{mmol}_{c} \text{ dm}^{-3}$	0.5	195.5	36.7	58.2	0	.4	200.0	40.3	62.9
H+Al, mmol _c dm ⁻³	8.0	996.0	193.0	317.0	8	.0	896.0	182.0	257.0
CEC, mmol _c dm ⁻³	56.2	1055.0	347.0	311.0	56	5.7	910.0	340.0	251.0
BS, %	2.0	98.0	49.5	39.2	1	.5	98.5	46.7	38.9
Cr, mg kg ⁻¹	11.5	6884.0	2600.0	2567.0		11.5	6774.0	2735.0	2475.0
Fe, mg kg ⁻¹	4965.0	81500.0	28540.0	32376.0	48	836.5	82600.0	32693.0	33619.0
Mn, mg kg ⁻¹	22.6	675.5	295.0	250.1		20.6	689.9	309.5	244.0
Pb, mg kg ⁻¹	15.0	34.0	19.7	7.3		15.0	34.1	19.7	6.4
Zn, mg kg ⁻¹	10.3	33.4	22.9	8.7		10.5	33.7	23.8	8.6

Table 17 - Descriptive statistics for soil attributes contents in the calibration and validation data sets

* Cr, Fe, Mn, Pb and Zn refer to pseudo-total contents

In our study the fractionation scheme is diverse for all the metals. The most significant differences in accuracy of prediction between mid-IR and vis-NIR for Cr were in fractions 2 (F2) and 4 (F4) in which RMSEs decrease 5.44 and 3.57 times, respectively. For Fe, Pb, Mn and Zn, the vis-NIR data showed models with higher accuracy. In this case, the differences in accuracy of predictions between vis-NIR and mid-IR higher than 2 times were observed for Fe (F5), Mn (F3) and Pb (F2) (Figures 34, 35 and 36).

For pseudo-total contents of metals, an extremely wide range of concentration was present (Table 17) but the RMSE values of all calibrations were lower than the chemical

standard deviation (figures 33 - 37), especially for Fe. For meaningful interpretation of spectral prediction error it is important to observe the within-laboratory uncertainty (COHEN et al., 2007). Judging the suitability of spectral methods based on spectral accuracy alone ignores the laboratory error.

Calibrations for Cr, especially in fraction 2 (vis-NIR) had a tendency to underpredict higher contents (more than 1000 mg kg⁻¹) (Figure 33c) and overpredict lower contents (less than 250 mg kg⁻¹). The tendency for under and over prediction was also observed for Fe, Mn, Zn and Pb (Figures 34, 35, 36 and 37). In general, only Pb contents of residual fraction (F5) and Mn of exchangeable fraction were still not predicted satisfactorily using the mid-IR data (Figure 37f and 36b), because there was a low R² between measured (chemically determined) and predicted contents. The predicted models of exchangeable fractions (F1) for Pb, Zn and Cr extracted with 15 mL 0.1 mol L⁻¹ CaCl₂ performed better than the available contents extracted with DTPA in Experiment I.



Figure 33 - Cross-validation scatter plot of laboratory-measured data versus vis-NIR and mid-IR predictions obtained from partial least square regression of pseudo-total content of Cr (a), Cr (F1) (b), Cr (F2) (c); Cr (F3) (d); Cr (F4) (e) and Cr (F5) (f). v and m refer to vis-NIR and mid-IR data



Figure 34 - Cross-validation scatter plot of laboratory-measured data versus vis-NIR and mid-IR predictions obtained from partial least square regression of pseudo-total content of Fe (a), Fe (F1) (b), Fe (F2) (c); Fe (F3) (d); Fe (F4) (e) and Fe (F5) (f). $_v$ and $_m$ refer to vis-NIR and mid-IR data



Figure 35 - Cross-validation scatter plot of laboratory-measured data versus vis-NIR and mid-IR predictions obtained from partial least square regression of pseudo-total content of Mn (a), Mn (F1) (b), Mn (F2) (c); Mn (F3) (d); Mn (F4) (e) and Mn (F5) (f). v and m refer to vis-NIR and mid-IR data



