UNIVERSIDADE FEDERAL DE VIÇOSA

SOIL ORGANIC MATTER STOCK AND QUALITY IN AGROFORESTRY AND FULL SUN COFFEE SYSTEMS

Francisco Alisson da Silva Xavier

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Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Solos e Nutrição de Plantas, para obtenção do título de *Doctor Scientiae.*

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APROVADA: 26 de junho de 2009.

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Dedico

À minha amada esposa Hélida Colares

pelo seu amor, carinho e paciência

durante esta caminhada.

Ofereço

Aos meus pais, Edilson e Lúcia, e irmãs,

Aline e Alice, que incondicionalmente me

apoiaram até aqui.

AGRADECIMENTOS

À Deus pela vida e por todas as coisas que a mim foram concedidas.

À Universidade Federal de Viçosa, por meio do Departamento de Solos, pela oportunidade da realização do curso de doutorado.

À Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), ao Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) e à Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) pela concessão das bolsas de estudo no país e no exterior e pela concessão do fomento utilizado no custeio das ações de pesquisa.

Ao professor Eduardo de Sá Mendonça pela orientação durante a condução deste estudo e, sobretudo, pela amizade e confiança construídas ao longo desses anos.

Aos professores Irene Maria Cardoso e Ivo Jucksch pelas preciosas e fundamentais contribuições para a melhoria deste estudo, pelo apoio e amizade a mim oferecidos sem restrições.

Aos conselheiros Ivo Ribeiro da Silva e Paulo César de Lima e examinadores Carlos Alberto Silva e Felipe Vaz Andrade pelas valiosas sugestões ao trabalho.

Ao Centro de Edafología y Biología Aplicada del Segura (CEBAS/CSIC-España) por meio dos pesquisadores Asunción Roig e Miguel Angel Sanchez-Monedero; e ao Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS/CSIC-España) por meio dos pesquisadores Francisco Javier González Vila e José Antonio González-Pérez pela orientação e amizade durante o período de doutorado sanduíche na Espanha. À laboratorista Trinidad Verdejo (IRNAS) durante a condução das análises em Sevilla.

Ao Centro de Tecnologias Alternativas da Zona da Mata (CTA-ZM) pela experiência conduzida durante longos anos em apoio à agricultura familiar na Zona da Mata mineira. Aos agricultores(as) familiares em Araponga (Ângelo e Lurdes; Romualdo e Avanir) e Divino (Alexandre e Josiane; Juarez e Ester) pela concessão do campo experimental, pelo apoio durante a coleta do material de estudo e pela troca de experiência de vida.

Aos bolsistas de iniciação científica Everson Freitas de Almeida e Monique Regina Carvalho Freitas pelas duras horas de trabalho e pela amizade construída.

Aos amigos Helton Nonato e Edivânia Duarte pelo convívio com intensas trocas de saberes e pelo companheirismo constante.

Aos colegas do Laboratório de Matéria Orgânica do Solo: Juliana Vanir, Emanuelle Soares, Marino, Alysson Mafia, Rafael Polizel e Lucas Gomes pela amizade quer nas horas de trabalho, quer no lazer (churrascos, cafezinhos, etc) durante todos esses anos. Em especial, meus sinceros agradecimentos ao laboratorista Brás Júlio (UFV) pela constante ajuda e pela amizade já de longas datas.

Aos novos amigos feitos na Espanha: Nuria, Mari Luz, Keiji, Guita, Encarnación, Marcelo, Marlio (Balo), Neila, Emerson, Janaína, Carla, Fábio e Lacau que durante o doutorado sanduíche me deram apoio longe da família e dos amigos no Brasil.

Aos meus amigos de república: Antônio Marcos, Fernando Schettini, Augusto Lima e Michel Moreira pelas poucas más e muitas boas horas de convivência. À Dona Rita que cuidava de nós como mãe.

A todos os amigos da Igreja Presbiteriana de Viçosa cujos nomes não serão relacionados para evitar a injustiça do esquecimento. Porém, não poderia deixar de agradecer pelo apoio e amizade de: Samuel, Filipinho, Jony, Lênia, Zilbinho, Marô, Lis, Júlia, Marcinho, Fred, Jeanne, Paulinho, Maressa, André Campos, Laura, PG, Carla, Marlon, Michele, Mauro, Tereza, Lissânder, Kelen, Gustavo Veríssimo, Lilian, Mel e Artur

Ao povo brasileiro que, por meio dos impostos, financiam a educação pública no país.

Meus sinceros agradecimentos a todos aqueles que, direta ou indiretamente, contribuíram para a realização deste trabalho.

SUMÁRIO

RESUMO

XAVIER, Francisco Alisson da Silva, D.Sc., Universidade Federal de Viçosa, junho de 2009. **Estoque e qualidade da matéria orgânica do solo em áreas cultivadas com café sob sistemas agroflorestal e a pleno sol**. Orientador: Eduardo de Sá Mendonça. Co-orientadores: Irene Maria Cardoso, Ivo Ribeiro da Silva e Paulo César de Lima.

A restauração dos níveis de matéria orgânica do solo (MOS) é considerada um dos mais importantes fatores para o aumento da qualidade do solo. A avaliação das mudanças nos níveis da MOS em função do manejo é fundamental para identificar estratégias para o aumento da produtividade, para evitar a degradação do solo e diminuir a emissão dos gases que proporcionam o aumento do efeito estufa. No Brasil, o manejo do solo com o plantio direto tem sido amplamente difundido como uma alternativa para o aumento do sequestro de C no solo em diferentes ecossistemas. Entretanto, pouca atenção tem sido voltada para outros tipos de uso do solo que promovem a restauração da MOS. O cultivo do café sob sistema agroflorestal (SAF) tem sido considerado uma opção de manejo do solo ideal para solucionar parte dos problemas agrícolas na região da Zona da Mata mineira, uma vez que tais sistemas contribuem para a redução da erosão do solo, melhoram a ciclagem de nutrientes e aumentam os teores de MOS. Em 1995, uma equipe composta por agricultores familiares e pesquisadores, com o apoio do Centro de Tecnologias Alternativas da Zona da Mata (CTA-ZM) em parceria com a Universidade Federal de Viçosa, especialmente com Departamento de Solos, iniciaram um processo de experimentação participativa com o cultivo de café sob SAFs. O potencial dos SAFs para o aumento dos estoques de C, N e P no solo e o efeito desse tipo de manejo sobre a qualidade da MOS não estão completamente elucidados em agroecossistemas específicos na região da Zona da Mata mineira. As hipóteses gerais envolvidas no presente estudo consideram que: (i) devido ao constante aporte de resíduos orgânicos derivados dos componentes arbóreos, os SAFs favorecem o aumento dos estoques de C, N e P do solo e nos diferentes compartimentos da MOS em comparação ao sistema de cultivo à pleno sol (PSOL); e que (ii) a diversidade e qualidade dos resíduos orgânicos nos SAFs afetam as características químicas e estruturais da MOS refletindo as diferentes formas com que esta atua na ciclagem de nutrientes. Os objetivos gerais deste estudo foram: (i) quantificar os estoques de C orgânico, N e P do solo e em diferentes compartimentos da MOS em áreas com cultivo de café sob SAF e PSOL, e (ii) avaliar a influência da diversidade e qualidade dos resíduos orgânicos sobre as características químicas e estruturais das substâncias húmicas em ambos os sistemas. O estudo foi conduzido em três propriedades de agricultores familiares em sistemas de cultivo de café sob SAF e PSOL em áreas situadas nos municípios de Divino e Araponga na região da Zona da Mata de Minas Gerais. Áreas sob fragmentos de mata nativa (MN) foram também amostradas e utilizadas como referência da condição de equilíbrio do solo. Amostras de solo foram coletadas nas profundidades de 0-5, 5-10, 10-20 e 20-40 cm. O capítulo 1 apresenta a introdução geral enfatizando os principais problemas do estudo. No capítulo 2 avaliaram-se os estoques totais de C orgânico, N e P no solo e nas substâncias húmicas. Os estoques de C orgânico nas áreas cultivadas variaram de 1,36 a 3,92 kg m^{-2} entre os diferentes sítios de estudo. De modo geral, não houveram diferenças significativas nos estoques de C, N e P do solo entre os sistemas SAF e PSOL em todos as áreas avaliadas. Tal efeito parece estar relacionado com outras características físicas do solo. O cultivo do solo reduziu os estoques de C em relação à MN. Nos SAFs tal redução foi menor quando comparado aos sistemas PSOL. A adoção dos SAFs resultou no aumento do índice de manejo de C em todos os sítios avaliados, sugerindo a reabilitação dos níveis de SOM. O potencial dos SAFs para o aumento do estoque de C no solo depende das condições ambientais particulares de cada sítio de estudo. A dinâmica do C, N e P no solo foi diretamente influenciada pela qualidade dos resíduos orgânicos nos SAFs. O estudo da dinâmica do C e N em diferentes classes de agregados é apresentado no capítulo 3. O teor de C na fração 250–2000 μm representou a maior parte do C orgânico total do solo. Em Divino, o conteúdo de matéria orgânica particulada livre no SAF foi 2,8 e 2,0 vezes maior que no sistema PSOL nas camadas de 0-5 e 5-10, respectivamente. Em Araponga(I) tais proporções foram 1,3 e 1,8 vezes maior no SAF comparado ao PSOL. Em Divino e Araponga(I) os SAFs melhoraram a agregação do solo devido ao aumento dos macroagregados estáveis e promoveram o aumento da proteção de C e N nos microagregados formados no interior do macroagregados. Portanto, a estabilidade dos teores de C e N no solo à longo prazo nestes sítios parece estar muito associada com a continuidade do cultivo sob manejo agroflorestal. No capítulo 4 foi realizada a caracterização da distribuição das formas inorgânicas e orgânicas de P (Pi e Po) em diferentes compartimentos em áreas sob SAF e PSOL. Para tal, utilizou-se a técnica de fracionamento sequencial. A distribuição dos compartimentos de Pi e Po variaram entre os diferentes sítios estudados, sugerindo que a ciclo do P depende das características particulares de cada agroecossistema. A dinâmica das frações de P nos SAFs dependeu do compartimento orgânico de P. Em Divino e Araponga(I), os SAFs aumentaram o compartimento de Po mineralizável ($NaHCO_3$-Po + HClconc.-Po), o que favorece os processos biológicos na ciclagem de P no solo. Em Araponga(II), o SAF aumentou o compartimento de Po moderadamente lábil (NaOH-Po), sugerindo que a ciclagem de P ocorre a médio prazo, uma vez que este compartimento é considerado como fonte de P quando formas de maior labilidade são utilizadas prioritariamente. A caracterização química e estrutural dos ácidos húmicos (AH) e ácidos fúlvicos (AF) foi o enfoque do capítulo 5. AH e AF foram extraídos das camadas de 0-5 e 5-10 cm e caracterizados comparativamente utilizando técnicas químicas e espectroscópicas específicas, incluindo: análise elementar (teores de C, H, N and O), análise dos grupamentos funcionais, termogravimetria (TG), espectroscopia na região do infra-vermelho transformada de Fourier (FTIR) e resonância magnética nuclear do ^{13}C (^{13}C CP-MAS/NMR). Em superfície, SAF em Divino apresentou AH com maior razão atômica H/C e menor O/C em relação ao cultivo PSOL, indicando que o manejo agroflorestal favoreceu a formação de AH com menor grau de oxidação. A tendência dos resultados obtidos com a análise elementar foi comprovada com a termogravimetria. De modo geral, os espectros de FTIR dos AHs e AFs foram semelhantes entre os tipos de manejo SAF e PSOL. Em todos os sítios estudados, os espectros de ^{13}C NMR de AH foram dominados pelo grupamento *O*-alquil C seguido de grupos alquil-C. Os dados de ^{13}C CP-MAS/NMR confirmaram os resultados obtidos com as demais técnicas, indicando que AH extraído de solos sob SAFs em Divino e Araponga(I) apresentaram menor grau de humificação, enquanto que em Araponga(II) esta clara evidência não foi verificada. Em conclusão, as mudanças químicas na estrutura de AHs e AFs em função do uso do solo sob manejo agroflorestal dependem das características particulares do ambiente nas quais este tipo de manejo é implantado. Desta forma, o efeito do manejo agroflorestal sobre as características químico-estruturais das substâncias húmicas em comparação ao

manejo a pleno sol não deve ser generalizado. Finalmente, o capítulo 6 apresenta o resumo geral e as considerações finais, apontando alguns aspectos importantes quanto às necessidades de pesquisas futuras considerando o cultivo do solo sob manejo agroflorestal na Zona da Mata.

ABSTRACT

XAVIER, Francisco Alisson da Silva, D.Sc., Universidade Federal de Viçosa, June 2009. **Soil organic matter stock and quality in agroforestry and full sun coffee systems**. Advisor: Eduardo de Sá Mendonça. Co-advisors: Irene Maria Cardoso, Ivo Ribeiro da Silva and Paulo César de Lima.

Soil organic matter (SOM) restoring is considered a main goal in the enhancement of soil quality. The evaluation of changes in the SOM as a result of soil management practices is fundamental to identify strategies to increase agricultural production, avoiding soil degradation and decreasing the emission of greenhouse gases. In Brazil, no-tillage has been broadly spread as a management alternative to enhance soil C sequestration in different ecosystems. However, little attention has been paid to other options of land use in restoring SOM. Agroforestry-coffee systems have been considered a suitable option of soil management to solve part of the agricultural problems in the Atlantic Costal Rain Forest domain, since it can contribute to reduce soil erosion, enhance nutrient cycling and increase SOM levels. In 1995, a group of farmers and researchers, supported by the Centre for Alternative Technologies of the Zona da Mata (CTA-ZM) in partnership with the Universidade Federal de Viçosa, especially with the Department of Soils, started a participatory agroforestry-coffee system experimentation. The potential of agroforestry systems to increase soil C, N and P stocks and the effect of this type of land use on the SOM quality are not completely understood in specific agro-ecosystems in the Zona da Mata. We hypothesized that (i) due to the constant input of organic residues derived from tree-components, agroforestry-coffee favors the increase of C, N and P stocks in the soil and in different SOM pools in comparison to a full sun coffee system; and (ii) that the diversity and quality of the organic residues in the agroforestry systems affect the chemical and structural characteristics of the SOM, reflecting the different forms of its role in the nutrient cycling. Our general objectives were: (i) to measure the stocks of C, N and P in the soil and in different pools of the SOM in areas under agroforestry-coffee and full sun coffee systems, and (ii) to evaluate the effect of the diversity and quality of the organic residues on the chemical and structural characteristics of humic substances in both systems. The work was carried out in three smallholding coffee production areas under agroforestry-coffee (AGF) and full sun coffee (FSC) systems situated at the municipalities of Divino and Araponga in the Atlantic Coastal Forest biome in the state of Minas Gerais, Brazil. In each selected site, areas under natural forest fragments (NF) were sampled and used to represent the native or steady state condition of soil. Soil samples were collected from 0-5, 5-10, 10-20 and 20-40 cm depth intervals. Chapter 1 presents a general introduction of the thesis, emphasizing the main study problems. In chapter 2, we evaluated the total organic C, N and P stocks in the soil and humic substances. Soil organic C stocks in the coffee-cultivated lands varied from 1.36 to 3.92 kg m^{-2} among all evaluated sites. In general, there were no significant differences in the soil C, N and P stocks between AGF and FSC systems in all evaluated sites. Other soil physical characteristics are likely related to this behavior. In comparison to a reference area, AGF systems presented lower C stock reductions than FSC systems. The adoption of AGF management resulted in the increase in the carbon management index in all sites, suggesting the rehabilitation or enhancement of SOM levels. The potential of agroforestry management to increase soil C storage depended on system-characteristics in each particular environmental condition. The dynamics of C, N and P in the soil has been strongly influenced by the quality of organic residues in the agroforestry systems. The study of C and N dynamics in aggregate-sized fractions is presented in Chapter 3. The C concentration in the 250–2000 μm fraction represented the most part of soil organic carbon. In Divino, free particulate organic matter amounts in AGF system were 2.8 and 2.0 times greater than in FSC in the 0-5 and 5-10 cm layers, respectively. In Araponga(I), these proportions were 1.3- and 1.8-fold greater in AGF, compared to the FSC system. In Divino and Araponga(I), agroforestry systems enhanced soil aggregation by increasing the amount of more stable macroaggregates as well as promoting an increased protection of C and N in the microaggregates within macroaggregates. Therefore, the long-term stability of C and N in these sites probably depends upon the continuation of agroforestry-coffee cultivation. In Chapter 4, we characterized the soil inorganic and organic P in different pools in agroforestry-coffee and full-sun coffee systems by adopting the sequential fractionation technique. The distribution of inorganic and organic P (Pi and Po) pools varied among the different studied sites, suggesting that P cycling depends on the inherent characteristic of each agro-ecosystem. The dynamics of P fractions in agroforestry systems seems depend on the organic P pool. In Divino and Araponga(I), agroforestry increased the proportion of mineralizable Po ($NaHCO_3$-Po + HClconc.-Po), which can favor biological processes of the soil P cycling. In Araponga (II), the agroforestry system increased moderately the labile Po pool (NaOH-Po), suggesting that P cycling occurs in a medium-term scale, since such pool has been considered as a source of P when most labile P fractions are depleted. The chemical and structural characterization of soil humic acids (HA) and fulvic acids (FA) was the focus of the study in Chapter 5. Soil HA and FA extracted from 0-5 and 5-10 cm layers were characterized comparatively by using chemical and spectroscopic techniques including: elemental analysis (C, H, N and O contents), analysis of functional groups, thermogravimetry (TG), Fourier transform infra-red (FTIR) and solid-state ^{13}C nuclear magnetic resonance (^{13}C CP-MAS/NMR). At soil surface, the HA from AGF presented higher H/C and lower O/C ratio than the FSC system in Divino, suggesting that AGF management favored the genesis of HAs with less oxidative character. The patterns of elemental composition were supported by the findings of the TG analysis. The FTIR spectra of the HAs and FAs were quite similar when comparing the AGF and FSC systems. In all sites ^{13}C NMR assignment of HAs was dominated by the *O*-alkyl C resonance in both soil layers followed by a resonance line assigned to alkyl C. Solid-state ^{13}C NMR spectroscopy confirmed the data from the previous analysis in which HA from the AGF system in Divino and Araponga(I) are less humified than in the FSC system, whereas in Araponga(II) this clear evidence was not verified. Conclusively, the chemical changes on the structure of HA and FA, as influenced by agroforestry management depend on inherent characteristics of the environment in which it is developed. Thus, the effect of this type of land use on the structural characteristics of humic substances in comparison to a monoculture system should not be broadly generalized. Finally, Chapter 6 describes a summary of the thesis and final remarks, pointing out that some important future research is necessary for the agroforestry in the Zona da Mata.

CHAPTER 1

GENERAL INTRODUCTION

The research area and description of the problems

The expansion of coffee (*Coffea arabica* L.) in the Atlantic Coastal Rainforest, one of most important biomes of the Brazilian vegetation, placed Brazil on the top of the production and exportation of this commodity in the world. Nevertheless, the exploitation of coffee in this region occurred at expense of a severe environmental damage, which brought about the decline of soil quality. It is estimated that the Brazilian Atlantic forest occupies only 7.5% of the original cover (Dean, 1998).

In the Zona da Mata, a region situated in the Atlantic Coastal Rainforest domain, the scenario of land degradation raised as a consequence of deforestation and further exploitation of coffee (Valverde, 1958). In this region, coffee is normally cultivated on hills which have steep slopes, ranging from 20 to 45%. In this case, the risk of degradation due to erosion is accentuated, especially if adequate practices of soil management are not adopted, as usually occurs in areas under intensive cultivation. As a result of the decreased soil quality, farmers usually occupy new and more fertile sites while the old coffee fields are normally converted into pasture. Most agro-ecosystems in the Zona da Mata show a decreasing productivity, even in areas with large use of chemical fertilizers, due to the loss of several soil functions as a consequence of its quality decline.

Despite many environmental constraints in the Zona da Mata, smallholder production is vital for food production in the region (Ferrari, 1996). Regarding the low soil fertility (e.g. Oxisols) in the region and the poor financial condition of smallholding farmers to buy large amounts of chemical fertilizers, there is an urgent need for a debate aiming at the proposition of new and more sustainable alternatives for soil conservation and food production in the Zona da Mata.