Figure 36 - Cross-validation scatter plot of laboratory-measured data versus vis-NIR and mid-IR predictions obtained from partial least square regression of pseudo-total content of Zn (a), Zn (F1) (b), Zn (F2) (c); Zn (F3) (d); Zn (F4) (e) and Zn (F5) (f). v and m refer to vis-NIR and mid-IR data



Figure 37 - Cross-validation scatter plot of laboratory-measured data versus vis-NIR and mid-IR predictions obtained from partial least square regression of pseudo-total content of Pb (a), Pb (F1) (b), Pb (F2) (c); Pb (F3) (d); Pb (F4) (e) and Pb (F5) (f). v and m refer to vis-NIR and mid-IR data

The validation results of the predictions produced using the PLS (vis-NIR and mid-IR) method and an independent validation data set are summarized on table 18.

Metal	Fraction	Sensor data	R_v^2	RMSE _v	Correlation	Slope	PLS factors	RPD
	F1	vis-NIR	0.65	304.00	0.83	0.53	11	1.72
		mid-IR	0.59	329.00	0.86	0.53	12	1.59
	F2	vis-NIR	0.61	244.00	0.80	0.75	9	1.63
		mid-IR	0.72	199.00	0.85	0.81	8	2.00
	F3	vis-NIR	0.77	473.00	0.88	0.84	6	2.11
Cr mg kg	1	mid-IR	0.83	401.00	0.92	0.92	6	2.48
	F4	vis-NIR	0.76	220.00	0.88	0.84	4	2.10
		mid-IR	0.80	200.00	0.90	0.91	4	2.31
	F5	vis-NIR	0.85	289.00	0.93	1.00	9	2.65
		mid-IR	0.52	528.00	0.75	0.74	7	1.45
	pseudo-total	vis-NIR	0.86	921.00	0.93	0.94	10	2.69
		mid-IR	0.86	915.00	0.93	0.87	6	2.70
	F1	vis-NIR	0.91	1.70	0.97	1.10	10	3.53
		mid-IR	0.90	1.96	0.95	0.81	4	3.06
	F2	vis-NIR	0.91	0.63	0.96	0.85	8	3.46
		mid-IR	0.58	1.41	0.80	0.70	4	1.55
	F3	vis-NIR	0.89	1.20	0.95	1.02	8	3.00
Zn mg kg	1	mid-IR	0.90	1.06	0.95	0.89	5	3.40
	F4	vis-NIR	0.62	1.35	0.79	0.59	2	1.46
		mid-IR	0.66	1.12	0.81	0.68	3	1.76
	F5	vis-NIR	0.21	4.69	0.67	0.73	5	1.19
		mid-IR	0.10	5.10	0.54	0.48	6	1.09
	pseudo-total	vis-NIR	0.47	7.61	0.70	0.50	4	1.13
		mid-IR	0.40	6.90	0.77	0.60	3	1.25
	F1	vis-NIR	0.53	1.52	0.74	0.68	4	1.26
		mid-IR	0.50	1.20	0.86	0.60	3	1.60
	F2	vis-NIR	0.20	1.47	0.43	0.61	10	1.09
		mid-IR	0.35	1.47	0.69	0.84	10	1.09
	F3	vis-NIR	0.86	2.40	0.93	0.91	7	2.67
Pb mg kg	1	mid-IR	0.63	3.90	0.79	0.67	12	1.64
	F4	vis-NIR	0.20	2.96	0.14	0.13	10	0.71
		mid-IR	0.61	1.29	0.83	0.81	4	1.64
	F5	vis-NIR	0.55	1.40	0.75	0.65	10	1.00
		mid-IR	0.35	1.87	0.50	0.35	4	0.84
	pseudo-total	vis-NIR	0.20	7.64	0.53	0.42	7	0.84
		mid-IR	0.20	8.10	0.39	0.25	6	0.79

Table 18 - Summary statistics of validation results of calibrations for Cr, Zn, Pb, Fe, Mn using an independent validation dataset (continues)

Metal	Fraction	Sensor data	R_v^2	$RMSE_v$	Correlation	Slope	PLS factors	RPD
	F1	vis-NIR	0.51	75.30	0.8	0.38	10	1.45
		mid-IR	0.30	79.80	0.80	0.33	3	1.32
	F2	vis-NIR	0.26	95.30	0.76	1.01	11	1.16
		mid-IR	0.36	87.30	0.82	1.08	3	1.27
	F3	vis-NIR	0.74	12.83	0.86	0.75	10	1.75
Fe mg kg	1	mid-IR	0.70	12.36	0.83	0.73	5	1.78
	F4	vis-NIR	0.55	3890.00	0.47	0.50	7	1.02
		mid-IR	0.50	3910.00	0.40	0.33	5	1.01
	F5	vis-NIR	0.4	17500.00	0.81	0.91	6	1.63
		mid-IR	0.30	21500.00	0.64	0.64	4	1.33
	pseudo-total	vis-NIR	0.98	3521.00	0.99	1.00	6	9.55
		mid-IR	0.33	3700.00	0.66	0.65	4	9.09
	F1	vis-NIR	0.87	46.54	0.95	1.11	9	2.91
		mid-IR	0.37	75.50	0.87	0.55	3	1.79
	F2	vis-NIR	0.73	3.43	0.87	0.86	9	2.31
		mid-IR	0.77	3.70	0.92	0.99	6	2.13
	F3	vis-NIR	0.91	30.52	0.96	0.98	12	3.41
Mn mg kg	g ⁻¹	mid-IR	0.50	74.80	0.74	0.69	3	1.39
	F4	vis-NIR	0.94	17.16	0.97	0.94	10	4.23
		mid-IR	0.85	28.34	0.93	0.90	4	2.56
	F5	vis-NIR	0.20	80.84	0.44	0.38	4	1.01
		mid-IR	0.10	79.80	0.48	0.41	5	1.03
	pseudo-total	vis-NIR	0.82	106.00	0.91	0.82	4	2.30
		mid-IR	0.55	90.00	0.97	0.90	3	2.71

Table 18 (continuation) - Summary statistics of validation results of calibrations for Cr, Zn, Pb, Fe, Mn using an independent validation dataset

It was possible to predict the pseudo-total contents of one metal (Cr) out of five with high precision with both sensors data (Table 18). Coefficients of determination for pseudototal Mn and Fe are also above 0.8 (vis-NIR).

Also, RPDs > 2 are indicative of very good models (KOOISTRA et al., 2001). Thus, the validation results for Cr (F3, F4 and F5), Zn (F1, F2 and F3), Pb (F3), Mn (F1, F3 and F4) gave R^{2} 's > 0.80 and RPDs between 2 and 4.23, which are considered good performances. The validation results for Cr (F1 and F2), Zn (F4), Pb (F3), Fe (F3) and Mn (F2) presented R^{2} 's between 0.6 and 0.8 and RPDs >1.7, which are also satisfactory. The others fractions of metals did not provide a significant prediction. These results showed that active soil components such as Fe oxides (related to F4) and organic matter (F3) allowed estimation of heavy metals with reflectance spectroscopy in accordance with Malley and Williams (1997), Kooistra et al. (2001) and Kemper and Sommer, (2002).

4.4 Conclusions

The available content of almost all metals studied, extracted by DTPA (pH 7), decreased over time, suggesting that metals were adsorbed to oxides, clay minerals, and/or soil organic matter. This adsorption regulates the concentration of ions and complexes in the soil solution, and plays an important role in its availability to the environment. The reflectance spectroscopy as a non destructive analytical method cannot be used to predict Cr, Zn and Pb extracted by DTPA (pH 7.0) accurately. However, it is important to highlight that the metals adsorption to soil constituents caused expressive changes in soil spectral curves, showing spectral differentiation between highly contaminated soil and soils that are relatively contaminant-free. However, the concentrations of metals below the agricultural intervention threshold (reported by Cetesb) do not show differences in the spectral curves. The metals were all negatively correlated with reflectance. The mid-IR spectra showed a larger number of features in comparison to vis-NIR. Such an approach although not useful for the exact quantification purposes, can be used to determine whether there is significant variability within a soil field.