Looking for solutions

In 1995, a group of farmers and researchers, supported by the Centre for Alternative Technologies of the Zona da Mata (CTA-ZM), in partnership with the Universidade Federal de Viçosa, especially the Soil Department, started participatory agroforestry-coffee system experimentation. The survey pointed out that agroforestry reduced the soil erosion process, improved soil quality and nutrient cycling, and increased the diversification of production (Souza, 2006). The main goals with the implementation of agroforestry systems were: i) land regeneration and conservation; ii) diversification of production; iii) decrease of the need of input; iv) increase or maintenance of production, and v) improvement of productivity (Cardoso, 2002). Cardoso et al. (2001) stated that the Zona da Mata meets all the criteria postulated by Young (1997) for the adoption of agroforestry. According to this author, agroforestry is particularly well developed in densely populated and sloping regions in the humid and sub-humid tropics, on which soils have often been degraded by erosion and forest cover has been extensively cleared for timber, charcoal and agriculture.

Several experimental works have been developed in different municipalities where agroforestry experiences were implanted. The challenge is to achieve a better understanding about the mechanisms of agroforestry in soil restoration and environmental quality. For instance, to optimize agroforestry systems it is necessary to study the interactions among the tree components, crop production and environmental resources, such as soil and water, which are included in the production.

Soil organic matter

A general soil–agroforestry hypothesis states that appropriate agroforestry systems have the potential to control soil erosion, maintain soil organic matter (SOM) and physical properties, and promote nutrient cycling and efficient nutrient use (Young, 1997). A more specific hypothesis among the twelve agroforestry hypotheses for soil management presented by Young (1997) consider that agroforestry systems can maintain SOM and biological activity at satisfactory levels for soil fertility. We studied more closely such hypothesis regarding the role of SOM in the different processes occurring in the soil.

The improvement of soil fertility as a result of trees in agroforestry is attributed to the maintenance of SOM through the supply of litter and root residues. SOM has been recognized as a major factor that controls the soil ability to deliver agricultural and environmental services and also to sustain human societies at both local (e.g. maintaining soil fertility) and global (e.g. increasing of C sequestration) scale (Manlay et al., 2007). Recent reviews discussing the potential of agroforestry for increasing C sequestration and promoting ecosystem services and environmental benefits are available in literature (Montagnini and Nair, 2004; Jose, 2009; Schoeneberger, 2009).

In agroforestry systems, the quality of organic residues differs according to the tree species. Therefore, the processes of decomposition of residues are different. In natural ecosystems and conventional agriculture systems, the main type of organic residues deposited on the soil surface is the senescent biomass. In agroforestry systems, besides the senescent material, inputs of fresh biomass derived from tree pruning also occur. Thus, the quality and the rates of litter and green leaf decomposition from the same plant may be quite different. This can differentiate agroforestry from natural ecosystems and conventional systems (Mafongoya et al., 1998).

The rate of SOM decomposition and mineralization depends on the balance of its labile and recalcitrant (non labile) components (Scholes et al., 1997). In general, the plant age influences the relative proportion of these components. Young plants or young tissues are richer in proteins, minerals and water soluble fractions. As plant age increases, the contents of cellulose, hemicellulose, lignin and polyphenols also increase (Scholes et al., 1997).

Decomposition is defined as the alteration of the original chemical structure of an organic compound or tissue, and in terms of SOM, is characterized by gradual changes in C functional groups that can be successfully assessed by specific spectroscopic techniques (Mathers et al., 2000). This process can be influenced by environmental factors such as temperature, nutritional status, and water content (Stevenson, 1994).

During the last decade, efforts to characterize the SOM were focused on the measurement of its different compartments by using techniques based on the degree of solubility of its components submitted to an acid or alkali medium (Swift, 1996). More recently, however, the development and adaptation of some techniques allowed the elucidation of important aspects of SOM quality. Besides SOM quantity, the quality (e.g., structure and composition) and distribution of individual organic fractions (e.g., fulvic and humic acids) are important to maintain soil structure and fertility (Ding et al., 2006). The SOM quality can be defined as its capacity to be used by soil biota as a source of energy, and/or as C skeleton on its own structure. The response to high SOM quality is an increase in the microbial activity promoting fast decomposition of residues and nutrient availability (Rovira and Vallejo, 2002). In tropical regions, especially in the areas with agroforestry systems, studies focused on the SOM quality are scarce. In studies performed in agroforestry experiments in the Zona da Mata, aspects of SOM quality were not investigated so far.

In Brazil, no-tillage has been broadly spread as a management alternative to increase SOM levels in different ecosystems (Machado and Silva, 2001; Bayer et al., 2000; D'Andrea et al., 2002; Leite et al., 2003; Sisti et al., 2004). However, little attention has been paid to other options of land use such as agroforestry systems in restoring SOM.

General hypotheses and objectives

The general hypotheses of this study were that (i) when compared to full sun coffee system, agroforestry coffee systems, due to constant input of organic residues derived from tree-components, increase C, N and P stocks in the soil and in different SOM pools; and (ii) that the diversity and quality of the organic residues in the agroforestry systems affect the chemical and structural characteristics of the SOM, with reflection in the nutrient cycling. Hence, the general objectives were: (i) to measure the stocks of C, N and P in the soil and in different pools of the SOM in areas under agroforestry-coffee and full-sun coffee systems, and (ii) to evaluate the influence of the diversity and quality of the organic residues on the chemical and structural characteristics of humic substances in both systems.

Outline of the Thesis

Chapter 2 describes the effect of agroforestry systems on the stocks of C, N and P in the soil and different SOM pools. The potential of agroforestry in sequestering C is discussed. Aspects including the lability of organic C were also investigated in a specific section. The study of C and N dynamics in aggregate-sized fractions was described in Chapter 3. In this study, I investigated the effect of agroforestry on soil aggregation. In addition, particulate organic matter concepts were discussed from a specific study of the most important aggregate-sized fraction for soil aggregate stability. In Chapter 4, I characterized the soil inorganic and organic P in different pools in agroforestry-coffee and full-sun coffee systems by adopting the sequential fractionation technique. The effect of agroforestry on the biological cycle of P was also discussed. The chemical and structural characterization of humic and fulvic acids was the focus of the study of Chapter 5. We used different chemical and spectroscopic techniques to evaluate the impact of the organic residues in agroforestry on the SOM quality. In this study, we discussed how the diversity and quality of organic residues can affect the characteristics of humic substances, and which effects regarding such characterization are involved in the nutrient cycling process. Finally, Chapter 6 describes a summary of the Thesis and final remarks, pointing out that some important future research is necessary for agroforestry systems in the Zona da Mata.

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CHAPTER 2

Soil organic C, N and P storage in areas under agroforestry- and full sun coffee systems at the Atlantic Coastal Rainforest, southeastern Brazil

Abstract – Although agroforestry can be considered a potential alternative for sequestering C on a global scale, quantitative data on specific systems in a field scale in Brazilian soils are still scarce. This study aimed i) to measure the stocks of organic C, N and P in bulk soil and different pools of soil organic matter (SOM) in areas under agroforestry-coffee and full-sun coffee systems, and ii) to detect the influence of the quality of organic residues derived from trees on the patterns of C, N and P storage. The work was carried out in three smallholding coffee production areas under agroforestry- (AGF) and full-sun coffee (FSC) systems located in the municipalities of Divino and Araponga in the Atlantic Coastal Forest biome in the state of Minas Gerais, Brazil. Soil samples were collected from 0-5, 5-10, 10-20 and 20-40 cm-deep intervals. C, N and P stocks were measured in the whole soil and in humic substances. Microbial C and N and C-CO_2 emissions were quantified. The lability of SOM was evaluated by the fractionation of soil organic C under different degree of oxidization. Soil organic C stocks in the coffee-cultivated lands varied from 1.36 to 3.92 kg m^{-2} in all evaluated sites. In general, there were no significant differences in the soil C, N and P stocks between AGF and FSC systems in all evaluated sites, exception to soil total P stocks in Araponga(II) at 20-cm soil depth. The stocks of C, N and P were variable across all evaluated sites. No clear tendency could be addressed to the effect of soil management. The potential of CO_2-C emission per month in the 0-10 cm soil depth in the AGF systems were 1,221; 594 and 1,005 kg CO_2-C ha^{-1} in Divino, Araponga(I) and Araponga(II), respectively. In Divino, soil relatively large metabolic quotient (qCO_2) in the AGF system seems to be more related to the greater levels of more available C content derived from tree-residues. In Divino and Araponga(I), the AGF system tend to increase the proportion of easily oxidizable C. The adoption of AGF management resulted in the increase of the carbon management index in all sites, suggesting the rehabilitation or enhancement of SOM levels. Under a qualitative point of view of SOM, agroforestry systems represent a more attractive option of management for increasing the proportion of more labile C forms. Other relevant aspects that were not object of our investigation, such as root-systems dynamics, need to be better understood and measured in order to obtain a more realistic analysis of the effect of agroforestry management on the C sequestration in the region.

Key words: Carbon sequestration; Carbon Management Index; Residue quality; qCO_2

1. Introduction

Carbon (C) sequestration in agricultural lands is considered an important strategy of management to deal with the problems of global warming (Lal, 1997; Scholes and Noble, 2001). Soil presents 3.5 times more C than the atmosphere (760 Gt) and 4.5 times the size of biotic pool (560 Gt) (Lal, 2004). This magnitude on the C storage makes soil one of most important factors in the changes of C cycling in the ecosystem.

The evaluation of changes in the SOM as a result of land use and management is important to identify strategies to increase agricultural production avoiding soil degradation and decreasing the emission of greenhouse gases (Freixo et al., 2002). The conversion of native forests into agricultural systems promotes decreases in soil C and N stocks due to reductions of organic inputs and increase of SOM mineralization and soil erosive process (Bayer and Mielniczuk, 1997; Marchiori Junior and Melo, 2000; Leite et al., 2003). The magnitude and extension of SOM decline, however, depends on the method of conversion, soil management intensity after conversion and physical and chemical soil properties (Lugo and Brown, 1993).

Among other factors, soil management has a marked influence on SOM dynamics in agricultural systems. It is assumed that: i) several SOM fractions respond in a specific way to management and land-use practices; ii) the synthesis and decomposition of these fractions are regulated by physical, chemical and biological factors that can be altered by management (Fernandes et al., 1997).

In Brazil, no-tillage has been broadly spread as a management alternative to enhance soil C sequestration in different ecosystems (Bayer et al., 2000; D’Andrea et al., 2002; Leite et al., 2003; Sisti et al., 2004). The potential of C storage in no-tillage management range from 0.1 to 0.3 Mg C ha^{-1} yr^{-1} (Lal, 2004; Carvalho et al., 2009). Machado and Silva (2001) reported that soils under no-tillage can storage (0-10 cm layer) on average 25.1 Mg C ha^{-1} compared to 19.9 Mg C ha^{-1} in conventional cultivation, and that the reductions of C in relation to a reference area were significantly lower in no-tillage compared to conventional systems. Despite the potential of no-tillage to increase C storage in Brazilian soils, little attention has been paid to other options of land use, such as agroforestry systems, in restoring SOM (Albrecht and Kandji, 2003).

Schroeder (1994) stated that regarding the climate change issue, agroforestry could be considered for at least two reasons: i) tree component fixes and stores C from the atmosphere via photosynthesis; and ii) agroforestry can reduce the need of deforestation for agriculture by providing alternatives to shifting cultivation.

Nevertheless, a realistic potential of agroforestry systems to increase SOM storage remain unknown due to the lack of reliable estimates on the extent of the area under agroforestry systems in different ecological zones. Furthermore, the C sequestered in agroforestry systems varies with system-specific characteristics, including climate, soil type, treeplanting densities, and tree management (Montagnini and Nair, 2004).

Despite agroforestry can be considered a potential alternative for sequestering C on a global scale (Schoeneberger, 2009), little quantitative data are available on specific systems in a field scale in Brazilian soils. For instance, Maia et al. (2007), studying soils from a semi-arid environment found that agrosilvopasture and silvopasture systems stored 49.08 and 68.65 Mg C ha^{-1}, respectively, considering soil thickness of 40cm. Montagnini and Nair (2004) stated that smallholder agroforestry systems have the potential to increase C storage in a rate of 1.5 to 3.5 Mg C ha^{-1} yr^{-1}.

Some attempts have been started in the region of Zona da Mata (Atlantic Coastal Rainforest Biome) by adopting agroforestry systems in smallholding coffee production areas (Ferrari, 1996). According to Mendonça and Stott (2003), agroforestry represents a potential to solve part of the agricultural problems in this region, since it can contribute to reduce soil erosion (Franco et al., 2002) and enhance nutrients and C cycling (Mendonça et al., 2001). However, only few data have been generated confirming the potential of agroforestry on the soil C sequestration in the Atlantic Forestry Biome. Besides, since C cycle is closely related to N and P cycles in the soil (Stevenson and Cole, 1999), data on the N and P stocks are equally necessary to improve the knowledge of the effects of agroforestry on the dynamics of these nutrients.

Actually, the amount of soil C, N and P stored in agroforestry systems will depend on the inherent environmental conditions in which it was implanted (e.g. soil, climate, topography, etc), the quality of organic residues derived from tree components and other socio-economic factors (Albrecht and Kandji, 2003). In this context, we hypothesized that agroforestry-coffee systems implanted in the region of Atlantic Forestry Biome increase the stocks of soil C, N and P pools in relation to a sole cropping system, and that the quality of organic residues (e.g. lignin, cellulose, hemicellulose, polyphenols contents) affects the amount of C, N and P stored in the soil. Hence, our objectives were i) to measure the stocks of organic C, N and P in bulk soil and different pools of soil organic matter in areas under agroforestry-coffee and full-sun coffee systems, and ii) to detect the influence of the quality of organic residues derived from trees on the patterns of C, N and P storage.

2. Materials and methods

2.1. General description of study area

The study was carried out in the Zona da Mata (about 36,000 km^2), located in the Atlantic Coastal Rainforest biome of the state of Minas Gerais, Brazil (Figure 1). The region is characterized by a tropical highland climate (average temperature and precipitation of 18 °C and 1500 mm, respectively, with 2 to 4 months of dry period), steep slopes (20 to 45%) and altitudes ranging from 200 to 1800 m (Cardoso, 2002). The parental rock is gneiss and the dominant soil types are deep and well drained Oxisols, which are acid and poor in nutrients (Ker, 1995; Mendonça and Stott, 2003). More detailed information on pedology, agriculture and sociology of the Zona da Mata region was previously published by Cardoso et al. (2001).

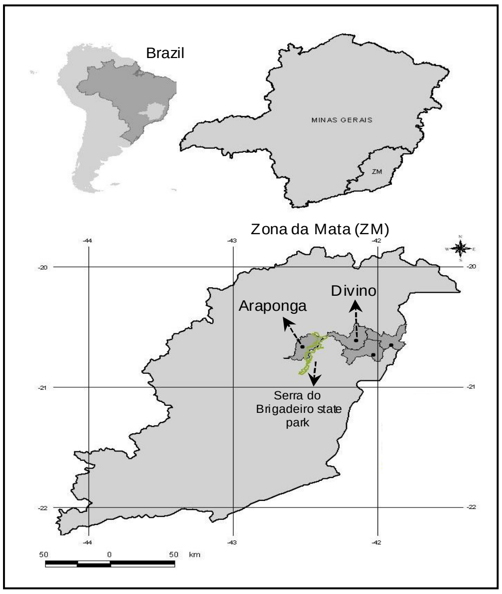

Figure 1. Localization of the municipalities of the study sites in the Zona da Mata (ZM), state of Minas Gerais.

2.2. *Specific study sites and soil sampling*

Three smallholder agroforestry coffee (*Coffea arabica* L.) systems (AGF) and three full sun coffee (FSC) systems fields with approximately 1.5 hectares and over 12 years of age were studied. These areas were situated at the municipalities of Divino and Araponga (Figure 1), managed by smallholding farmers. More detailed information about the historical land-use and management of the studied systems are presented in Box 1.

In each selected site, areas under natural forest fragments (NF) were sampled and used to represent the native or steady state condition of the soil. In all cases, NF fragments were at the same position on the landscape of the coffee-cultivated areas.

The chemical composition of senescent leaves of the main trees species used in the agroforestry systems was previously measured by Duarte (2007) and a summary is presented in Table 1.

Table 1. Chemical composition and C:N, LG:N, LG:PP and LG+PP:N ratios of senescent leaves of the main tree species in areas under agroforestry-coffee systems at three municipalities of Zona da Mata, Minas Gerais state

Site/ species	Chemical composition[/a]							Ratio			
	C	N	P	LG	HC	CL	PP	C:N	LG:N	LG:PP	LG+PP:N
	%										
Divino											
Luechea grandiflora	65.8	2.02	0.119	13.6	19.2	17.2	8.3	32.6	6.7	1.6	10.8
Araponga(I)											
Persea americana	60.7	2.05	0.163	21.0	13.4	12.8	7.3	29.6	10.2	2.9	13.8
Araponga(II)											
Inga subnuda	54.6	3.17	0.141	27.3	23.9	21.3	4.8	17.2	8.6	5.7	10.1

[/a] C:carbon; N: nitrogen; P: phosphorus; LG: lignin; HC: Hemicellulose; CL: Cellulose; PP: total polyphenols. Adapted from Duarte (2007).

Box 1. Historical of land use and management of selected sites

Divino (coordinate: 20º33'S, 42º11'W; altitude: 1,160 m)

Agroforestry-coffee system: Prior cultivation this area was deforested and use as pasture, cultivated with *Melinis minutiflora* P. Beauv. (common name: Capim gordura). Some tree species of *Piptadenia gonoacantha* J.F. Macbr. (Jacaré) spontaneously grew in the pasture area. The intensive use of soil with pasture for several years (exact time unknown) declined the soil quality. Agroforestry-coffee system was implemented in 1994. The study was concentrated in an area of approximately 3,150 m^2 with 600 coffee-trees (*Coffea Arabica* L.) spaced in 3.5 m x 1.5 m. Native tree species were intercropped with coffee. The main tree species is *Luehea grandiflora* Mart (Açoita-cavalo), although other species such as *Aegiphila sellowiana* Cham. (Papagaio), *Erythrina verna* Vell (Mulungu), *Musa sp.* L. (Banana) and *Zeyheria tuberculosa* (Vell.) Bur. (Ipê-preto) can be found. Fertilizers and limestone were not applied during the two first years of the establishment of agroforestry systems. After this period, 3 Mg of limestone were applied in the projection of coffee-tree canopy. From 1999 to 2002, 50 g per plant of a mixture of ammonium sulfate, potassium chloride and monocalcium phosphate in a proportion of 3-1-1 was applied in a rate of 4 applications per year, totalizing 200 g per plant. In 2000, the trees species intercropped with coffee were drastically pruned, and the residues were left on the soil surface between the coffee rows. From 2003 to 2006 the farmer started the transition to organic coffee and stopped the inorganic fertilization. During this period, cow manure, castor bean cake, residues of leguminous species, supermagro[/1] and cattle urine were applied (Table 2). The productivity during organic cultivation was approximately 1.5 kg of coffee (pulp removed) per plant. In 2007, the organic coffee production was interrupted. Since this year, 100 g per plant of N-P-K fertilizer (20-5-20) has been applied twice a year (Table 2). The lower branches of the trees are pruned every 2 years and the residues are left on the soil surface, between coffee rows. Sporadically, jackbean, pumpkin and castor bean are cultivated between coffee rows. The mean annual productivity in 2007, 2008 and 2009 were about 0.90, 0.72 and 0.60 kg of coffee per plant. Full sun coffee system: the historical of land use is identical to the previous described site. The forest was converted in pasture for several years (exact time unknown) and further in coffee cultivation. The area has approximately 2,000 m^2 with 1,000 coffee trees spaced in 2 m x 1 m. There are no trees intercropped with coffee. Soil liming is not performed and there is no application of organic manure. Chemical fertilization of soil in 2007, 2008 and 2009 was done by applying 300, 200 and 150 g per plant of N-P-K (20-5-20). The mean annual productivity in 2007, 2008 and 2009 were 0.93, 1.2 and 0.06 kg of coffee per plant, respectively.

Araponga(I) (coordinate: 20º48'S, 42º32'W; altitude: 1,040 m)

Agroforestry-coffee system: In the past this area was deforested and used as pasture for several years (exact time is unknown). Then, coffee was cultivated under conventional management during 15 years, which resulted in severe reduction of soil fertility mainly caused by soil erosion. In 1995, agroforestry-coffee system was implemented in an area of approximately 5,040 m^2 with 1,200 coffee-trees spaced in 3 m x 1.2 m. The system was established in the highest slope area of the farm. The main tree species intercropped with coffee is *Persea americana* Mill. (Abacate). Soil is limed once a year, and there is no chemical fertilizer application. Chicken manure was used in the organic fertilization in 2001. Cow manure is applied annually and foliar fertilization is done by using supermagro twice a year (Table 2). Spontaneous vegetation is slashed 1- or 2-times per year and the residues are kept on the soil. Bean straw is applied annually on the rows. The lower branches of the tree-canopy are pruned during the dry season (June-July), after coffee harvesting. The residues of prune are kept on the soil surface avoiding soil erosion. The annual productivity is around 0.62 kg of coffee per plant. Full sun coffee system: the historical of land use is identical to the previous described site. The area has approximately 4,000 m^2 with 2,000 coffee trees spaced in 2 m x 1 m. The system was implanted in the lowest slope position, immediately below of the agroforestry-coffee area. There are no trees intercropped with coffee, but corn and beans had been planted between coffee rows. Soil liming and N-P-K fertilizer (20-5-20) applications are performed annually (Table 2) and there is no organic fertilization. The annual coffee productivity is approximately 0.79 kg of coffee per plant.

Araponga(II) (coordinate: 20º41'S, 42º31'W; altitude: 1,040 m)

Agroforestry-coffee system: In the past this area was deforested and used as pasture for several years (exact time is unknown). Further, it was burned and cultivated with rice during 7 years. During rice cultivation the soil was usually plowed by animal traction. Rice cultivation caused severe soil erosion leading to a decline of soil quality. After rice the area was cultivated with corn and beans, and finally, it was converted in pasture for 3 years when soil achieved its lowest level of fertility. In order to reclaim the land, in 1994 *Pennisetum purpureum* Schum. cv. Napier (capim-napier) and trees species such as, *Colubrina glandulosa* Perkins (sobrasil), *Hovenia dulcis* Thunb. (uva-do-japão), *Inga sessilis* Mart. and *Inga subnuda* subsp. *luschnathiana* (Benth.) T.D. Penn. were planted. The Inga species were introduced later on and the other tree species were removed. In 1998, Agroforestry-coffee was implemented. Soil liming was done in 1999, 2001, 2004 and 2006 by adding 200 g of limestone per m^2. The coffee field which includes the area covered by Inga species has approximately 1,500 m^2 with 500 coffee-trees spaced in 3 m x 1 m. At the beginning, corn and beans was usually intercropped between coffee rows, but since four years ago such inter-cropping is not performed. In the cultivation of corn and/or beans, N-P-K fertilizer (4-18-8) was applied on a rate of 30 g per m^2. Trees are not pruned but the herbaceous spontaneous vegetation is slashed three times per year. The residues of slashing are kept on the soil surface. N-P-K (20-5-20) and foliar fertilizer are applied annually (Table 2). There is no organic fertilization. The mean of coffee productivity in 2007 was 0.36 kg of coffee per plant. Full sun coffee system: the historical of land use is identical of the previous described site. This area corresponds to the other part in which Inga species were not planted. It has approximately 7,500 m^2 with 2,500 coffee trees spaced in 3 m x 1 m. The main difference in relation to agroforestry-coffee is the absence of trees. The mean of coffee productivity in 2007 was 0.45 kg of coffee per plant. Other information about chemical fertilization is presented in Table 2.

[/1] Liquid biofertilizer for foliar application prepared from fresh manure diluted in water and enriched with bone meal, blood, fish scraps (the latter two contributing minerals), and unrefined sugar and milk to stimulate fermentation. This mix is fermented anaerobically for about 1.5 months. Other organic liquid fertilizers include fermented, cattle urine and an infusion prepared from manure (Velásquez, 2002).

The more detailed characterization of the sites studied is presented in Table 2.

Table 2. Characterization of the agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino and Araponga.

	Divino		Araponga(I)		Araponga(II)	
Item	**AGF**	**FSC**	**AGF**	**FSC**	**AGF**	**FSC**
Area size, m^2	3,150	2,000	5,040	4,000	1,500	7,500
Number of coffee trees	600	1,000	1,200	2,000	500	2,500
Spacing of coffee trees, m	3.5 x 1.5	2 x 1	3 x 1.2	2 x 1	3 x 1	3 x 1
Number of trees per ha	150 - 200	-	200	-	~150	-
Fertilizer N-P-K (20-5-20), g/plant	100[/b]	150[/c]	na	180	200[/d]	200[/d]
Cow manure, kg	10,000[/e]	na	2,880	na	na	na
Castor bean residue, kg	600[/e]	na	na	na	na	na
Compost, kg	5,000[/e]	na	na	na	na	na
Limestone, g/m^2	950[/f]	na	20[/g]	40[/g]	200[/h]	200[/h]
Foliar fertilization (supermagro)	yes	na	yes	na	na	na
Biomass production[/a] (litter)						
Coffee trees, kg/year	720	890	1,440	1,780	600	2,225
Trees, kg/year	2,398	-	2,004	-	4,331	-

[/a] Coffee trees: estimated from Campanha et al. (2007) where litter production (dry matter) in agroforestry is 50.7 g m^{-2} $month^{-1}$ and sun coffee system is around 37.2 g m^{-2} $month^{-1}$; Other trees: measured by Duarte (2007);

[/b] From 2006 to 2009, applied twice a year; From 1999 to 2002: 200 g $plant^{-1}$ $year^{-1}$ of a mixture of ammonium sulfate, potassium chloride and monocalcium phosphate in a proportion of 3-1-1;

[/c] Performed in 2008; In 2006 and 2007, N-P-K (20-5-20) was applied on a rate of 150 and 100 g per plant, respectively, twice a year;

[/d] applied once a year;

[/e] Total applied during organic cultivation from 2003 to 2006; supermagro applied twice a year;

na: not applied;

[/f] applied in 1997;

[/g] applied annually;

[/h] total applied in 1999, 2001, 2004 and 2006.

The soil samples were collected at intervals of 0-5, 5-10, 10-20 and 20-40 cm of depth from December 2006 to March 2007 (rainy season). In order to guarantee a representative sampling procedure, four sub-samples randomly distributed between coffee rows were taken from each site, and then combined to form one replicate. Four replicates were collected. Before the samples were taken, the litter layer was removed. Immediately after sampling, approximately 300 grams of soil from 0-5 and 5-10 cm layers were separated and frozen to perform a further microbiological analysis. Once in the laboratory, the moist soil was air-dried, sieved through a 2-mm sieve and stored at room temperature. Selected physical and chemical characteristics of the studied soils are shown in Table 3.

Table 3. Values of particle sized fractions, pH (H_20), cation exchange capacity (CEC) and base saturation of soils under native forest (NF), agroforestry coffee (AGF) and full sun coffee (FSC) systems at 0-10 cm layer in the municipalities of Divino, Araponga(I) and Araponga(II)

	Divino			Araponga(I)			Araponga(II)		
Soil characteristic	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
Particle size, g kg^{-1}									
Sand	504	573	519	493	520	495	474	388	444
Silt	237	122	165	108	119	124	124	113	134
Clay	259	305	316	399	361	381	402	499	422
pH H_2O (1:2.5)	6.4	6.0	6.1	4.9	5.8	5.8	4.8	5.6	6.2
CEC, cmol$_c$ dm^{-3}	21.4	11.1	11.6	16.6	11.1	10.1	17.7	12.2	11.0
Base saturation, %	77.0	69.0	63.0	2.0	46.0	51.0	1.0	30.0	40.0

2.3. Total soil organic carbon, nitrogen and phosphorus stocks

Soil organic C (SOC) was quantified by wet combustion with a mixture of potassium dichromate and sulfuric acid (Yeomans and Bremner, 1988). Soil total N (STN) was measured after sulfuric digestion followed by Kjedahl distillation (Tedesco et al., 1995). Soil total P (STP) was determined colorimetrically (Murphy and Riley, 1962) after digestion with H_2SO_4 – H_2O_2 (Bowman, 1988). For each soil layer (0-5, 5-10, 10-20 and 20-40 cm), the C, N and P stocks were calculated by multiplying the element concentration (g kg^{-1}) by the soil bulk density (g cm^{-3}) and to the thickness of the soil layer (cm). The result was divided by 100 to obtain stocks in kg m^{-2} (Fidalgo et al. 2007).

2.4. Soil microbial properties

For measuring CO_2-C emissions, 100 g (oven-dry basis) of the moist soil sample was adjusted to 70% of its water-holding capacity, and then placed in hermetically sealed glass jars. The CO_2-C produced was trapped in 30 ml 0.5 M

NaOH and the excess of NaOH was quantified by titration with 0.25 M HCl. The CO_2 production was then measured for 30 days (Anderson, 1982).

The microbial biomass C and N (MB-C, MB-N) were estimated by the irradiation-extraction method (Islam and Weil, 1998; Ferreira et al., 1999) by using 0.5 M K_2SO_4 as extractant. The MB-C and MB-N were measured in aliquots of irradiated and non-irradiated samples by wet combustion with a mixture of potassium dichromate and sulfuric acid (Yeomans and Bremner, 1988) and by digestion followed by Kjedahl distillation (Tedesco et al., 1995), respectively. The conversion factors for the calculation of MB-C and MB-N (Kc and Kn), used to convert the flux of soil C and N into microbial C and N, were 0.33 and 0.54, respectively (Brookes et al., 1985; Sparling and West, 1988). The metabolic quotient ($q$$CO_2$) was calculated as follows: [basal respiration (mg CO_2-C kg soil day^{-1})/MB-C] x 100. The results were expressed in mg CO2-C mg^{-1} MB-C day^{-1}.

2.5. Soil humic substances

Extraction and fractionation of soil humic substances in fulvic acids (FAs), humic acids (HAs) and humin (HUM) were obtained adopting the principle of differential solubility in basic and/or acid media according to the International Humic Substances Society (IHSS) methodology (Swift, 1996). Briefly, FAs and HAs were extracted and separated by using 0.1 M NaOH solution with a soil:solvent ratio of 1:10, and then precipitated with 6 M HCl added to the extract until a pH of 2.0 was reached. Total organic C and N contents in humic fractions were measured by wet digestion with potassium dichromate in an acid medium (Yeomans and Bremner, 1988) and Kjedahl distillation (Tedesco et al., 1995), respectively. The P concentration in each extracted humic fraction was determined colorimetrically (Murphy and Riley, 1962) after digestion with H_2SO_4 – H_2O_2 (Bowman, 1988). The stocks of C, N and P (Mg ha^{-1}) in the humic substances were calculated by multiplying the element concentration (%) by the soil bulk density (g cm^{-3}) and to the thickness of the soil layer (cm).

2.6. Soil organic carbon fractionation

Soil organic C fractionation was performed through adaptation of the method described by Chan et al. (2001). Organic C fractions were quantified by organic matter oxidation with potassium dichromate in an acid medium (Yeomans and Bremner 1988), by using different H_2SO_4 concentrations without external heating. The final H_2SO_4 concentrations were 3, 6 and 9 mol L^{-1}, at a constant concentration of potassium dichromate. The amount of SOC oxidized in each concentration was separated into four fractions with different degrees of lability: *Fraction 1* (3 mol L^{-1} of H_2SO_4): oxidized SOC in 3 mol L^{-1} of H_2SO_4; *Fraction 2* (6 – 3 mol L^{-1} of H_2SO_4): oxidized SOC between 6 and 3 mol L^{-1} of H_2SO_4; *Fraction 3* (9 – 6 mol L^{-1} of H_2SO_4): oxidized SOC between 9 and 6 mol L^{-1} of H_2SO_4, and *Fraction 4* (Total SOC – 9 mol L^{-1} of H_2SO_4): oxidized SOC between Total SOC and 9 mol L^{-1} of H_2SO_4.

Based on the differences between the SOC in a native forest (NF) area and in the cultivated systems, a Carbon Pool Index (CPI) was created and estimated as follows: CPI = $SOC_{\text{cultivated system}}/SOC_{NF}$. According to changes in the proportion of labile and non-labile organic C (C_L and C_{NL}) in the soil (i.e. L = C_L/C_{NL}), a Lability Index (LI) was calculated as: LI = $L_{\text{cultivated}}$ /L_{NF}. The C concentration in the Fraction 1 and in the sum (Fraction 3 + Fraction 4) were assumed as being C_L

and C_{NL}, respectively. The CPI and LI indexes were used to determine the Carbon Management Index (CMI), which was calculated as following: CMI = CPI x LI x 100. The CMI has been considered a sensitive index to measure the impact of soil management on the SOM levels (Blair et al., 1995).

2.7. Statistical analysis

The effect of soil management was tested by performing the analysis of variance (ANOVA) followed by the least significant difference (LSD at $P < 0.05$) post-hoc test. The *t*-test ($P < 0.05$) was applied assess the differences among estimated means (e.g. C_L, C_{NL}, CPI, L and LI indexes).

3. Results and discussion

3.1. Soil bulk density

The soil bulk density (Table 4) varied from 1.00 to 1.43 g cm^{-3} among the cultivated areas and was significantly affected by the management in Araponga(II). At this site, the FSC system showed higher ($P < 0.05$) values of bulk density compared to AGF in all evaluated soil layers. Such response in AGF system can be attributed to the effect of the larger input of organic residues in comparison to FSC that, among other factors, protect soil surface against the direct impact of rainfall, decreasing the potential of soil compaction and avoiding the downward transport of fine particles through the soil profile (Osunbitan et al., 2005). These results suggest that agroforestry management favors a better soil structure, whereas in the FSC system, the increase in bulk density can lead to an inappropriate development of the root systems of the plants.

Table 4. Soil bulk density (g cm^{-3}) in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino, Araponga(I) and Araponga(II)

Soil depth (cm)	Divino				Araponga(I)				Araponga(II)			
	NF	AGF	FSC	lsd$_{0.05}$	NF	AGF	FSC	lsd$_{0.05}$	NF	AGF	FSC	lsd$_{0.05}$
0-5	0.93	1.21	1.23	0.06	0.69	1.08	0.99	0.13	0.70	1.00	1.21	0.19
5-10	0.80	1.19	1.21	0.16	0.79	1.10	1.04	0.12	0.75	1.06	1.32	0.10
10-20	0.97	1.27	1.25	0.21	0.81	1.11	1.15	0.17	0.88	1.06	1.40	0.11
20-40	1.03	1.28	1.27	0.22	0.89	1.08	1.06	0.11	1.02	1.06	1.43	0.23

lsd: least significant difference ($P < 0.05$).

3.2. Total organic C contents in the soil and humic substances

Organic C contents in the soil and humic substances are presented in Table 5. The SOC contents ranged from 13.36 to 97.02 g kg^{-1} in Divino; from 17.20 to 77.00 g kg^{-1} in Araponga (I) and from 13.65 to 55.06 g kg^{-1} in Araponga(II). In general, the SOC reduction in the cultivated areas in relation to the reference (NF) in the whole soil profile (0 – 40 cm) was about 56%. In Divino and Araponga(II), such reduction was lower in the AGF than FSC systems, whereas in Araponga(II) the SOC reduction was lower in the FSC (47.9%) than in AGF (54,4%) system. The main changes in the SOC contents occurred at soil surface (0-10 cm). At this soil depth interval, AGF reduced 67, 58 and 45% of SOC in the NF area in Divino, Araponga(I) and Araponga(II), respectively, whereas FSC reduced 71, 55 and 47%, respectively. The lower SOC reductions in the AGF systems in Divino and Araponga(II) suggest that agroforestry has greater potential to recover the SOM levels in relation to a steady state area, when compared to a sole cropping system.

Table 5. Total soil organic C (SOC) contents, organic C in fulvic acids (FA) and humic acids (HA), proportions of C in FA and HA in relation to SOC and humification rate (HR) index in soils under native forest (NF), agroforestry coffee (AGF) and full sun coffee (FSC) systems at 0- to 40-cm soil depth in the municipalities of Divino, Araponga(I) and Araponga(II)

System	Soil depth (cm)	SOC (g kg^{-1})	Carbon, g kg^{-1}		% SOC		
			FA	HA	FA	HA	HR[/a]
			- - - - - - - - - - - - - - - - - - - -	***Divino***	- - - - - - - - - - - - - - - - - - - -		
NF	0-5	97.02	5.40	15.35	6	16	21.4
	5-10	63.86	5.72	13.16	9	21	29.6
	10-20	53.34	3.95	14.47	7	27	34.5
	20-40	44.21	3.03	12.16	7	28	34.4
AGF	0-5	26.59	2.77	6.89	10	26	36.3
	5-10	25.70	2.45	5.45	10	21	30.7
	10-20	18.21	2.64	4.97	14	27	41.8
	20-40	15.30	2.39	4.78	16	31	46.9
FSC	0-5	24.48	2.95	7.05	12	29	40.8
	5-10	22.50	2.83	6.61	13	29	42.0
	10-20	18.33	2.29	5.78	12	32	44.0
	20-40	13.36	2.49	5.36	19	40	58.8
			- - - - - - - - - - - - - - - - - -	***Araponga(I)***	- - - - - - - - - - - - - - - - - -		
NF	0-5	77.00	7.23	18.30	9	24	33.2
	5-10	60.96	8.21	13.84	13	23	36.2
	10-20	47.94	7.05	9.77	15	20	35.1
	20-40	22.87	5.54	3.34	24	15	38.8
AGF	0-5	31.05	6.01	8.89	19	29	48.0
	5-10	26.78	5.77	8.60	22	32	53.7
	10-20	20.09	6.01	7.81	30	39	68.8
	20-40	17.20	5.49	4.60	32	27	58.7
FSC	0-5	34.58	4.07	7.15	12	21	32.4
	5-10	27.93	3.76	6.11	13	22	35.3
	10-20	24.11	4.02	6.29	17	26	42.8
	20-40	22.36	3.61	4.87	16	22	37.9
			- - - - - - - - - - - - - - - - -	***Araponga(II)***	- - - - - - - - - - - - - - - - -		
NF	0-5	55.06	6.56	14.15	12	26	37.6
	5-10	46.32	6.68	8.47	14	18	32.7
	10-20	33.68	6.09	6.30	18	19	36.8
	20-40	30.77	4.69	3.78	15	12	27.5
AGF	0-5	29.62	4.63	7.56	16	26	41.2
	5-10	26.33	4.31	6.80	16	26	42.2
	10-20	16.90	4.63	6.49	27	38	65.8
	20-40	17.91	7.50	4.57	42	26	67.4
FSC	0-5	29.05	5.43	5.93	19	20	39.1
	5-10	24.68	5.59	6.89	23	28	50.6
	10-20	15.27	9.77	4.41	64	29	92.9
	20-40	13.65	7.18	2.12	53	16	68.1

[/a] HR = [C_{FA+HA}/SOC] x 100.

The opposite pattern found in Araponga(I) can be directly related to the inherent conditions of the slope position of both cropped fields. The AGF system was implanted in a condition of upslope, which can facilitate the processes of translocation, whereas FSC is located at the downslope position which can be considered a condition of accumulation on the landscape.

In general, C contents in HA were higher than in FA in all evaluated sites (Table 5). The reductions of C contents in FA with the increase of soil depth were less accentuated than in HA due to the greater mobility of the FA fraction in the soil compared to HA (Stevenson, 1994). Regarding the whole soil profile (0-40 cm), C content in FA in the NF and cultivated sites accounted on average for 12 and 22% of SOC, respectively, whereas C contents in HA represented 21 and 27% of SOC, respectively. Humification rate (HR%) is a parameter that can provide quantitative information about the humic substance content normalized with respect to the total SOM (Dell'Abate et al., 2002). The HR was greater in FSC than AGF systems in Divino and Araponga(II) (Table 5), suggesting that at these sites, FSC systems favored the accumulation of humified compounds. A contrary pattern occurred in Araponga(I). Such behavior was more pronounced at soil surface (0-10 cm), where the effect of soil management is more expressive.