The distribution of Cr, Fe, Mn, Zn and Pb species in the soils varied according to pH and CEC and the fractionation scheme is diverse for all the metals and soils studied. Generally, adding tannery sludge caused an increase in soil pH, which led to a decline in metals contents in the exchangeable fractions. It can be attributed to precipitation reactions and by increasing adsorption to variable-charged colloids. The soils treated with tannery sludge showed more different spectral signatures in the vis-NIR region than those treated with CrCl₃.6H₂O. However, this was not the case for the mid-IR data. We observed that the organic matter played a more important role in determining the soil spectral signatures than the mineralogical characteristics of soils, in high SOC concentrations.

For pseudo-total contents of metals, an extremely wide range of concentration was present and the RMSE values of all models were lower than the chemical standard deviation. It showed that although sequential extraction methods allow one to selectively measure the distribution of metals in soils, this method is not very precise. The results indicate that the Cr pseudo-total content can be predicted by spectroscopy reflectance with both sensors data. Fe and Mn also can be predicted accuratley by vis-NIR. The vis-NIR models outperformed the mid-IR. Besides these results, the vis-NIR instrument has less complicated sample and can be used directly in the field using portable spectrorradiometers. Thus it should be preferred over mid-IR.

References

ABREU, C.A.; ABREU, M.F.;ANDRADE, J.C. Determinação de cobre, ferro, manganês, zinco, cádmio, níquel e chumbo em solos usando a solução de DTPA em pH 7,3. In: RAIJ, B.van; ANDRADE, J.C.; CANTARELLA, H.;QUAGGIO, J.A.(Ed.).. Análise química para avaliação da fertilidade de solos tropicais. Campinas:Instituto Agronômico, 2001. p. 240-250.

ABREU, C.A.; RAIJ, B. VAN; ABREU, M.F.; GONZÁLEZ, A.P. Routine soil testing to monitor heavy metals and boron. **Scientia Agricola**, Piracicaba, v. 62/6, p. 564-571, 2005.

ADRIANO, D.C. **Trace elements in terrestrial environment**. New York: Springer Verlag, 1986. 533p.

ALLEONI, L.R.F.; IGLESIAS, C.S.M.; MELLO, S.C.; CAMARGO, O.A.; CASAGRANDE, J.C. & LAVORENTI, N.A. Atributos do solo relacionados à adsorção de cádmio e cobre em solos tropicais. Acta Scientia Agronomica, v27, p. 729-737, 2005.

ARAÚJO, S.R. Sensoriamento remoto laboratorial na detecção de alterações químicas no solo pela aplicação de corretivos. 2008. 130p. Dissertação (Mestrado em Solos e Nutrição de Plantas) – Escola Superior de agricultura "Luiz de Queiroz", Universidade de São Paulo, Piracicaba, 2008.

BELLINASO H.; DEMATTÊ J.A.M.; ARAÚJO S.R.A. Soil spectral library and its use in soil classification. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 34, p. 861-870, 2010.

BEN-DOR, E.; IRONS, J.R.; EPEMA, G. Soil Reflectance. In: RENCZ, A.N. (Ed.). **REMOTE SENSING for the Earth Sciences**. Canada: John Wiley, 1999. cap. 3, p. 111-188.

BEN-DOR, E.; HELLER, D.; CHUDNOVSKY, A. A novel method of classifying soil profiles in the field using optical means. **Soil Science Society of American Journal**, Madison, v. 72, p. 1113-1123, 2008.