3.3. Soil total C, N and P stocks

The total SOC, STN and STP stocks in different soil layers are shown in Figure 2. In general, all three agroecosystems presented similar levels of C, N and P stocks although they presented different aboveground biomass residual inputs (data not shown). The SOC stocks in the coffee-cultivated lands varied from 1.36 to 3.92 kg m^{-2} among all evaluated sites. STN stocks varied from 0.12 to 0.42 kg m^{-2}, whereas STP ranged from 0.02 to 0.15 kg m^{-2}. There were significant reductions of SOC stocks in the cropped areas in relation to their respective reference area, suggesting that soil cultivation leads to a decline in the SOM levels regardless of the type of soil management.

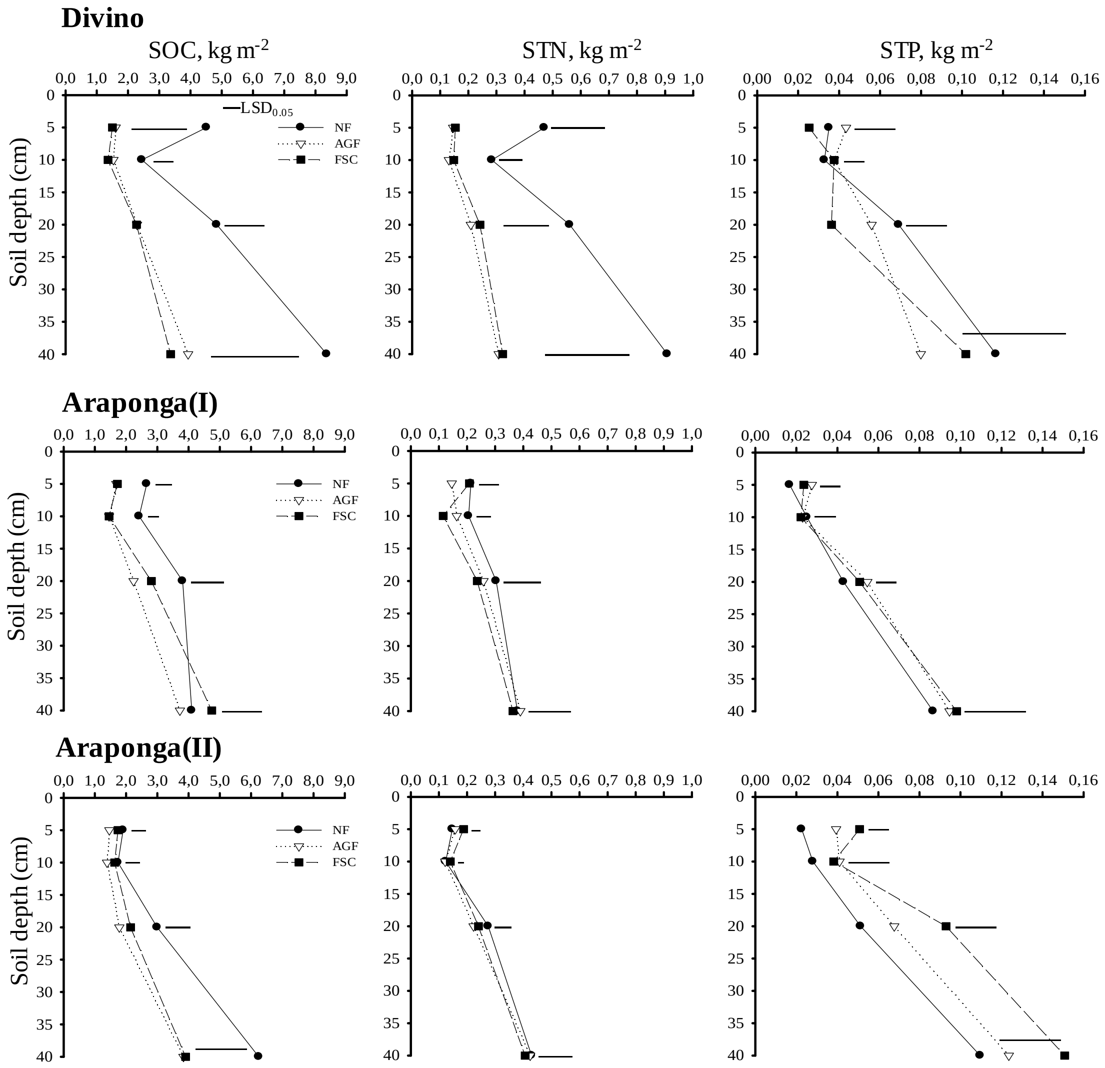

Figure 2. Soil total organic C, N and P stocks (SOC, STN, STP) at different soil depths in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino, Araponga(I) and Araponga(II). Horizontal bars indicate the least significant difference (LSD, $P < 0.05$).

In general, there were no significant differences in the soil C, N and P stocks between the AGF and FSC systems in all evaluated sites, exception to STP stocks in Araponga (II) in the 20-cm soil depth. Even in Araponga(II), where the largest input of aboveground biomass occurred (4.3 Mg ha^{-1} $year^{-1}$), SOC stocks were similar in both AGF and FSC systems. Since SOC stock calculation takes into account the bulk density, this response is probably more associated to the increase of soil bulk density in the FSC (Table 4) than the lack of effect of the SOM storage in the AGF system.

An increase of soil C storage has been pointed out as one of the most important benefits of AGFs in a global scale (Schoroeder, 1994; Albrecht and Kandji, 2003). Our results, however, suggest that it could not be generalized when evaluated in field scale because inherent factors such as climate, soil, topography, etc, can play a decisive role in the C dynamics. Besides, the quality of organic residues derived from trees also rules the pattern of SOM cycling (Mafangoya et al., 1998; Mendonça and Stott, 2003). Basically, two reasons can be drawn to explain the lack of changes in C, N and P storage in AGF comparison to FSC systems: i) there is a slow decomposition rate of the organic residues that, in turn, results in a slow rate of transfer of C and other nutrients from litter to soil; ii) On the contrary, there is a fast rate of decomposition of the residues that can accelerate SOM cycling, retarding C storage in a short-time.

We believe that the first hypothesis can be addressed to the Araponga(II). At this site, a thick layer of organic residues derived from Inga (*I. subnuda*) remaining under soil is easily verified in the field. The chemical composition of organic residues of Inga in the litter showed higher content of lignin and lignin/polyphenols ratio compared to other tree species (Table 1), which can help to explain its slow rate of decomposition. The second hypothesis can be credited to Divino, where the lowest biomass input was observed, included leaves, and lignin/polyphenols ratio (Table 1). An intermediated condition seems to occur in

Araponga(I), in which leaves had a smaller contribution on the total of biomass input compared to the other two sites, meanwhile flowers and fruits accounted with a greater proportion to C input (data not shown). The AGF system in Araponga(I) was implanted in a condition of huge slope, and it was common to verify the gravitational transportation of fruits from upper to lower positions of the slope. As a result of this behavior, there is a loss in the storage of C and other nutrients, especially at the upper soil depths in the AGF system.

Albrecht and Kandji (2003) highlighted that C sequestration in agroforestry systems is a dynamic process. At establishment, many systems used to lose C and N from vegetation and soil to atmosphere. Then, the following phase is characterized by a quick accumulation of tons of C that are stored in the trunks, stems, leaves and roots of trees and in the soil. At the end of the rotation period, part of the C will be released back to the atmosphere (Dixon, 1995). The benefits of agroforestry systems go beyond providing C restoration. These systems improve land cover in agricultural fields, as observed in Araponga(II). This has often reduced soil erosion (Franco et al., 2002), which is an essential process in the soil C dynamics.

The potential of C storage in the different land use is shown in Table 6. Soil cultivation reduced C stocks in relation to the reference area in 57, 38 and 15% in the soil surface (0-10 cm layer) in Divino, Araponga(I) and Araponga(II), respectively. In Divino, the C reduction was lower in the AGF (55%) than in the FSC (59%) system. At this site, AGF increased the C stock in 2.7 Mg ha^{-1} in the 0-10 cm soil layer and 8.5 Mg ha^{-1} in the whole soil profile (0-40 cm) in relation to the FSC system. In Araponga(I), C stocks at soil surface were very similar between the AGF and FSC systems. At this site, the FSC system seems to be affected by the slope position, and probably has influence of the deposition of materials from AGF, which is located in the upslope position. In Araponga(II), FSC increased C stocks in relation to the AGF system in 5.2 and 9.5 Mg ha^{-1} in the 0-10 and 0-40 cm layers, respectively. At this site, the increase of C storage in the FSC system has been influenced by the increasing of soil bulk density in all soil layers (Table 4). Therefore, the potential of the AGF system to restore soil quality must be analyzed not only with respect to the increase of SOM levels but it needs to take into account other benefits such as the enhancement of the soil physical quality and protection against erosive processes.

Table 6. Organic carbon storage (Mg ha^{-1}) in soils under native forest, agroforestry-coffee and full sun-coffee systems in the municipalities of Divino, Araponga(I) and Araponga(II). Values in brackets are ± standard error (n=4)

Soil depth (cm)	Native Forest	Agroforestry-coffee	Full sun-coffee
		Divino	
0-5	45.1 (9.4)	16.0 (0.5)	15.0 (0.7)
5-10	24.4 (3.3)	15.3 (0.7)	13.6 (0.7)
Total 0-10	69.5	31.3	28.6
Total 0-40	201.6	93.5	85.0
		Araponga(I)	
0-5	26.6 (1.5)	16.9 (1.2)	17.2 (2.0)
5-10	24.2 (1.2)	14.5 (0.8)	14.5 (1.1)
Total 0-10	50.8	31.4	31.7
Total 0-40	129.9	91.0	107.3
		Araponga(II)	
0-5	19.0 (0.7)	14.6 (0.7)	17.4 (0.9)
5-10	17.4 (0.6)	13.9 (0.5)	16.3 (1.5)
Total 0-10	36.4	28.5	33.7
Total 0-40	128.8	84.7	94.2

3.4. Soil microbial parameters

The estimate of CO_2-C emission by the microbial biomass in the different agroecosystems is presented in Figure 3. In order to make comparable values among the systems, in each area the total amount of CO_2-C produced was related to their respective total SOC content.

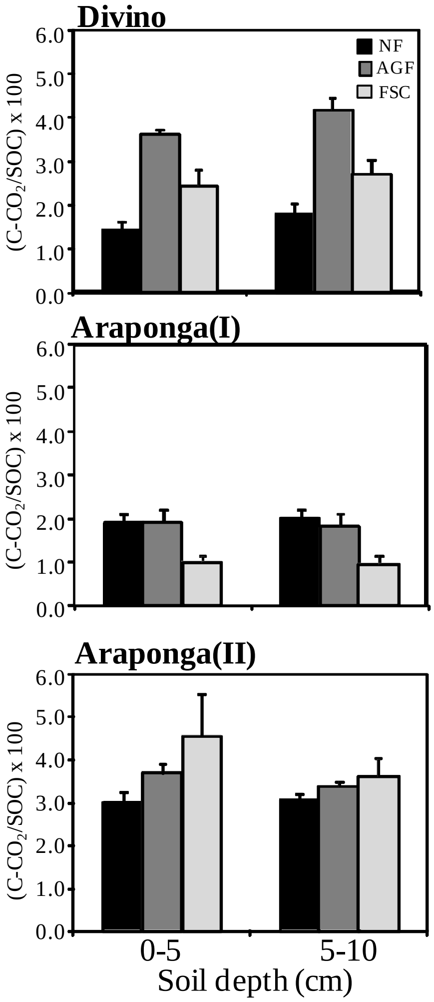

Figure 3. CO_2-C emissions in function of total soil organic carbon (SOC) at different soil depths in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in three municipalities of Zona da Mata, Minas Gerais state.

In Divino, the CO_2-C emissions in the AGF system accounted for 3.6 and 4.2% of SOC at the 0-5 and 5-10 cm layers, respectively, against 2.4 and 2.7% in the FSC system. A higher amount of CO_2-C was also verified in AGF when compared to the FSC system in Araponga(I) for both soil layers. However, a similar pattern was not observed in Araponga(II). The larger emission of CO_2-C in AGFs in Divino and Araponga(I) imply that this system presented the highest level of microbial activity, which may result in a higher potential to act as sink of C to the atmosphere under a possible condition of soil disturbance. The CO_2-C production trends reinforce the hypothesis of two opposite patterns on SOM cycling between Divino and Araponga(II), and it seems to be directly influenced by the quality of the organic residues in each situation.

The potential of CO_2-C emission per month of evaluation in the 0-10 cm soil depth (Table 7) for the AGF systems were 1,221; 594 and 1,005 kg CO_2-C ha^{-1} in Divino, Araponga(I) and Araponga(II), respectively. At the same sites, the CO_2-C emissions in the FSC systems were 720; 302 and 1,347 kg CO_2-C ha^{-1}, respectively. As a result of the intense microbial activity, the basal soil respiration tended to be higher in AGF when compared to the FSC systems in Divino and Araponga(I) (Table 7).

Table 7. Microbial biomass C and N, microbial-C to N ratio, microbial-C to organic C ratio, microbial-N to total N ratio, basal respiration, metabolic quotient and total CO_2-C production in soils under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at three municipalities of Zona da Mata, Minas Gerais state

	Divino				Araponga(I)				Araponga(II)			
Microbial parameters	NF	AGF	FSC	LSD[b]	NF	AGF	FSC	LSD	NF	AGF	FSC	LSD
0-5 cm depth												
MB-C, $\mu g\ g^{-1}$ soil	698	102	110	266	572	145	89	419	313	208	65	116
MB-N, $\mu g\ g^{-1}$ soil	nd[a]	51.2	79.9	66.5	49.8	25.3	32.6	7.8	77.8	25.2	44.3	15.6
Microbial C:N	-	2.0	1.4	1.4	11.5	5.7	2.7	3.4	4.0	8.3	1.5	2.4
MB-C: organic C, %	0.7	0.4	0.4	-	0.8	0.5	0.3	-	0.6	0.7	0.2	-
MB-N: total soil N, %	-	2.1	3.1	-	0.8	0.9	0.8	-	1.9	0.8	1.4	-
Basal soil respiration, mg CO_2-C kg^{-1} soil day^{-1}	45.9	33.2	19.7	16.4	50.6	20.7	11.5	10.0	55.5	37.5	43.7	14.9
Metabolic quotient (qCO_2), mg CO_2-C μg^{-1} MB-C day^{-1}	6.6	32.5	17.9	19.7	8.8	14.3	12.9	15.5	17.8	18.0	67.6	60.7
CO_2-C emission, kg ha^{-1}	623	581	353	232	503	328	165	121	571	540	766	274
5-10 cm depth												
MB-C, $\mu g\ g^{-1}$ soil	309	121	108	162	563	139	92	190	177	120	188	90.7
MB-N, $\mu g\ g^{-1}$ soil	nd	27.6	83.7	19.5	69.0	24.7	22.6	25.7	53.7	15.0	30.5	26.0
Microbial C:N	-	4.4	1.3	4.5	8.2	5.6	4.1	6.1	3.3	8.0	6.2	4.1
MB-C: organic C, %	0.5	0.5	0.4	-	0.9	0.5	0.3	-	0.4	0.5	0.8	-
MB-N: total soil N, %	-	1.3	3.4	-	1.3	0.9	1.1	-	1.6	0.7	1.4	-
Basal soil respiration, mg CO_2-C kg^{-1} soil day^{-1}	36.6	37.1	20.9	10.0	42.1	16.4	9.2	8.2	48.3	30.4	30.3	8.0
Metabolic quotient (qCO_2), mg CO_2-C μg^{-1} MB-C day^{-1}	11.8	30.7	19.3	32.4	7.5	11.9	9.9	18.8	27.3	25.3	16.1	18.3
CO_2-C emission, kg ha^{-1}	418	640	367	161	485	266	137	132	527	465	581	147

[a] nd: not determined; [b] LSD: least significant difference ($P < 0.05$).

In Araponga(I), MB-C contents tended to be higher in AGF than FSC even though larger $q\mathrm{CO}_2$ was observed in AGF in both soil layers (Table 7), reinforcing the previous patterns found in Divino. In Araponga(II), the $q\mathrm{CO}_2$ in AGF tended to be lower than the FSC system at soil surface (Table 7), suggesting a better efficiency in the use of substrate-C, which reflected a significant increase in the MB-C. The improvement of the microbial efficiency in the AGF system might be attributed to a shift in the soil microbial community from bacteria to fungal dominance. It has been suggested because there was a significant increase on MB-C:N ratio, from 1.5 in FSC to 8.3 in AGF (Table 7). An increase in fungal-to-microbial biomass ratios has been reported as a result of large microbial biomass C-to-N ratios (Salamanca et al., 2001). Zhang et al. (2007), studying microbial biomass dynamics and soil wettability, also found that the intensity and frequency of wetting and drying cycles caused an increase in soil microbial C-to-N ratio due to a dominance of fungal instead of bacterial community. Regarding the high content of lignin in the litter from the AGF system in Araponga(II) (Table 1), our findings are well consistent with the previous findings, since fungi are considered the most important degraders of lignin (Fukushima and Kirk, 1995; Tuor et al., 1995). Therefore, further direct measurements of fungal biomass and microbial community are needed.

The proportions of microbial C and N in the total soil C and N contents were represented by MB-C: organic C and MB-N: total soil N ratios, respectively (Table 7). MB-C accounted for less than 1% of SOC, varying from 0.2 to 0.8% among all cultivated sites, which is below the values commonly found in literature, normally comprising between 1 to 5% of organic C (Sparling, 1992; Stevenson and Cole, 1999). In Araponga(II) MB-C: organic C ratio from the upper soil layer tended to be consistently higher in AGF than FSC, probably as a result of the increase in the efficiency of the substrate used by the microbiota. MB-N: the total N ratio averaged 2.5; 0.9 and 1.0% in Divino, Araponga(I) and Araponga(II), respectively. In general, FSC systems showed larger MB-N: total N ratio than AGF systems. The immobilization of N into microbial biomass in the FSC systems can be associated to the incorporation of fresh residues of leguminous species (e.g. beans) into soil surface, which are often cropped between coffee rows. These results are in accordance with the findings of Xavier et al. (2006) in areas under organic cropping cultivation.

3.5. C, N and P stocks in the humic substances

The stocks of C, N and P in the soil FA and HA fractions are presented in Figures 4, 5 and 6. In Divino soils (Figure 4), stocks of C, N and P were relatively greater in HA than FA. At this site, FA, HA and Humin (HUM, data not shown) from cultivated areas accounted for 13, 28 and 56% of SOC and 15, 38 and 47% of STN, respectively. The proportions of P contents in humic substances in relation to STP varied according to soil management. In the FSC system, FA, HA and HUM represented 5, 10 and 86% of STP, respectively. However, these proportions changed to 10, 20 and 23% in the AGF system.

These results indicate that most part of STP in the FSC system is allocated in the most stable humic pool, whereas AGF promoted an increase of organic P in the most dynamic humic fractions. Such results indicate that AGF can favor a faster organic P cycling than FSC system. In general, there were no significant differences in the C and N stocks of FAs and HAs between the AGF and FSC systems (Figure 4). This pattern was similar to the previously findings for SOC and STN stocks (Figure 2). On the other hand, AGF showed significant increases on the P stocks in the FAs and HAs compared to the FSC system.

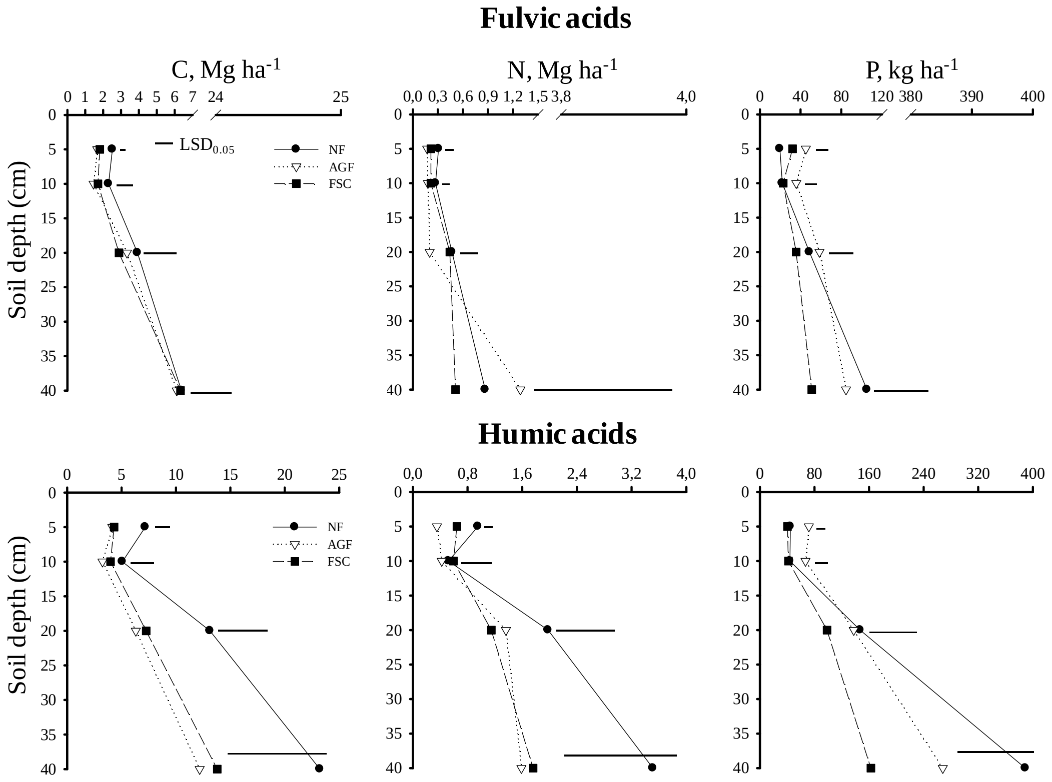

Figure 4. Stocks of carbon, nitrogen and phosphorus in fulvic and humic acids fractions in soils under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipality of Divino, Minas Gerais state. Horizontal bars indicate the least significant difference (LSD, $P < 0.05$).

In Araponga(I), the stocks of C and N were quite similar in FAs and HAs (Figure 5). The P stocks, in turn, were higher in HAs than FAs. A significant increase in the C stocks occurred in FAs in AGF, compared to the FSC system in almost all soil profile. At this site, FAs accounted for 26 and 15% of SOC in AGF and FSC, respectively. A similar pattern was verified in HAs, where greater C stocks were registered in AGF compared to FSC, mainly at soil surface.

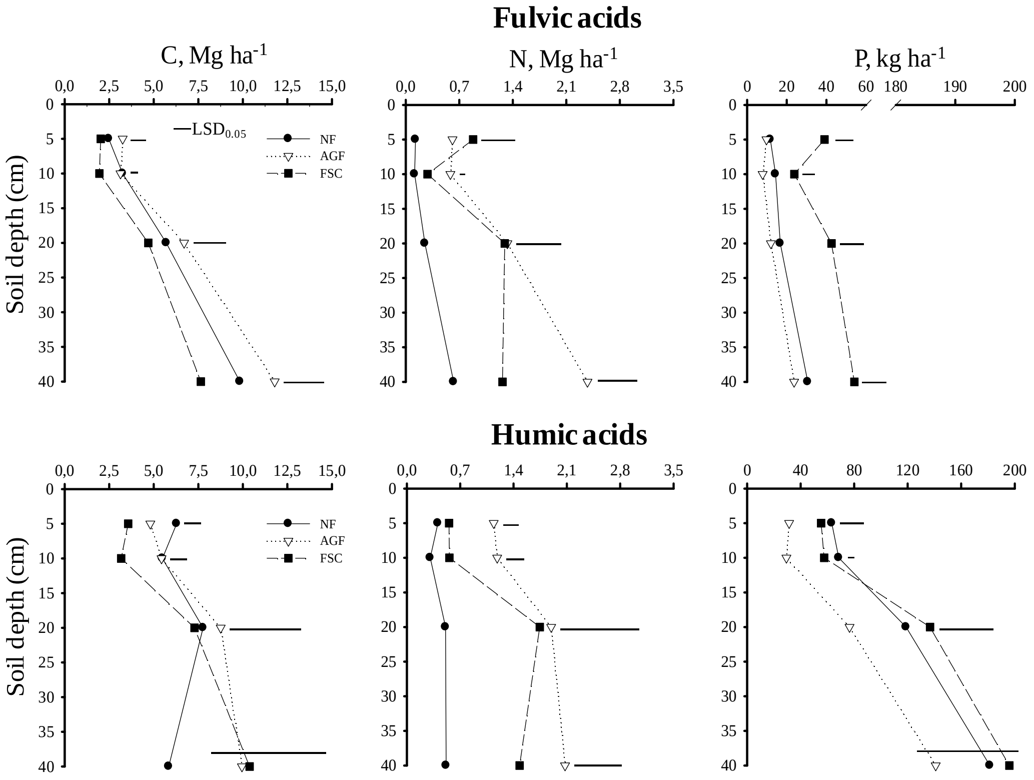

Figure 5. Stocks of carbon, nitrogen and phosphorus in fulvic and humic acids fractions in soils under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipality of Araponga(I), Minas Gerais state. Horizontal bars indicate the least significant difference (LSD, $P < 0.05$).

In general, the N stocks followed a behavior similar to that of C, but significant differences between the AGF and FSC systems were only verified at 40-cm depth for FAs and at 0-to 5- and 5- to 10-cm depths for HAs. In both conditions, AGF presented significant higher N contents. The trends for P stocks in the humic substances in Araponga(I) were conversely different from Divino (Figure 4). Significant higher P stocks occurred in FSC compared to the AGF system for both FAs and HAs, except for HAs at 20 to 40-cm soil depth. It suggests that most part of the organic P in AGF is associated to the most stable humic fraction (Humin), whereas FSC favors increases of P in the least stable fractions. It might indicate that P cycling in the FSC system can occur faster than in AGF, which has most part of organic P stabilized. One possible explanation for this behavior is that in the AGF system, the organic P in FAs and HAs has been potentially mineralized in order to supply the requirements for available P, since no inorganic P fertilizers are used in this area. NaOH-Po pool has been considered an important P source for the crop in low P-input systems (Guo et al., 2000; Verma et al., 2005).

In Araponga(II), no significant differences occurred in the C and N stocks for both FAs and HAs between the AGF and FSC systems at the soil surface (Figure 6). However, there were significant increases in the C stocks of the FAs fraction in FSC, compared to the AGF system at 20 and 40-cm soil depth. Opposite trend occurred in the HAs at 40-cm soil depth, where AGF presented higher C and N stocks than FSC system.

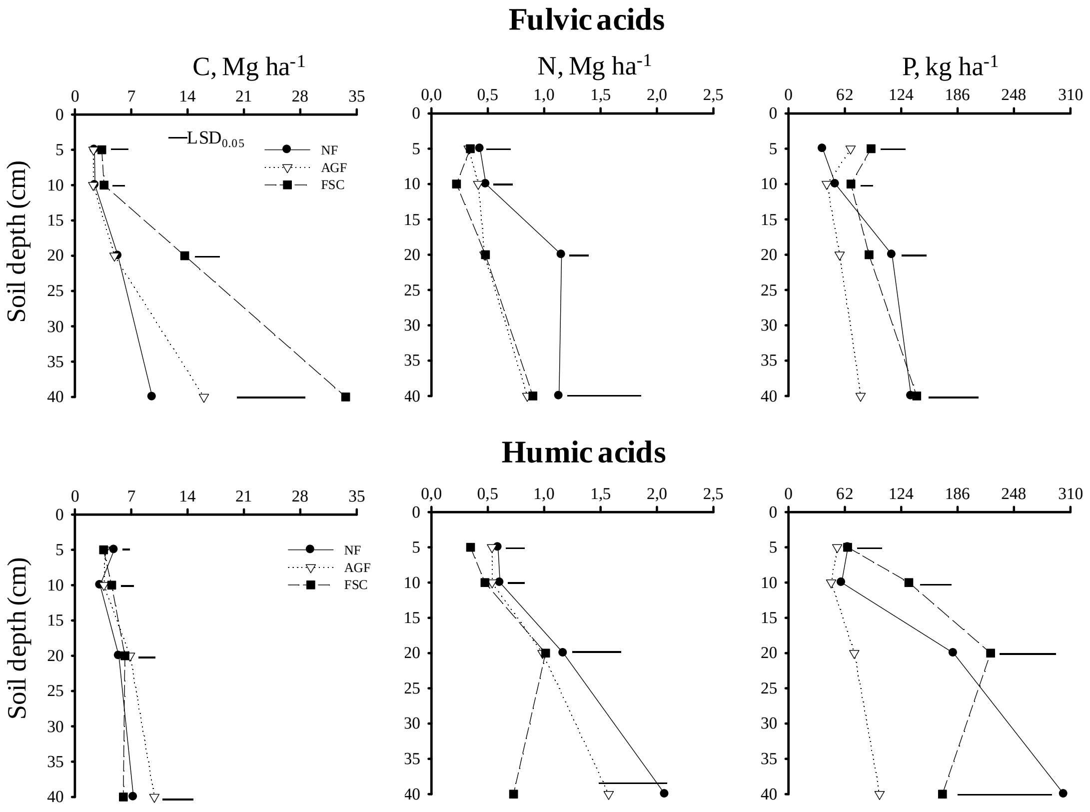

Figure 6. Stocks of carbon, nitrogen and phosphorus in fulvic and humic acids fractions in soils under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipality of Araponga(II), Minas Gerais state. Horizontal bars indicate the least significant difference (LSD, $P < 0.05$).

The increase of C stocks in FAs with increase of soil deep in the FSC systems indicate that larger amounts of most easily oxidizible humic fraction have been lost to the deepest soil layers, whereas in AGF system C stocks in FAs followed similar trend of the reference area. The greater C and N stocks in HAs at the deepest soil layer in AGF compared to FSC can be an indicative of the influence of cycling of the tree root system. The stocks of P in FAs and HAs in the FSC system tended to be higher than AGF. Similar patterns were verified in Araponga(I) soils (Figure 5) but differed from site at Divino (Figure 4).

The organic P dynamics in the humic substances seems to be closely related to the quality of organic residues in the AGF systems. For instance, C:P ratios of litter at Divino (553) was larger than the sites at Araponga (I) (372) and Araponga(II) (387). We believe that organic P in humic substances has been an important source for P supplying in the AGF systems. Further investigations are needed to stress the role of organic P in areas under agroforestry management.

3.5. Soil organic carbon fractionation

The fractions of organic C extracted under different gradients of oxidizing conditions are shown in Table 8. In general, in all sites there was no significant effect of soil management on the C contents in almost all soil fractions, even in those considered most easily oxidizible (Fractions 1 and 2). These results are not in accordance with the findings of Chan et al. (2001), which reported significant changes in the F1 as a result of different management practices. However, when the proportions of each C fraction in relation to the total SOC were calculated, the effect of soil management could be better evaluated. In Divino, for instance, C contents in the F1 at the soil surface accounted for 32 and 24% of the total SOC in

AGF and FSC systems, respectively (Table 8), suggesting that agroforestry increased the proportion of easily oxidizable organic C.

Table 8. Fractionation of soil organic carbon (g kg^{-1}) from soils under full-sun coffee (FSC) and agroforestry-coffee (AGF) systems in different municipalities of Zona da Mata, Minas Gerais state (values in parentheses are percentages of total soil organic carbon)

Organic C	Divino			Araponga(I)			Araponga(II)		
fractions[a]	AGF	FSC	LSD[b]	AGF	FSC	LSD	AGF	FSC	LSD
				0-5 cm					
F1	8.59 (32)	5.95 (24)	10.3	10.1 (33)	10.0 (29)	2.0	9.23 (31)	9.66 (31)	4.4
F2	5.45 (21)	6.10 (25)	8.2	6.96 (22)	7.19 (21)	4.2	7.80 (26)	7.08 (23)	4.5
F3	7.77 (29)	7.69 (31)	6.8	9.72 (31)	11.0 (32)	3.2	9.54 (32)	9.88 (32)	3.3
F4	4.79 (18)	4.73 (19)	15.3	4.24 (14)	6.42 (19)	4.3	3.04 (10)	4.27 (14)	6.5
				5-10 cm					
F1	9.53 (37)	8.79 (39)	4.4	7.74 (29)	7.44 (27)	2.3	8.63 (33)	6.50 (26)	2.1
F2	6.05 (24)	4.66 (21)	6.7	5.97 (22)	5.24 (19)	3.6	7.22 (27)	6.12 (25)	3.1
F3	6.61 (26)	5.96 (26)	9.9	6.90 (26)	8.49 (30)	3.6	5.41 (21)	7.68 (31)	3.5
F4	3.52 (14)	3.09 (14)	5.6	6.17 (23)	6.76 (24)	8.0	5.06 (19)	4.39 (18)	6.1

[a] F1 = 3 mol L^{-1} H_2SO_4; F2 = 6–3 mol L^{-1} H_2SO_4; F3 = 9–6 mol L^{-1} H_2SO_4; F4 = Total SOC – 9 mol L^{-1} H_2SO_4; [b] LSD: least significant difference ($P < 0.05$).

In Araponga(I), a similar pattern was verified at the upper soil layer. At this site, the proportional increase of C in the F1 in the AGF system was followed by a decrease in the relative proportion of F4. A reverse trend occurred in the FSC system. In Araponga(II), such trends were not evident at the soil surface, but it also occurred at 5-10 cm layer.

The proportional changes in the most oxidizible C fraction (F1) indicate that it can be considered a more sensitive indicator of changes in the SOM as a result of different soil management practices, in comparison to isolated measurements of total SOC contents (Chan et al., 2001; Maia et al., 2007).

The lability of SOC and the C management index (CMI) are presented in Table 9. The CMI has been used to provide a sensitive measure of the rate of change in soil C dynamics of agricultural systems related to a more stable reference soil (Blair et al., 1995). Actually, the absolute values of CMI are not important, but the changes reflect how different management strategies are affecting the soil C dynamics over time.

Table 9. Labile and non-labile C and Carbon Management Index from areas under full-sun coffee (FSC) and agroforestry-coffee (AGF) systems in the municipalities of Divino, Araponga(I) and Araponga(II)

	Lability[a]		Indexes[b]			
Site/system	Labile carbon (C_L)	Non-labile carbon (C_{NL})	Carbon pool index (CPI)	Lability of carbon (L)	Lability index (LI)	Carbon management index (CMI)
	----------- g kg^{-1} --------					
Divino			*0-5cm*			
AGF	8.59	12.55	0.31	0.69	1.09	34
FSC	5.95	12.43	0.28	0.48	0.77	22
$t_{(0.05)}$	ns	ns	ns	*	*	
Araponga(I)						
AGF	10.08	14.10	0.41	0.73	0.97	40
FSC	10.00	17.39	0.45	0.58	0.85	38
$t_{(0.05)}$	ns	ns	ns	*	ns	
Araponga(II)						
AGF	9.23	12.58	0.51	0.73	1.73	89
FSC	9.66	14.15	0.51	0.69	1.58	81
$t_{(0.05)}$	ns	ns	ns	ns	ns	
Divino			*5-10cm*			
AGF	9.53	10.12	0.46	0.96	1.07	49
FSC	8.79	9.05	0.39	0.98	1.06	41
$t_{(0.05)}$	ns	ns	ns	ns	ns	
Araponga(I)						
AGF	7.74	13.07	0.44	0.62	1.07	47
FSC	7.44	15.25	0.46	0.50	0.86	39
$t_{(0.05)}$	ns	ns	ns	ns	ns	
Araponga(II)						
AGF	8.63	10.48	0.57	0.88	1.52	87
FSC	6.50	12.07	0.54	0.55	0.97	53
$t_{(0.05)}$	*	ns	ns	ns	ns	

[a] Labile C assumed as being organic C extracted from F1; Non-labile C assumed as being organic C extracted from F3+F4; [b] Calculated indexes: CPI = $SOC_{sample}/SOC_{reference}$; L = C_L/C_{NL}; LI = $L_{sample}/L_{reference}$; CMI = CPI x LI x 100.

The adoption of agroforestry management resulted in the increase in the CMI in all sites, suggesting the rehabilitation or enhancement of the SOM levels (Leite et al., 2003). Increases on the CMI in AGF systems seem to be mainly related to the patterns of the lability of C. Since derivation of the CMI take into account CPI and LI indexes, our data showed that increases on LI index were more representative than in CPI in the calculation of CMI in the AGF systems soils (Table 9). These results stress the importance of agroforestry in promoting increases in more labile C components, which represent an important source of energy to the soil microbial community.

4. Conclusions

The potential of Agroforestry in increasing C storage depended on the characteristics of the systems in each particular environmental condition. In Divino, agroforestry increased soil C stocks at the soil surface in 9% in relation to full-sun coffee system. In other particular conditions, such as Araponga(II) soils, the C storage was influenced by soil bulk density. A similar pattern can be drawn to N stocks, but not in relation to the P dynamics. However, the increase on the P stocks as influenced by agroforestry management could not be generalized to all sites, being only evident in Divino soils. Similar patterns occurred in different pools, such as humic substances, suggesting a great heterogeneity among the studied sites.

The dynamics of C, N and P in the soil has been strongly influenced by the quality of organic residues in the agroforestry systems. The difference in the chemical composition of litter at the three sites seems to drive the patterns of nutrient dynamics and soil microbiota.

Under a qualitative point of view of soil organic matter, agroforestry systems represent a more attractive option of management for increasing the proportion of more labile C forms. It has been considered an important contribution for the enhancement of soil organic matter levels, as indicated by the carbon management index.

Since there are no previous studies providing baseline data similar to those reported by the present study, these data represent only one step in a scale of time, limiting a final prediction of the potential of agroforestry systems in sequestering C. Furthermore, other relevant aspects that were not object of our investigation, such as root-system dynamics, need to be better understood and measured in order to obtain a more realistic analysis of the effect of agroforestry management in the region.

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CHAPTER 3

Soil aggregation and distribution of C and N in different fractions under agroforestry- and full sun coffee systems

Abstract – The role of soil organic matter in the mechanisms of soil aggregates stabilization in tropical soils (e.g. Oxisols) and needs to be better understood. The objectives of the present study were i) to evaluate the distribution of different classes of aggregates; ii) to measure the organic C within aggregate fractions and iii) to evaluate the distribution of intra-aggregate particulate organic matter (iPOM) in macroaggregates in soils under agroforestry and full-sun coffee systems. The work was carried out in three smallholding coffee production areas under agroforestry-coffee (AGF) and full-sun coffee (FSC) systems situated at the municipalities of Divino and Araponga in the Atlantic Coastal Forest biome in the state of Minas Gerais, Brazil. The soil was collected at 0-5 and 5-10-cm deep intervals and was fractionated in large macroaggregates (> 2000 µm), small macroaggregates (250–2000 µm) and microaggregates (53–250 µm). Free POM, coarse and fine iPOM were isolated from small macroaggregates. Total C and N contents in each aggregate-size fractions were measured. The distribution of aggregate fractions in a bulk soil basis increased in the following order: small macroaggregates > large macroaggregates > microaggregates. The C concentration in the 250–2000 µm fraction represented most part of soil organic carbon (SOC) in both soil layers. In Divino, C contents in the > 2000 µm fraction in the AGF system accounted for 37% of total SOC against 19% in FSC at 0-5 cm soil layer. In Araponga(I), soils with these proportions were 22% and 8% in the AGF and FSC systems, respectively. In Divino, the free POM amounts in the AGF system were 2.8 and 2.0 times greater than in FSC in the 0-5 and 5-10 cm layers, respectively. In Araponga(I), these proportions were 1.3- and 1.8-fold greater in AGF compared to the FSC system. The fine iPOM-C contents were on average 51% higher in the AGF than FSC system in Divino at the soil surface, suggesting that this aggregate fraction may be considered as an early indicator of increased C sequestration under the AGF system. In Divino and Araponga(I), the agroforestry systems enhanced soil aggregation by increasing the amount of more stable macroaggregates and promoted an increased protection of C and N in the microaggregates within macroaggregates. Therefore, the long-term stability of C and N in these sites is likely dependent on the continuation of agroforestry-coffee cultivation. The influence of the agroforestry management on the dynamics of C and N storage within different aggregates fractions depends on inherent characteristics of the environment in which it is developed.

Key words: wet-sieving; particulate organic matter; aggregate-stabilization; Oxisols.