BRAY, J.G.P.;ROSSEL, R.V.;MCBRATNEY, A.B. Diagnostic screening of urban soil contaminants using diffuse reflectance spectroscopy. **Australian Journal Soil Research**, Melbourne, v. 47, p. 433–442, 2009

BROWN, D.J.; SHEPHERD, K.D.; WALSH, M.G.; DEWANE MAYS, M.; REINSCH, T.G. Global soil characterization with Vis-NIR diffuse reflectance spectroscopy. Geoderma, Amsterdam, v. 132, p. 273-290, 2006.

BOWERS, S.A.; HANKS, J.R. Reflection of radiant energy from soil. **Soil Science**, Philadelphia, v. 100, n. 2, p. 130-138, 1965.

CAMARGO, M.S.; ANJOS, A.R.M.; ROSSI, C.; MALAVOLTA, E. Adubação fosfatada e metais pesados em Latossolo cultivado com arroz. **Scientia Agricola**, Piracicaba, v. 57, p. 513-518, 2000.

CHANG, A.C.; PAGE, A.L.; WARNEKE, J.E.; GRGUREVIC, E. Sequencial extraction of soil heavy metals following a sludge application. **Journal Environmental Quality**, Stanford, v. 13, p. 33-39, 1984.

CHOE, E.; KIM, K.W.; BANG, S.; YON, I.H.; LEE, K.Y. Quantitative analysis and mappinp of heavy metals in an abandoned Au-Ag mine area using Nir spectroscopy. **Environmental Geology**, New York, 2008.

COHEN, M.; PRENGER, J.P.; DEBRUSK, W.F. Visible-near infrared reflectance spectroscopy for rapid, non-destructive assessment of wetland soil quality. **Journal of Environmental Quality**, Stanford, v. 34, p.1422–1434, 2005.

COMPANHIA DE TECNOLOGIA DE SANEAMENTO AMBIENTAL - CETESB. Valores orientadores para solos e águas subterrâneas no Estado de São Paulo. Decisão da diretoria No 195-2005- E, de 23 de nov. de 2005. 4p.

Conselho Nacional do Meio Ambiente - CONAMA, Ministério do Meio Ambiente, 375/2006.

CUNHA, R.C.A.; CAMARGO, O.A.; KINJO, T. Retenção de zinco em solos paulistas. **Bragantia**, Campinas, v. 53, p. 291-301, 1994.

DALMOLIN, R.S.D. **Matéria orgânica e características físicas, químicas, mineralógicas e espectrais de Latossolo de diferentes ambientes**. 2002. 151 p. Tese (Doutorado em Ciência do Solo) – Universidade Federal do Rio Grande do Sul, Porto Alegre, 2002.

DALMOLIN, R.S.D.; GONÇALVES, C.N.; KLAMT, E. ; DICK, D.P. Relação entre os constituintes do solo e seu comportamento espectral. **Ciência Rural**, Santa Maria, v. 35, n. 2. p. 481-489, 2005..

DEMATTÊ, J.A.M. Characterization and discrimination of soils by their reflected electromagnetic energy.**Pesquisa Agropecuária Brasileira**, Brasília, v. 37, n. 10, p. 1445-1458, 2002.

DEMATTÊ, J.A.M; GENÚ, A.; FIORIO, P. R.; ORTIZ, J. L.; MAZZA, J. A.; LEONARDO, H. C. L. Comparação entre mapas de solos obtidos por sensoriamento remoto espectral e pelo método convencional. **Pesquisa Agropecuária Brasileira**, Brasília, v. 39, n. 12, p. 1219-1229, 2004a.

DEMATTÊ, J.A.M.; CAMPOS, R.C.; ALVES, M.C.; FIORIO, P. R.; NANNI, M.R. Visible-NIR reflectance: a new approach on soil evaluation. **Geoderma**, Amsterdan, v. 121, p. 95-112, 2004.

DIXON J.B.; SCHULZE, D.G. **Soil mineralogy with environmental applications.** Madison: Soil Science Society of America, 2002. 866p.