1. Introduction

The intensive use of any ecosystem leads to an inevitable condition of degradation of its resources. The deforestation of the Atlantic Coastal Rainforest, one of most important Brazilian biomes, and the further expansion of coffee cultivation (*Coffea arabica* L.) during the mid-19th century caused a severe damage to the ecosystem, which has lead to land degradation (Valverde, 1958). Coffee is normally cultivated on hills, which results in a sensitive environmental condition for soil erosion and other degrading processes. As a consequence of the decline of soil quality, farmers usually abandon the old coffee fields, which are converted into pasture, and use new more fertile sites, creating a non-sustainable agricultural scenario. Agroforestry systems have been pointed out as a major opportunity to deal with the problems related to land-use in this region (Cardoso et al., 2001; Mendonça et al., 2001; Mendonça and Stott, 2003).

Soil organic matter (SOM) has been considered as a useful indicator of soil quality due to its close relationship with important soil functions (Doran and Parkin, 1994; Reeves, 1997; Manlay et al., 2007). In agroforestry systems, the constant input of organic residues enhances SOM levels, in comparison to monoculture agricultural systems (Mendonça et al., 2001; Perez et al., 2004; Maia et al., 2007).

In tropical soils (e.g. Oxisols), it has been stated that minerals such as Fe- and Al-oxides and 1:1 clays are the dominant stabilizing agents of soil aggregation, since they can act basically i) as a flocculant like calcium, ii) as links between clay and polymers and iii) as cement after precipitation, as gel on clay surfaces (Bissonnais, 1995). However, other studies have stressed the role of SOM on the mechanisms of soil aggregates stabilization (Denef et al., 2007;

Zotarelli et al., 2007). On these works, the focus of SOM effects on the mechanical strength of aggregates lies on the fact that aggregates are arranged in a hierarchy of organo-mineral complexes and it has been assumed that different mechanisms act combining clay, silt, sand and organic matter into floccules and microaggregates (< 250 µm), and increasing macroaggregates(< 250 µm) (Tisdall and Oades, 1982).

The formation rate of new macro- and microaggregates is directly influenced by the dynamics of the particulate organic matter (POM). According to the conceptual model of aggregate formation postulated by Six et al. (2000), macroaggregates (250–2000 µm) are formed around fresh residue which then becomes coarse intra-aggregate POM (iPOM). As a result of decomposition and subsequent fragmentation of coarse iPOM, the fine iPOM is originated within macroaggregate. As fine iPOM is formed, it gradually becomes encrusted with clay particles and microbial products to form microaggregates within macroaggregates (Six et al., 1998; Six et al., 1999). Consequently, the fine iPOM is expected to be older than coarse iPOM and can be an important factor contributing to C-sequestration since its fraction has a slower turnover than C into macroaggregates (Six et al., 2002).

In a recent work performed in two Brazilian Oxisols (Zotarelli et al., 2007), the concept of microaggregate formation from macroaggregates explained the POM-C distribution in the aggregate size classes in experiments under no-tillage. In conclusion, the authors stated that in Oxisols the conceptual model of macroaggregate turnover determining the stabilization of SOM as fine iPOM-C in microaggregates (Six et al., 1998, 1999) can be applied.

There is scant information on the mechanism of SOM storage in aggregate fractions in areas under agroforestry systems in Brazilian soils. Most available information derives from studies performed under conventional and no-tillage management. In agroforestry systems, some questions still need to be answered: do the recent tree-derived residual inputs influence on SOM storage within soil aggregate fractions as found in no-tillage experiments? How does agroforestry management contribute to C sequestration during aggregate formation? We hypothesize that agroforestry systems enhance C-sequestration by increasing C storage in different aggregate fractions (especially macroaggregates) due to the recent inputs of organic residues derived from trees. The present study aims i) to evaluate the distribution of different classes of aggregates by adopting the standard wet-sieving procedure ; ii) to measure the organic C within aggregates fractions and iii) to evaluate the distribution of iPOM in macroaggregates in soils under agroforestry-coffee and full-sun coffee systems in three agricultural smallholding-farms in the Atlantic Coastal Rainforest.

2. Materials and methods

2.1. General description of study area

The study was carried out in the Zona da Mata (about 36,000 km^2), located in the Atlantic Coastal Rainforest biome of the state of Minas Gerais, Brazil (Figure 1). The region is characterized by a tropical highland climate (average temperature and precipitation of 18 °C and 1500 mm, respectively, with 2 to 4 months of dry period), steep slopes (20 to 45%) and altitudes ranging from 200 to 1800 m (Cardoso, 2002). The parental rock is gneiss and the dominant soil types are deep and well drained Oxisols, which are acid and poor in nutrients (Ker, 1995; Mendonça and Stott, 2003). More detailed information on pedology, agriculture and sociology of the Zona da Mata region was previously published by Cardoso et al. (2001).

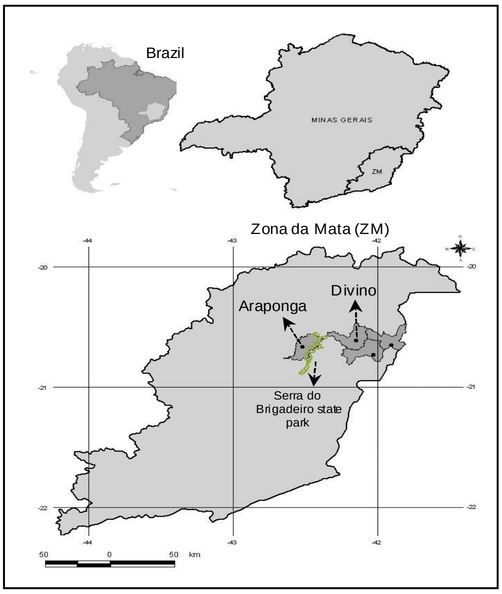

Figure 1. Localization of the municipalities of the study sites in the Zona da Mata (ZM), state of Minas Gerais.

2.2. *Specific study sites and soil sampling*

Three smallholder agroforestry coffee (*Coffea arabica* L.) systems (AGF) and three full sun coffee (FSC) systems fields with approximately 1.5 hectares and over 12 years of age were studied. These areas were situated at the municipalities of Divino and Araponga (Figure 1), managed by smallholding farmers. More detailed information about the historical land-use and management of the studied systems are presented in Box 1.

Box 1. Historical of land use and management of selected sites

Divino (coordinate: 20º33'S, 42º11'W; altitude: 1,160 m)
Agroforestry-coffee system: Prior cultivation this area was deforested and use as pasture, cultivated with *Melinis minutiflora* P. Beauv. (common name: Capim gordura). Some tree species of *Piptadenia gonoacantha* J.F. Macbr. (Jacaré) spontaneously grew in the pasture area. The intensive use of soil with pasture for several years (exact time unknown) declined the soil quality. Agroforestry-coffee system was implemented in 1994. The study was concentrated in an area of approximately 3,150 m^2 with 600 coffee-trees (*Coffea Arabica* L.) spaced in 3.5 m x 1.5 m. Native tree species were intercropped with coffee. The main tree species is *Luehea grandiflora* Mart (Açoita-cavalo), although other species such as *Aegiphila sellowiana* Cham. (Papagaio), *Erythrina verna* Vell (Mulungu), *Musa sp*. L. (Banana) and *Zeyheria tuberculosa* (Vell.) Bur. (Ipê-preto) can be found. Fertilizers and limestone were not applied during the two first years of the establishment of agroforestry systems. After this period, 3 Mg of limestone were applied in the projection of coffee-tree canopy. From 1999 to 2002, 50 g per plant of a mixture of ammonium sulfate, potassium chloride and monocalcium phosphate in a proportion of 3-1-1 was applied in a rate of 4 applications per year, totalizing 200 g per plant. In 2000, the trees species intercropped with coffee were drastically pruned, and the residues were left on the soil surface between the coffee rows. From 2003 to 2006 the farmer started the transition to organic coffee and stopped the inorganic fertilization. During this period, cow manure, castor bean cake, residues of leguminous species, supermagro[/2] and cattle urine were applied (Table 1). The productivity during organic cultivation was approximately 1.5 kg of coffee (pulp removed) per plant. In 2007, the organic coffee production was interrupted. Since this year, 100 g per plant of N-P-K fertilizer (20-5-20) has been applied twice a year (Table 1). The lower branches of the trees are pruned every 2 years and the residues are left on the soil surface, between coffee rows. Sporadically, jackbean, pumpkin and castor bean are cultivated between coffee rows. The mean annual productivity in 2007, 2008 and 2009 were about 0.90, 0.72 and 0.60 kg of coffee per plant. Full sun coffee system: the historical of land use is identical to the previous described site. The forest was converted in pasture for several years (exact time unknown) and further in coffee cultivation. The area has approximately 2,000 m^2 with 1,000 coffee trees spaced in 2 m x 1 m. There are no trees intercropped with coffee. Soil liming is not performed and there is no application of organic manure. Chemical fertilization of soil in 2007, 2008 and 2009 was done by applying 300, 200 and 150 g per plant of N-P-K (20-5-20). The mean annual productivity in 2007, 2008 and 2009 were 0.93, 1.2 and 0.06 kg of coffee per plant, respectively.

Araponga(I) (coordinate: 20º48'S, 42º32'W; altitude: 1,040 m)
Agroforestry-coffee system: In the past this area was deforested and used as pasture for several years (exact time is unknown). Then, coffee was cultivated under conventional management during 15 years, which resulted in severe reduction of soil fertility mainly caused by soil erosion. In 1995, agroforestry-coffee system was implemented in an area of approximately 5,040 m^2 with 1,200 coffee-trees spaced in 3 m x 1.2 m. The system was established in the highest slope area of the farm. The main tree species intercropped with coffee is *Persea americana* Mill. (Abacate). Soil is limed once a year, and there is no chemical fertilizer application. Chicken manure was used in the organic fertilization in 2001. Cow manure is applied annually and foliar fertilization is done by using supermagro twice a year (Table 1). Spontaneous vegetation is slashed 1- or 2-times per year and the residues are kept on the soil. Bean straw is applied annually on the rows. The lower branches of the tree-canopy are pruned during the dry season (June-July), after coffee harvesting. The residues of prune are kept on the soil surface avoiding soil erosion. The annual productivity is around 0.62 kg of coffee per plant. Full sun coffee system: the historical of land use is identical to the previous described site. The area has approximately 4,000 m^2 with 2,000 coffee trees spaced in 2 m x 1 m. The system was implanted in the lowest slope position, immediately below of the agroforestry-coffee area. There are no trees intercropped with coffee, but corn and beans had been planted between coffee rows. Soil liming and N-P-K fertilizer (20-5-20) applications are performed annually (Table 1) and there is no organic fertilization. The annual coffee productivity is approximately 0.79 kg of coffee per plant.

Araponga(II) (coordinate: 20º41'S, 42º31'W; altitude: 1,040 m)
Agroforestry-coffee system: In the past this area was deforested and used as pasture for several years (exact time is unknown). Further, it was burned and cultivated with rice during 7 years. During rice cultivation the soil was usually plowed by animal traction. Rice cultivation caused severe soil erosion leading to a decline of soil quality. After rice the area was cultivated with corn and beans, and finally, it was converted in pasture for 3 years when soil achieved its lowest level of fertility. In order to reclaim the land, in 1994 *Pennisetum purpureum* Schum. cv. Napier (capim-napier) and trees species such as, *Colubrina glandulosa* Perkins (sobrasil), *Hovenia dulcis* Thunb. (uva-do-japão), *Inga sessilis* Mart. and *Inga subnuda* subsp. *luschnathiana* (Benth.) T.D. Penn. were planted. The Inga species were introduced later on and the other tree species were removed. In 1998, Agroforestry-coffee was implemented. Soil liming was done in 1999, 2001, 2004 and 2006 by adding 200 g of limestone per m^2. The coffee field which includes the area covered by Inga species has approximately 1,500 m^2 with 500 coffee-trees spaced in 3 m x 1 m. At the beginning, corn and beans was usually intercropped between coffee rows, but since four years ago such inter-cropping is not performed. In the cultivation of corn and/or beans, N-P-K fertilizer (4-18-8) was applied on a rate of 30 g per m^2. Trees are not pruned but the herbaceous spontaneous vegetation is slashed three times per year. The residues of slashing are kept on the soil surface. N-P-K (20-5-20) and foliar fertilizer are applied annually (Table 1). There is no organic fertilization. The mean of coffee productivity in 2007 was 0.36 kg of coffee per plant. Full sun coffee system: the historical of land use is identical of the previous described site. This area corresponds to the other part in which Inga species were not planted. It has approximately 7,500 m^2 with 2,500 coffee trees spaced in 3 m x 1 m. The main difference in relation to agroforestry-coffee is the absence of trees. The mean of coffee productivity in 2007 was 0.45 kg of coffee per plant. Other information about chemical fertilization is presented in Table 1.

[/2] Liquid biofertilizer for foliar application prepared from fresh manure diluted in water and enriched with bone meal, blood, fish scraps (the latter two contributing minerals), and unrefined sugar and milk to stimulate fermentation. This mix is fermented anaerobically for about 1.5 months. Other organic liquid fertilizers include fermented, cattle urine and an infusion prepared from manure (Velásquez, 2002).

In each selected site, areas under natural forest fragments (NF) were sampled and used to represent the native or steady state condition of the soil. In all cases, NF fragments were at the same position on the landscape of the coffee-cultivated areas.

The more detailed characterization of the studied sites is presented in Table 1.

Table 1. Characterization of the agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino and Araponga.

	Divino		Araponga(I)		Araponga(II)	
Item	**AGF**	**FSC**	**AGF**	**FSC**	**AGF**	**FSC**
Area size, m^2	3,150	2,000	5,040	4,000	1,500	7,500
Number of coffee trees	600	1,000	1,200	2,000	500	2,500
Spacing of coffee trees, m	3.5 x 1.5	2 x 1	3 x 1.2	2 x 1	3 x 1	3 x 1
Number of trees per ha	150 - 200	-	200	-	~150	-
Fertilizer N-P-K (20-5-20), g/plant	100[/b]	150[/c]	na	180	200[/d]	200[/d]
Cow manure, kg	10,000[/e]	na	2,880	na	na	na
Castor bean residue, kg	600[/e]	na	na	na	na	na
Compost, kg	5,000[/e]	na	na	na	na	na
Limestone, g/m^2	950[/f]	na	20[/g]	40[/g]	200[/h]	200[/h]
Foliar fertilization (supermagro)	yes	na	yes	na	na	na
Biomass production[/a] (litter)						
Coffee trees, kg/year	720	890	1,440	1,780	600	2,225
Trees, kg/year	2,398	-	2,004	-	4,331	-

[/a] Coffee trees: estimated from Campanha et al. (2007) where litter production (dry matter) in agroforestry is 50.7 g m^{-2} month^{-1} and sun coffee system is around 37.2 g m^{-2} month^{-1}; Other trees: measured by Duarte (2007);

[/b] From 2006 to 2009, applied twice a year; From 1999 to 2002: 200 g plant^{-1} year^{-1} of a mixture of ammonium sulfate, potassium chloride and monocalcium phosphate in a proportion of 3-1-1;

[/c] Performed in 2008; In 2006 and 2007, N-P-K (20-5-20) was applied on a rate of 150 and 100 g per plant, respectively, twice a year;

[/d] applied once a year;

[/e] Total applied during organic cultivation from 2003 to 2006; supermagro applied twice a year;

na: not applied;

[/f] applied in 1997;

[/g] applied annually;

[/h] total applied in 1999, 2001, 2004 and 2006.

The chemical composition of senescent leaves of the main trees species used in the agroforestry systems was previously measured by Duarte (2007) and a summary is presented in Table 2.

Table 2. Chemical composition and C:N, LG:N, LG:PP and LG+PP:N ratios of senescent leaves of the main tree species in areas under agroforestry-coffee systems at three municipalities of Zona da Mata, Minas Gerais state

Site/ species	Chemical composition[a] C	N	P	LG	HC	CL	PP	Ratio C:N	LG:N	LG:PP	LG+PP:N
	---------------------------- % ----------------------------										
Divino											
Luechea grandiflora	65.8	2.02	0.119	13.6	19.2	17.2	8.3	32.6	6.7	1.6	10.8
Araponga(I)											
Persea americana	60.7	2.05	0.163	21.0	13.4	12.8	7.3	29.6	10.2	2.9	13.8
Araponga(II)											
Inga subnuda	54.6	3.17	0.141	27.3	23.9	21.3	4.8	17.2	8.6	5.7	10.1

[a] C:carbon; N: nitrogen; P: phosphorus; LG: lignin; HC: Hemicellulose; CL: Cellulose; PP: total polyphenols. Adapted from Duarte (2007).

The soil samples were collected at intervals of 0-5, 5-10, 10-20 and 20-40 cm of depth from December 2006 to March 2007 (rainy season). In order to guarantee a representative sampling procedure, four sub-samples randomly distributed between coffee rows were taken from each site, and then combined to form one replicate. Four replicates were collected. Before the samples were taken, the litter layer was removed. Immediately after sampling, approximately 300 grams of soil from 0-5 and 5-10 cm layers were separated and frozen to perform a further microbiological analysis. Once in the laboratory, the moist soil was air-dried, sieved through a 2-mm sieve and stored at room temperature. Selected physical and chemical characteristics of the studied soils are shown in Table 3.

Table 3. Values of particle sized fractions, pH (H_20), cation exchange capacity (CEC) and base saturation of soils under native forest (NF), agroforestry coffee (AGF) and full sun coffee (FSC) systems at 0-10 cm layer in the municipalities of Divino, Araponga(I) and Araponga(II)

	Divino			Araponga(I)			Araponga(II)		
Soil characteristic	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
Particle size, g kg^{-1}									
Sand	504	573	519	493	520	495	474	388	444
Silt	237	122	165	108	119	124	124	113	134
Clay	259	305	316	399	361	381	402	499	422
pH H_2O (1:2.5)	6.4	6.0	6.1	4.9	5.8	5.8	4.8	5.6	6.2
CEC, cmol$_c$ dm^{-3}	21.4	11.1	11.6	16.6	11.1	10.1	17.7	12.2	11.0
Base saturation, %	77.0	69.0	63.0	2.0	46.0	51.0	1.0	30.0	40.0

Mean weight diameter (MWD) were determined as Castro Filho et al. (2002):

$$\mathrm{MWD} = \sum x_i y_i \qquad (1)$$

where y_i is the proportion of each size fraction with respect to the total sample and x_i is the mean diameter of the size classes (mm).

The study of particulate organic matter (POM) was concentrated in small macroaggregates (250–2000 μm) fraction due to its close relationship with microbiological activity (Six et al., 2001). Briefly, a subsample of 10-g of slaking-resistant small macroaggregates was then suspended in 1.85 g cm^{-3} NaI to isolate the free POM (fPOM) (Six et al., 1998, Sohi et al., 2001). After flotation of fPOM, small macroaggregates were dispersed in 0.5% Na-hexametaphosphate and passed through 250- and 53-μm sieves to isolate the coarse and fine intra-aggregate POM (iPOM) fractions, respectively (Fig. 2) (Six et al., 2001). Considering that the dispersion of aggregates by using NaI was minimal, the release of iPOM was only a small proportion of the fPOM (Six et al., 1999).

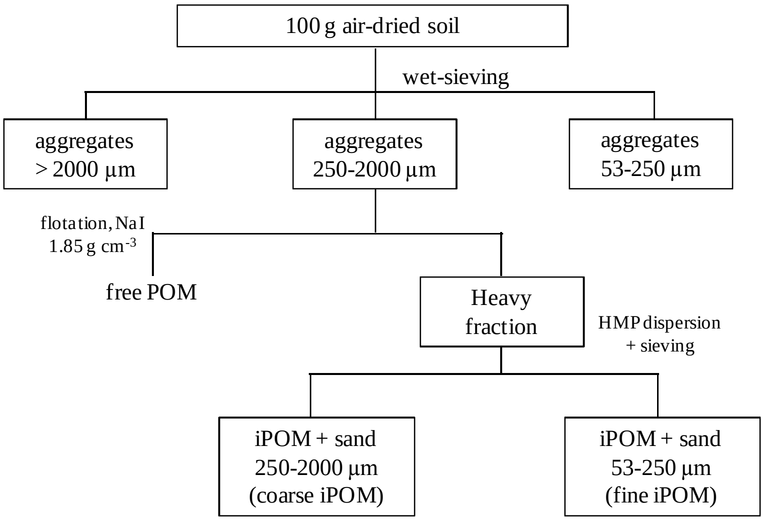

Figure 2. Fractionation scheme to isolate aggregate and aggregate-associated organic matter fractions. POM = particulate organic matter; i = intra-aggregate; HMP = Hexametaphosphate-Na (Adapted from Six et al., 2002).

2.3. Carbon and Nitrogen analysis

Total C and N analyses were performed on: (1) total soil, (2) water-stable aggregate fractions (> 2000, 250–2000 and 53–250 μm) and (3) fPOM and coarse- and fine iPOM fractions. Total C and N contents in total soil and water-stable aggregate fractions were measured, respectively, by the oxidation of $K_2Cr_2O_7$ in the presence of H_2SO_4 and the titration of the excess dichromate with standardized $FeSO_4$ (Yeomans and Bremner, 1988) and by digestion with concentrated H_2SO_4 and dosed by Kjedahl distillation (Tedesco et al., 1995). The C and N content in fPOM and coarse and fine iPOM were determined by dry combustion on a CHNS analyzer (Perkin Elmer 2400).

Sand-free C concentrations (g kg^{-1} sand-free macroaggregates) in coarse- and fine iPOM were calculated as proposed by Six et al. (1998)

$$\text{Sand - free C}_{\text{fraction}} = \frac{\text{C}_{\text{fraction}}}{[1 - (\text{sand proportion})_{\text{fraction}}]} \qquad (2)$$

where C_{fraction} was the C [%] in the respective aggregate and sand proportion fraction was the relative proportion of sand in the aggregate fraction. Although both coarse and fine iPOM fractions consisted of sand plus POM, the weight of the POM was considered negligible compared to the weight of the sand (Denef et al., 2004).

2.4. Statistical analysis

The field experiment was arranged in a randomized complete design with four replicates. Each evaluated site was considered as an independent experiment and were not compared. The effect of soil management was tested by performing the one-way ANOVA at $P < 0.05$, followed by the least significant difference (LSD at $P < 0.05$) post-hoc test.

3. Results

3.1. Distribution of water-stable aggregates

The distribution of aggregate size classes in the 0-5 and 5-10 cm soil layers is presented in Table 4. In general, the proportion of each aggregate fraction in a bulk soil basis increased in the following order: small macroaggregates (250–2000 μm) > large macroaggregates (> 2000 μm) > microaggregates (53–250 μm) ≅ < 53 μm. On average, the proportions of each class in relation to the total amount of soil fractions following this order were: 68, 19 and 8%, respectively.

The effect of soil management on the behavior of aggregate size classes was mainly observed in Araponga(I) in both soil layers (Table 4). At this site, the AGF system favored the formation of large aggregate size fraction, whereas the FSC system promoted a significant increase in the 53–250 μm fraction. A similar behavior was found in Araponga(II) at the 5-10 cm soil layer.

The mean weight diameter (MWD) varied from 0.79 to 2.10 mm and was significantly affected by land use, mainly in Araponga(I) and Araponga(II) soils. In Araponga(I), the MWD was higher in the FSC than AGF system for both soil layers (Table 4). In Araponga(II), higher MWD was registered in AGF (1.14 mm) compared to FSC (0.91 mm) in the 0-5 cm soil layer. However, the opposite was observed at 5-10 cm layer. In Divino, there was no significant effect of crop systems on the MWD.

Table 4. Soil water-stable aggregate size distribution and mean weight diameter (MWD) in the 0-5 and 5-10 cm layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at three municipalities of Zona da Mata, Minas Gerais state

			Soil fractions (μm)				
			>2000	250–2000	53–250	< 53$^{/a}$	MWD
Sites	Land use		----------	g aggregate kg^{-1}	unsieved bulk soil	---------	mm
					0-5 cm		
Divino	NF		5.3	767.8	85.3	141.6	0.84
	AGF		305.5	610.1	42.9	41.5	0.79
	FSC		210.3	684.5	62.3	42.9	1.15
		lsd$_{0.10}$	124.8	231.9	39.8	60.0	0.59
Araponga(I)	NF		175.6	634.4	64.6	125.4	1.05
	AGF		197.8	622.0	111.0	69.2	1.56
	FSC		96.2	661.8	170.4	71.6	2.10
		lsd$_{0.10}$	46.8	50.8	28.8	14.9	0.26
Araponga(II)	NF		190.8	615.9	70.0	123.3	1.11
	AGF		176.0	693.8	66.5	63.8	1.14
	FSC		175.7	666.8	49.3	108.3	0.91
		lsd$_{0.10}$	55.2	44.8	23.5	31.6	0.22
					5-10 cm		
Divino	NF		15.0	726.2	139.0	119.9	1.70
	AGF		283.1	642.0	45.2	29.7	1.06
	FSC		186.9	735.1	48.1	29.9	0.97
		lsd$_{0.10}$	37.7	36.6	30.7	39.0	0.24
Araponga(I)	NF		211.8	621.2	62.0	105.0	1.08
	AGF		216.4	656.6	74.8	52.2	1.27
	FSC		110.8	701.2	117.6	70.5	1.62
		lsd$_{0.10}$	30.3	16.7	19.1	18.2	0.16
Araponga(II)	NF		172.4	670.6	71.8	85.2	1.16
	AGF		126.4	770.6	58.2	44.9	1.01
	FSC		110.8	701.2	117.6	70.5	1.62
		lsd$_{0.10}$	33.5	22.6	27.0	31.6	0.29

$^{/a}$ calculated by difference; lsd$_{0.10}$: least significant difference ($P < 0.10$).

3.2. C and N storage and C/N ratio in water-stable aggregates

The total C an N contents and C/N ratio in water-stable aggregates are shown in Table 5. Considering the NF area as a reference, with C and N content considered as 100%, there were several reductions on the C and N contents in different soil fractions as a result of soil cultivation. Such reductions were higher in Divino and Araponga(I) soils than in Araponga(II). On average, considering a mean of C content in all aggregate fractions, the C reductions at the upper soil layer were 73, 67 and 40% in Divino, Araponga(I) and Araponga(II), respectively.

A similar behavior was verified at 5-10 cm layer. In Divino, the reductions in the C contents in large macroaggregates were higher in the FSC than AGF system, reaching 81% and 71% in FSC and 64% and 57% in the AGF systems at 0-5 and 5-10 cm soil layers, respectively. Similar pattern occurred in the microaggregate fraction at this site.

Table 5. Total C and N distribution (g per kg of aggregate) and C-to-N ratio in different soil water-stable aggregates size fractions from 0-5 and 5-10 cm layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at three municipalities of Zona da Mata, Minas Gerais state

		Soil fractions (μm)								
		> 2000			250–2000			53–250		
		C	N	C/N	C	N	C/N	C	N	C/N
Site	Land use	g kg^{-1}			g kg^{-1}			g kg^{-1}		
					0-5 cm					
Divino	NF	93.0	8.7	11	92.9	9.2	10	98.8	8.2	12
	AGF	33.9	3.1	11	27.3	2.5	11	30.4	2.8	11
	FSC	18.1	2.0	9	20.8	2.2	9	23.6	2.7	9
	lsd$_{0.10}$	6.1	3.5		3.5	2.0		6.8	2.7	
Araponga(I)	NF	92.1	6.5	14	93.2	6.2	15	74.7	5.2	14
	AGF	32.7	2.2	15	31.9	2.5	13	28.5	2.0	14
	FSC	22.2	1.7	13	31.5	2.3	14	24.4	2.2	11
	lsd$_{0.10}$	6.4	0.5		10.3	0.8		8.3	0.6	
Araponga(II)	NF	58.2	4.2	14	60.2	4.2	14	42.9	3.1	14
	AGF	38.6	3.0	13	34.3	3.1	11	27.7	2.4	12
	FSC	33.0	3.1	11	37.5	3.4	11	23.6	2.2	11
	lsd$_{0.10}$	6.2	0.5		10.1	0.7		7.8	0.7	
					5-10 cm					
Divino	NF	57.3	5.4	11	59.2	6.3	9	75.3	6.4	12
	AGF	24.6	2.2	11	21.0	1.9	11	25.0	2.1	12
	FSC	16.4	1.7	10	18.5	2.0	9	19.7	2.1	9
	lsd$_{0.10}$	5.6	1.8		8.6	2.3		5.3	3.0	
Araponga(I)	NF	70.9	5.3	13	62.3	4.6	14	61.9	5.0	12
	AGF	30.4	2.6	12	28.7	2.5	11	21.8	2.1	10
	FSC	22.8	2.1	11	27.4	2.5	11	22.3	2.2	10
	lsd$_{0.10}$	5.7	0.4		4.4	0.4		9.4	0.5	
Araponga(II)	NF	42.8	3.4	13	40.9	3.3	12	33.7	2.9	12
	AGF	28.0	2.4	12	27.9	2.2	13	20.9	1.8	12
	FSC	24.3	2.3	11	22.1	2.2	10	15.8	1.7	9
	lsd$_{0.10}$	7.8	0.6		8.9	0.7		8.2	0.6	

lsd$_{0.10}$: least significant difference ($P < 0.10$).

The C contents were significantly higher in the AGF than FSC system in almost all aggregate sized fractions in Divino for both soil layers. Similar trends occurred in the N contents in large macroaggregates. Higher C and N contents were also registered in large macroaggregates from the AGF than FSC system in Araponga(I) (Table 5).

In general, the highest C concentrations occurred in macroaggregates in all sites, whereas N contents were almost constant among the different fractions. The C/N ratio ranged from 9 to 15 (Table 5) and it was not related to aggregate size, being relatively uniform across aggregate classes. At the soil surface, the AGF systems tended to show higher C/N ratios in large macroaggregates compared to the FSC systems in all evaluated sites, as a result of the highest C contents in this fraction.

The C contents in each aggregate size fraction expressed on a whole soil basis are shown in Figure 3. In all sites and soil layers, the C concentrations increased in the following order: microaggregates (7%) < large macroaggregates (20%) < small macroaggregates (74% of total). C concentration in small macroaggregates (250–2000 μm) represented the most part of soil organic C (SOC) in both soil layers (Figure 3). Similar trends were found for N contents (data not shown). In all sites, the AGF systems promoted the highest proportion of C in large macroaggregates compared to FSC. In Divino, C contents in the > 2000 μm fraction in the AGF system accounted for 37% of total SOC against 19% in FSC at 0-5 cm soil layer. In Araponga(I) soils, these proportions were 22% and 8% in the AGF and FSC systems, respectively.

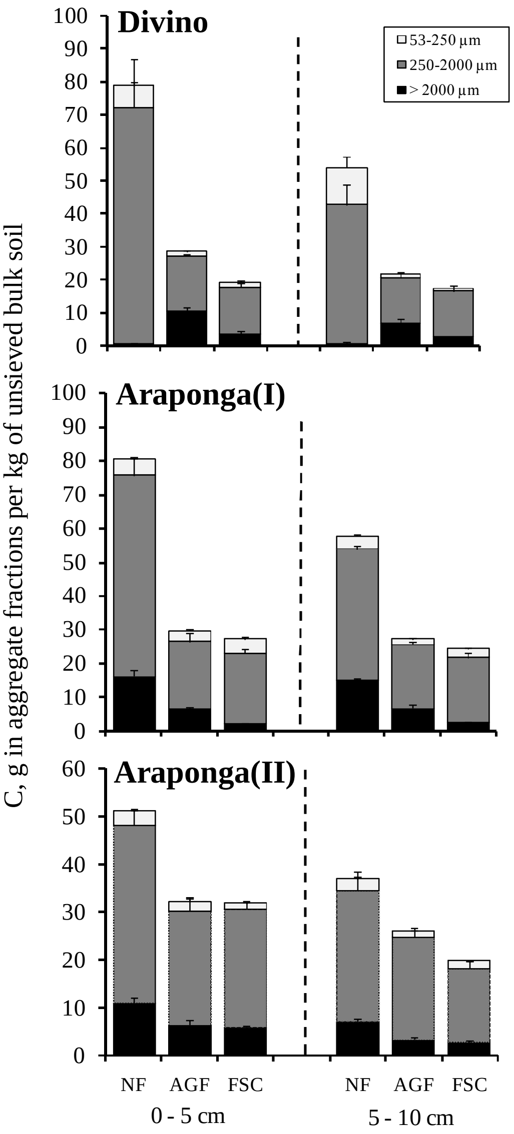

Figure 3. Distribution of organic C per kg of bulk soil in water-stable aggregates fractions extracted from 0-5 and 5-10 cm soil layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in three municipalities of Zona da Mata, Minas Gerais state. Bars represent mean ± standard error (*n*=4).

3.3. C and N contents in free- and intraparticulate organic matter

Figures 4 and 5 shown C and N contents in free, coarse and fine intra-POM fractions isolated from small macroaggregates (250 – 2000µm).

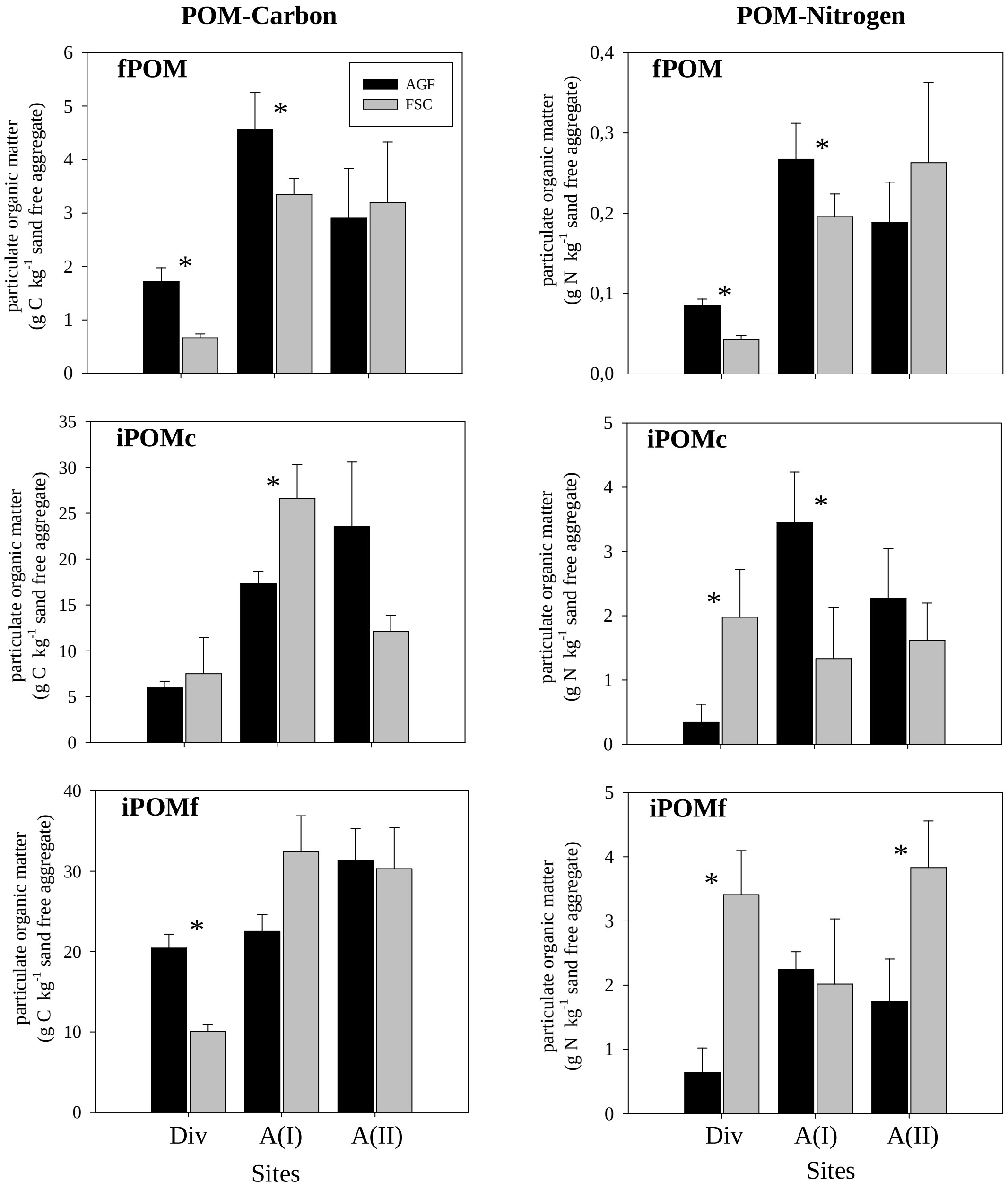

Figure 4. Free- and intra-aggregate particulate organic matter (fPOM, iPOM) C and N contents in the 0-5 cm soil layer from areas under agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino (Div), Araponga(I) (A(I)) and Araponga(II) (A(II)). (fPOM = free POM on an aggregate basis; iPOMc and iPOMf = coarse (250–2000 µm) and fine (53–250 µm) iPOM, respectively). Bars represent mean ± standard error. *: significantly different at $P < 0.05$ by LSD test.

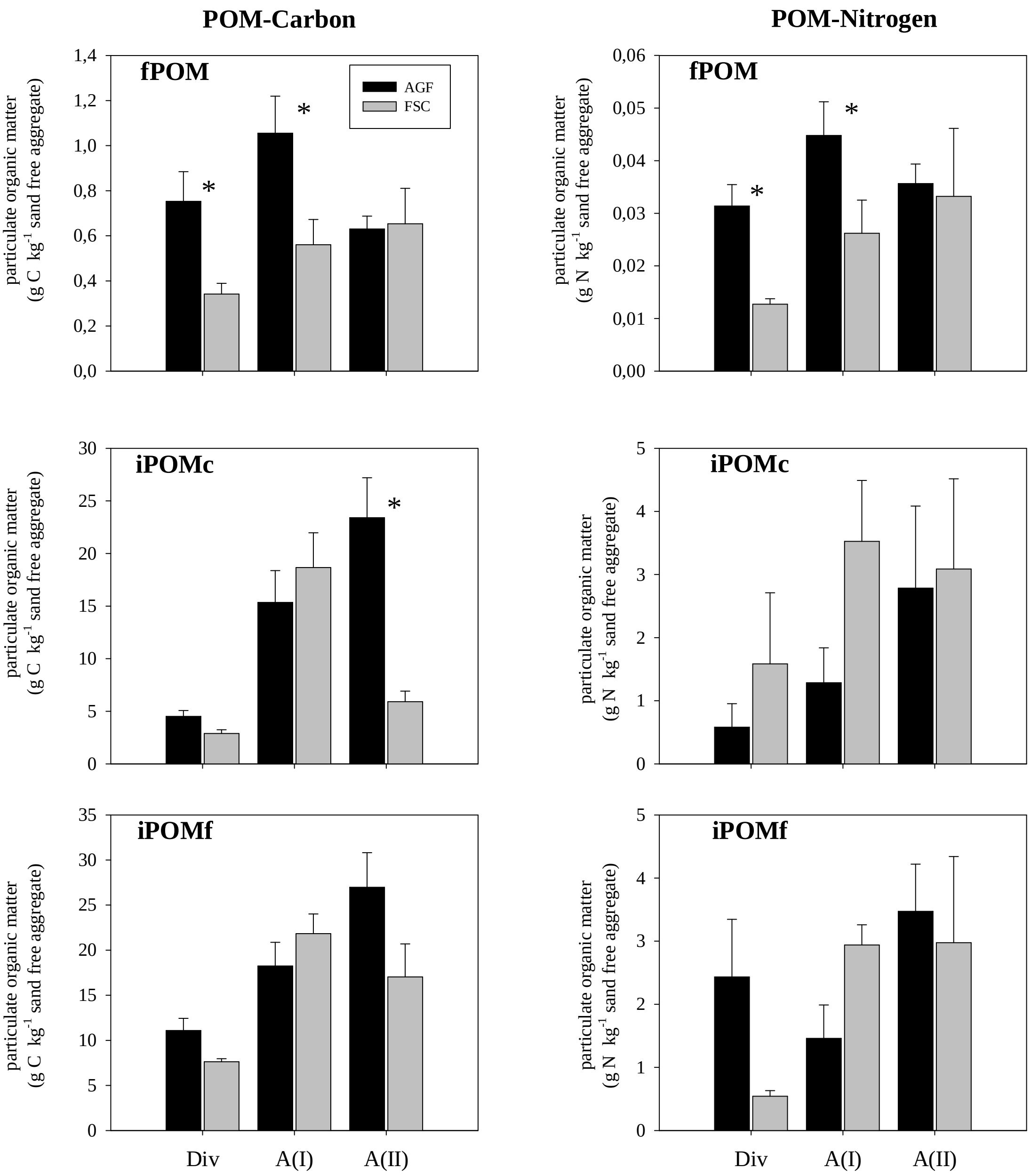

Figure 5. Free- and intra-aggregate particulate organic matter (fPOM, iPOM) C and N contents in the 5-10 cm soil layer from areas under agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino (Div), Araponga(I) (A(I)) and Araponga(II) (A(II)). (fPOM = free POM on an aggregate basis; iPOMc and iPOMf = coarse (250–2000 μm) and fine (53–250 μm) iPOM, respectively). Bars represent mean ± standard error. *: significantly different at $P < 0.05$ by LSD test.