DUNN, B.W.; BEECHER, H.G.; BATTEN, G.D.; CIAVARELLA, S. The potential of nearinfrared reflectance spectroscopy for soil analysis – a case study from the Riverine Plain of south-eastern Australia. **Australian Journal of Experimental Agriculture**, Melbourne, v. 42, p. 607-614, 2002. FORMAGGIO, A.R.; EPIPHANIO, J.C.N.; VALERIANO, M.M.; OLIVEIRA, J.B. Comportamento espectral (450-2.450 nm) de solos tropicais de São Paulo. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 20, p. 467-474, 1996.

GALVÃO, L.S.; VITORELLO, I.; PARADELLA, W.R. Spectroradiometric discrimination of laterites with principal components analysis and additive modeling. **Remote Sensing of Environment**, New York, v. 53, p. 70-75, 1995.

GUILHERME, L.R.G. Poluição do solo e qualidade ambiental. In: CONGRESSO BRASILEIRO DE CIÊNCIAS DO SOLO, 1999.Brasília-DF. **Anais...** Brasília-DF, 1999. p 275.

ISLAM, K.; SINGH, B.; McBRATNEY, A. Simultaneuous estimation of several properties by ultra-violet, visible, and near-infrared reflectance spectroscopy. **Australian Journal of Soil Research**, Sidney, v. 41, p. 1101-1114, 2003.

JANIK, L.J.; SKJEMSTAD, J. O.; SHEPHERD, K. D.; SPOUNCER, L. R. The prediction of soil carbon fractions using mid-infrared-partial least square analysis. **Australian Journal of Soil Research**, Collingwood, v. 45, p. 73-81, 2007.

JANIK, L.J.; FORRESTER, S.T.; RAWSON, A. The prediction of soil chemical and physical properties from mid-infrared spectroscopy and combined partial least-square regression and neural networks (PLS-NN) analysis. **Chemometrics and Intelligent Laboratory Systems**, Amsterdam, v. 97, p. 179-188, 2009.

JARMER, T.; VOHLAND, M.; LILIENTHAL, H.; SCHNUG, E. Estimation of some chemical properties of an agricultural soil by spectroradiometric measurements. **Pedosphere**, Amsterdam, v. 18, n. 2, p. 163-170, 2008.

KABATA-PENDIAS, A.; MUKHERJEE, A.B. **Trace elements from soil to human**. Berlin:Springer, 2007. 576p.

KABATA-PENDIAS, A.; PENDIAS, H. **Trace elements in soils and plants**. 3rd .ed. Boca Raton:CRC Press, 2001. 413p.

KEMPER, T.; SOMMER, S. Estimate of heavy metal contamination in soils after a mining accident using reflectance spectroscopy. **Environmetal Science Technology**, v. 36, p. 2742–2747, 2002

KOOISTRA, L.; WEHRENS, R.;LEUVEN, R.S.E.W.;BUYDENS, L.M.C. Possibilities of visible-near-infrared spectroscopy for the assessment of soil contamination in river floodplains. **Analytical Chemistry Acta**, New York, v. 446, p. 97–105, 2001.

LIMA, M.C.; GIACOMELLI, M.B.O.; STÜPP, V.; ROBERGE, F.D. Epeciação de cobre e chumbo em sedimento do rio tubarão (sc) pelo método Tessier. **Quimica Nova**, São Paulo, v. 24, p. 734-742, 2001.

McBRIDE, M.B. Reactions controlling heavy metal solubility in soils. Advances in Soil Science, New York, v. 10, p. 1-56, 1989.
__. Environmental chemistry of soils. New Yok: Oxford University Press, 1994. 406p.

MADEIRA NETTO, J.S. Spectral reflectance properties of soils. **Photogrametric Interpretation**, v.34, p.59-70, 1996.

MADEIRA NETTO, J.S.; BÉDIDI, A.; CERVELLE, B.; FLAY, N. Spectral (MIR) Determination of Kaolinite and Gibbsite Contents in Lateritic Soils. **Comptes Rendus de l'Àcademie des Science,** Serie Ila, Paris, v. 321, p. 119-128, 1995.

MADEJOVÁ, J.; KOMADEL, P. Baseline studies of the clay minerals society source clays: infrared methods. **Clay and Clay Minerals**, Chantilly, v. 49, n. 5, p. 410-432, 2001.

MALAVOLTA, E. Fertilizantes e seu impacto ambiental: micronutrientes e metais pesados, mitos, mistificações e fatos. São Paulo: Produquímica, 1994. 153p.

MALLEY, D.F.; YESMIM, I.; EDWARDS, W.D. Application of near-infrared spectroscopy in analysis of soil mineral nutrients. **Communications in Soil Science and Plant Analysis**, New York, v.30, p. 999-1012, 1999.

MARTINES, A.M.; NOGUEIRA, M.A.; SANTOS, C.A.; CANTARELLA, H.; SOUSA, J.P., CARSODO, E.J.B.N. Ammonia volatilization in soil treated with tannery sludge. **Bioresourse Technology,**New York, v. 101, p. 4690-4696, 2009.

NASCIMENTO, C.W.A.; FONTES, R.L.F.; MELÍCIO, A. Copper availability as related to soil copper fractions in oxisols under liming. **Scientia Agricola**, Piracicaba, v. 60, p. 167-173, 2003.

NGUYEN, T.T.; JANIK, L.J.; RAUPACH, M. Diffuse reflectance infrared fourier treansform (DRIFT) spectroscopy in soil studies. **Australian Journal of Soil Research,** Collingwood, v. 29, p. 49-67, 1991.

POST, J. L.;NOBLE, P.N. The near-infrared combination band frequencies of dioctahedral smectites, micas, and illites. **Clays Clay Minerals**, New York, v.41, p.639–644, 1993.

RAIJ, B. van.; ANDRADE, J.C.; CANTARELA, H.; QUAGGIO, J.A. Análise química para avaliação de solos tropicais. Campinas: IAC, 2001. 285p.

SAS Institute. 2007. JMP Version 7.0.1, SAS Institute, Cary, NC.

SASTRE, I.; VICENTE, M.A.; LOBO, M.C. Behaviour of cadium and nickel in a soil amended with sewage sludge. Land Degradation and Development, New York, v. 12, p. 27-33, 2001.

SHEPHERD, K.D.; WALSH, M.G. Development of reflectance spectral libraries for characterization of soil properties. **Soil Science Society of America Journal**, Madison, v. 66, p. 988–998, 2002.

SHUMAN, L.M. Separating soil iron and manganese-oxide fractions form microelement analysis. **Soil Science Society of America Journal**, Madison, v. 46, p. 1099-1102, 1982.

_____. Effect of ionic strength and anions on zinc adsorption by two soils. **Soil Science Society of America Journal**, Madison, v.50, p.1438-1442, 1986.

_____. Effect of organic waste amendments on cadmium and lead in soil fractions of two soils.**Communications in Soil Science and Plant Analysis**, New York, v. 29, p. 2939-2952, 1998.

SIEBIELEC, G.; MCCARTY, G.W.; STUCZYNSKI, T.I.;REEVES, J.B. III. Near- and midinfrared diffuse reflectance spectroscopy for measuring soil metal content. **Journal of Enviromental Quality**, New York v. 33, p. 2056–2069, 2004.

SILVA; C.A.; BERNARDI, A.C.C.; VAN RAIJ, B. **Infra-estrutura e qualidade das análises de solo realizadas em laboratórios de fertilidade do Nordeste participantes do PAQLF**. Rio de Janeiro: EMBRAPA, 2001. 4p. (Circular Técnica, 11)

SILVEIRA, M.L.A.; ALLEONI, L.R.F; O'CONNOR, G.A.; CHANG, A.C. Heavy metal sequential extraction methods - A modification for tropical soils. **Chemosphere**, Oxford, v. 64, p. 1929-1938, 2006.

SIMS, J.T. Soil pH effects on the distribution and plant availability of manganese, copper and zinc. **Soil Science Society of America Journal**, Madison, v. 50, p. 367-373, 1986.

SIMS, J.T.; KLINE, J.S. Chemical fractionation plant uptake of heavy metals in soils amended with co-composted sewage sludge. **Journal Environmental Quality**, Madison, v. 20, p. 387- 395, 1991.

SPARKS, D.L. Environmental soil chemistry. San Diego: Academic Press, 1995. 267p.

SPOSITO, G. **The chemistry of soils**. 2nd .ed. New York:Oxford University Press, 2008. 330p.

STENBERG, B.; VISCARRA ROSSEL, R.A.; MOUAZEN, A.M.; WETTERLIND, J. Visible and near infrared spectroscopy in soil science. Advances in Agronomy, Amsterdam, v. 107, n. 107, p. 163-215, 2010.

STONER, E.R.; BAUMGARDNER, M.F. Characteristic variations in reflectance of surface soils. **Soil Science Society of American Journal**, Madison, v. 45, p. 1161-1165, 1981.

SCHWERTMANN, U. Die fraktionierte extraction der freien eisenoxyde in boden, ihre mineralogischen formen und ihre entste-hunsweisen. Zeitung Pflanzenernähr Düng BodenKontrolle, Berlin, v. 84, p. 194-204, 1959.

_____. Differezierung der eisenoxide des bodens durch photochemische extraktion mit saurer ammoniumoxalate-lösung. **Zeitung Pflanzenernähr Düng Bodenkontrolle**, Berlin, v.105, p. 194-202, 1964.

_____. The influence of aluminium on iron oxides: IX. Dissolution of Al-goethites in 6M HCl. **Clay Minerals**, Middlesex, v. 19, p. 9-19, 1984.

TERRA, F.S. **Espectroscopia de reflectância do visivel ao infravermelho médio aplicado aos estudos quantitativos e qualitativos de solos.** 2012. 198p. Tese (Doutorado na área de Solos e Nutrição de Plantas) – Escola Superior de Agricultura "Luiz de Queiroz", Universidade de São Paulo, Piracicaba, 2012.

TILLER, K.G. Heavy metals in soils and their environmental significance. Advances in soil Science, v. 9, p. 113-142, 1989.

VAN GROENIGEN, J. W.; MUTTERS, C. S.;HORWATH, W.R.;VAN KESSEL, C. NIR and DRIFT-MIR spectrometry of soils for predicting soil and crop parameters in a flooded field. **Plant Soil, Dordrecht,** v.250, p. 155–165, 2003.

VISCARRA ROSSEL, R.A.; WALVOORT, D.J.J.; McBRATNEY, A.B.; JANIK, L.J.; SKJEMSTAD, J.O. Visible, near infrared, mid infrared or combined diffuse reflectance spectroscopy for simultaneous assessment of various soil properties. **Geoderma**, Amsterdam, v.131, p.59–75, 2006.

VISCARRA ROSSEL, R.A. The Soil Spectroscopy Group and the development of a global soil spectral library. NIR News, v. 20, p. 17–18, 2009.

WU, Y.; CHEN, J.;JI, J.; TIAN, Q.;QIN, Z.; WU, X. Possibilities of reflectance spectroscopy for the assessment of contaminant elements in suburban soils. **Applied Geochemistry**, v.20, p. 1051-1059, 2005.

WU, Y.;CHEN, J.; JI, J.;GONG, P.;LIAO, Q.; TIAN, Q.;MA, H. A mechanism study of reflectance spectroscopy for investigating heavy metals in soils. **Soil Science Society of America Journal**, Madison, **v.** 71, p.918–926, 2007.

XIANG, H.F.; TANG, H.A.; YING, Q.H. Transformation and distribution of forms of zinc in acid, neutral and calcareous soils of China. **Geoderma**, Amsterdam, v. 66, p. 121-135, 1995.

ZHANG, T.; SHAN, X.; FULIANG, L. Comparison of two sequential extraction procedures for speciation analysis of metals in soils and plant availability. **Communications of Soil Science and Plant Analysis**, New York, v. 29, p. 1023-1034, 1998.