In the NF areas, the C concentration in free- and and iPOM was substantially higher than its respective cultivated sites (data not shown). The reductions in the C contents regarding the effect of soil cultivation when evaluated by coarse and fine iPOM fractions were proportionally greater than those analyzed by total SOC, suggesting that both fractions can be used as an early and more sensitive indicator for tillage effects on SOM contents.

In Divino and Araponga(I) sites, higher C and N contents in the fPOM fraction were greater in the AGF than FSC system in both soil layers (Figures 4 and 5). In Divino, fPOM amounts in AGF were 2.8 and 2.0 times greater than in FSC in the 0-5 and 5-10 cm layers, respectively (Figure 6). In Araponga(I), these proportions were 1.3- and 1.8-fold greater in AGF compared to FSC.

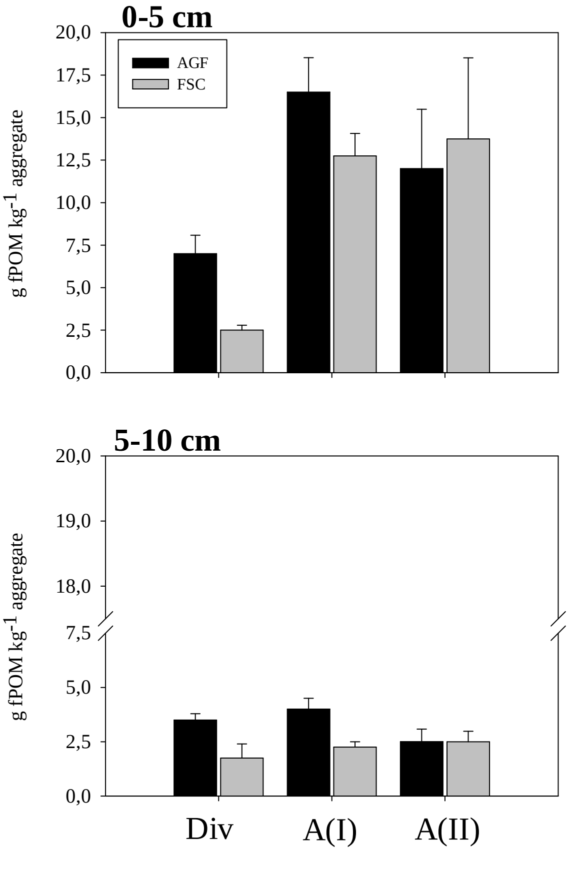

Figure 6. Free-particulate organic matter (fPOM) amount extracted from 250–2000 µm aggregate size in the 0-5 and 5-10 cm soil layers in areas under agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino (Div), Araponga(I) (A(I)) and Araponga(II) (A(II)). Bars represent mean ± standard error.

In Araponga(I), the coarse iPOM-C was higher in the FSC than AGF system in the 0-5 cm soil layer, whereas the opposite was found in Araponga(II) (Fig. 4). Similar patterns were found in the 5-10 cm layer (Fig. 5). The coarse iPOM-N content in Araponga(I) was higher in the AGF than FSC system, contrary to the behavior of C contents.

There was a significant effect of crop system on the fine iPOM-C contents in the upper soil layer. In Divino, the fine iPOM-C concentration was two times greater in the AGF than FSC system in the 0-5 cm layer (Figure 4). However, the fine iPOM-N content was greater in FSC compared to the AGF system. A similar trend was found in Araponga(II). In Araponga(I), higher fine iPOM-C occurred in FSC in comparison to AGF system, similar to the behavior of the coarse iPOM-C.

In general, iPOM-C contents in Araponga(I) and Araponga(II) soils tended to be higher than in Divino in both soil layers, suggesting that, in Divino, the mechanism of protection of SOM within aggregates is less intensive than in the other sites.

The C/N ratio in fPOM and iPOM was larger in AGF than in FSC system in Divino and Araponga(II) in the 0-5 cm layer (Figure 7). In opposition, larger C/N ratio was found in FSC in comparison the AGF system in Araponga(I). No consistent pattern on the C/N ratio could be described at the 5-10 cm soil layer.

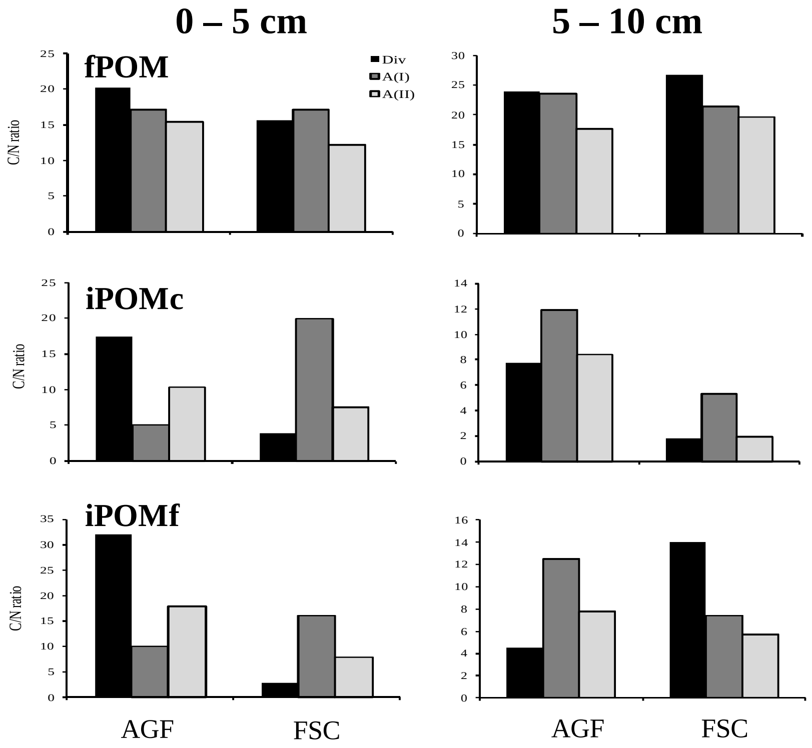

Figure 7. C-to-N ratio of free and intra-particulate organic matter (fPOM, iPOM) in the 0-5 and 5-10 cm soil layers in areas under agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino (Div), Araponga(I) (A(I)) and Araponga(II) (A(II)). (fPOM = free POM on an aggregate basis; iPOMc and iPOMf = coarse (250–2000 μm) and fine (53–250 μm) iPOM, respectively).

The ratio fine iPOM-C: coarse iPOM-C is presented in Figure 8. It has been used as a relative measurement of the turnover of macroaggregates (Six et al., 2000; Zotarelli et al., 2007). Two opposite behaviors were verified among the evaluated sites. In Divino, the ratio was greater in AGF than in FSC at the soil surface, whereas in Araponga(II), the contrary trend was registered for both depth intervals. In Araponga(I), there were no significant differences between the AGF and FSC systems in the fine iPOM-C: coarse iPOM-C ratio and the values were relatively lower than those found in Divino and Araponga(II).

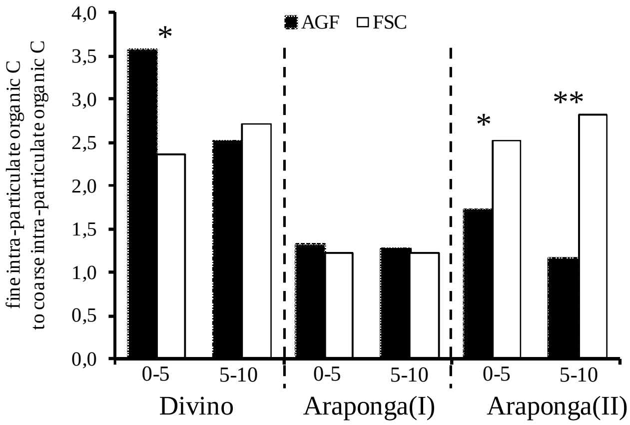

Figure 8. Ratio of fine- to coarse- intra particulate organic matter (iPOMf: iPOMc) in the 0-5 and 5-10 cm soil layers in areas under agroforestry-coffee (AGF) and full-sun coffee (FSC) in the municipalities of Divino, Araponga(I) and Araponga(II). Significant differences between cropped areas are indicated by *, ** ($P < 0.05$ and 0.01, respectively according to *F* test).

4. Discussion

Our results showed that small macroaggregates (250–2000 μm) predominated over all aggregate size classes, being in line to other studies with similar soil type (Razafimbelo et al., 2008). This result also highlights the importance of this fraction for the mechanisms of soil aggregation and reinforces its close relationship with the microbiological activity (Six et al., 2001).

The decrease of the large macroaggregates followed by a concomitant increase of the microaggregates in the FSC system in Araponga(I) suggests that this type of management can lead to a decrease in soil aggregation by favoring the process of macroaggregate disruption. The proportion of the water-stable aggregate size > 2000 μm has been considered as the most important fraction to evaluate the effect of management practices on soil aggregation (Jiao et al., 2006). Thus, the AGF system in Araponga(I) seems to increase the soil aggregation as a consequence of the constant input of organic residues derived from trees, mainly at soil surface. This result becomes more desirable in sites with accentuated slopes, such as those found in Araponga(I). Organic residues can promote 1.3-times more macroaggregate formation (Lichter et al., 2008).

In Araponga(I), the FSC system presented higher MWD compared to the AGF system in both soil layers. In an initial evaluation, it could express that the FSC management promoted a better soil aggregation, since MWD is considered a comprehensive index for evaluating soil aggregation (John et al., 2005; Jiao et al., 2006; Litchter et al., 2008). However, the increase of MWD in the FSC system was more associated to an increase in the proportion of microaggregate size class than macroaggregates. Thus, this index should be interpreted with caution. On the other hand, in Araponga(II), the higher MWD index in the AGF management compared to FSC represents a better condition of soil aggregation, since it was correlated with the increase in macroaggregates. There is a lack of information necessary to evaluate the effect of organic residues derived from trees in agroforestry management on soil aggregation in Brazilian soils, making it difficult to compare our results. Several works have been carried out in areas under conventional and no-tillage management (Silva et al., 2000; Bayer et al., 2002; Costa et al., 2003; Pinheiro et al., 2004).

The greater potential of the AGF systems compared to FSC in sequestering C in different soil fractions was confirmed by the smallest C reductions as a result of soil cultivation in relation to a reference area. These results can be credited to the influence of the constant additions of organic residues into soil due to the adoption of the agroforestry system. The positive effect of the maintenance of organic residues in the soil on the C and N storage in different aggregate fractions was also reported elsewhere (Wright and Hons, 2005; Razafimbelo et al., 2008).

The higher C contents in macroaggregates in the AGF systems compared to FSC in Divino and Araponga(I) can explain the higher amount of these water-stable fractions in AGF in comparison to FSC at these sites (Table 3). The direct relationship between the aggregate size proportions and their respective C concentrations is well documented in literature (Pinheiro et al., 2004; John et al., 2005; Wright and Hons, 2005; Razafimbelo et al., 2008). Macroaggregates are generally formed by joined soil particles and organic residues (roots and hyphae) which are highly concentrated in C (Tisdall and Oades, 1982; Oades, 1984). Furthermore, the increase in C concentration with increasing aggregate-size class occurs because larger aggregate-size classes are composed of smaller aggregate-size classes plus organic binding agents (Six et al., 1999; Denef et al., 2004).

The largest C/N ratios in large macroaggregates at the soil surface in AGF systems suggest that the organic matter on these fractions derived mainly from plants (Six et al., 2001) and reveals that agroforestry can be an important strategy of soil management to increase C storage in macroaggregates. The increase in C/N ratios with the increase in aggregate size suggests that C in macroaggregates is younger and more labile than C in microaggregates (John et al., 2005). It may represent a greater potential for substrate utilization by microbial biomass as a source of energy and may imply in the enhancement of nutrient cycling.

The 250–2000 μm aggregate fraction was the most abundant fraction and accounted for the major part of the SOC in all studied sites, when expressed on a whole soil basis. John et al. (2005) found that the relation between the total C stored in macroaggregates (>250 μm) per kg of bulk soil and the total SOC had a greater slope and a greater correlation coefficient (r=0.99) than the relation between the total C stored in microaggregates (< 250 μm) and the total SOC storage (r=0.72). Our findings are in line with this behavior and suggest that, especially in the AGF systems, the increase in SOC storage was closer associated with macro- than microaggregates.

Our data suggest that free-, fine- and coarse iPOM fractions were more sensitive indicators for tillage effects on SOM than the total SOC, since they registered greater C reductions in cultivated soils in relation to a reference area. Such behavior was also supported by Six et al. (1999) in soils under no-tillage and conventional systems.

The higher amounts of free POM in AGF compared to the FSC system mainly at the soil surface for both Divino and Araponga(I) soils (Figure 6) can be credited to the additional input of organic residues derived from tree-components in the AGF systems. Free POM consists in a transitory pool between litter and mineral-associated organic matter and can be considered a source of readily available C and energy for soil microorganisms (Janzen et al., 1992; Christensen, 2001). These results support that the AGF systems can promote better conditions to the soil microbial community and enhance the enrichment of SOC in macroaggregates. The quality of residue and input as well as soil microclimatic conditions are the main factors that determine the balance between free POM accumulation and loss (Six et al., 1999). Although free POM accounted for a minimal part of SOC in aggregates, this fraction plays an important role in the dynamics of macroaggregates. Oades (1984) stressed that the resistance to slaking of macroaggregates is associated with larger pieces of organic debris from litter and roots and from the activity of soil macro- and microfauna. In contrast with Divino and Araponga(I), soils in Araponga(II) did not show any effect of crop systems on the free POM contents. We hypothesized that, at this site, the slow turnover of organic residues under soil surface in the AGF system is likely the most important factor controlling the cycling of free POM into macroaggregates. Such behavior can be ascribed to the high lignin and polyphenols contents of the litter (Duarte, 2007), which seems to delay the cycling of free light fraction from the soil surface to aggregate structure in a short-time scale. Christensen (2001) also emphasized that the proportion of SOM recovered as free POM is affected, among other factors, by vegetation type and litter input and decomposition.

The coarse iPOM-C was affected by the crop system in Araponga(I) and Araponga(II) (Figure 4) and revealed an opposite pattern between the AGF and FSC systems. In Araponga(I), the SOM recovered as coarse iPOM-C was higher in FSC compared to the AGF system, suggesting a greater level of protection of organic matter in the FSC system. It can be an indication that i) the cycling of the coarse iPOM-C has been faster in the AGF than FSC system or ii) the rate of transformation of free POM into coarse iPOM-C in the macroaggregate is lower in the AGF than FSC system. A contrary trend was observed in Araponga(II), highlighting the greater potential of the AGF system in sequestering C within macroaggregate.

The fine iPOM-C contents were on average 51% higher in AGF than in the FSC system in Divino at the soil surface, suggesting that this aggregate fraction may be considered as an early indicator of increased C sequestration under AGF. Our results were in line with the findings reported by Denef et al. (2004) in soils under no-tillage management. Enhanced C sequestration through C stabilization in the microaggregates within macroaggregates has been also found in afforested (Del Galdo et al. 2003) and forested soils (Denef et al., 2007). The relatively large C/N ratio of both coarse and fine iPOM in the AGF system in Divino in the 0-5 cm layer indicates that these fractions derived mainly from plants (Six et al., 2001; Liao et al., 2006) and supports the idea that the free POM has been recently cycled within the macroaggregate structure.

In general, Araponga(I) and Araponga(II) soils presented higher levels of complexed organic matter (recovered as iPOM) compared to Divino (Figures 4 and 5), probably due to a higher content of clay on soils from Araponga, which can act directly on the mechanism of SOM protection (Feller and Beare, 1997).

The fine/coarse iPOM-C ratio (Figure 8) can be used as a relative measure of the macroaggregate turnover. Largest ratio values indicate slow breakdown or turnover of macroaggregates (Six et al., 2000). In Divino, the higher ratio in AGF compared to FSC suggests that AGF reduced the macroaggregate turnover, especially at soil surface. According to Six et al. (1998, 2000) microaggregate formation occurs inside of macroaggregates as fine iPOM is gradually encrusted with clay and microbial products. The higher concentration of fine iPOM-C under AGF compared to FSC is consistent with the concept of enhanced C stabilization in microaggregates due to a slower macroaggregate turnover. Such behavior is well established in conservation tillage systems in Brazilians soils, particularly under no-tillage (Denef et al., 2004; Denef et al., 2007; Zotarelli et al., 2007). However, our study showed that the pattern of the mechanism of aggregation depended on the conditions of the environment of the site studied. In Araponga(II), for instance, a higher fine/coarse iPOM-C ratio in FSC than AGF management indicated a faster turnover of macroaggregates in AGF compared to the FSC system, which is opposed to the trends found in Divino. This result can be closely related to the quality of tree-derived organic residues in the AGF system (high lignin and polyphenols contents), as previously reported by Duarte

(2007). At this site, the higher coarse iPOM-C content as well as larger C/N ratio in AGF compared to the FSC system suggests that this fraction is influenced by recent residual inputs. Furthermore, considering that as the coarse iPOM becomes decomposed and fragmented it originates fine iPOM inside macroaggregates (Six et al., 1998), the residue type in the AGF system does not seem to favor the faster turnover of coarse iPOM-C into fine iPOM. We concluded that in Araponga(II), the SOC stored within macroaggregates as coarse iPOM-C is less protected in AGF than in FSC, which could represent a greater potential of coarse iPOM-C to be used as a source of energy for soil microorganisms.

5. Conclusions

The influence of soil management on the dynamics of C and N storage within different aggregate fractions varied with the sites studied. In Divino and Araponga(I), when compared to the sole crop systems, agroforestry systems enhanced soil aggregation by increasing the amount of more stable macroaggregates as well as promoted an increased protection of C and N in the microaggregates within macroaggregates (enhanced C-sequestration). Thus, the long-term stability of SOM in these soils may depend on the maintenance of small macroaggregate fraction. Therefore, the long-term stability of C and N in these sites probably depends on the continuation of agroforestry-coffee cultivation. On the other hand, in Araponga(II), the agroforestry system failed to increase C and N in small macroaggregates, especially at soil surface, suggesting that the residue quality greatly affects the C and N sequestration potential at this site. Hence, new studies on the role of the residue quality in the potential of C storage in different aggregate fractions at this site are needed.

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CHAPTER 4

Soil phosphorus pools under agroforestry- and full-sun coffee systems in Atlantic Forest biome, Brazil

Abstract – In highly weathered soils, such as tropical Oxisols, P deficiency is one of the most important constraints to food production. Hence, management systems that favor the increase of available P forms are desirable. This study aimed to characterize the inorganic and organic P pools in the soil in three coffee cultivation fields managed under either agroforestry or full-sun cultivation systems. The work was carried out in three smallholding coffee production areas under agroforestry-coffee (AGF) and full-sun coffee (FSC) systems situated at the municipalities of Divino and Araponga in the Zona da Mata in the state of Minas Gerais, Brazil, within the Atlantic Coastal Forest biome domain. Soil P forms including H_2O-Pi; $NaHCO_3$-Pi,Po; NaOH-Pi,Po; 1*M* HCl-Pi; concentrate HCl-Pi,Po and Residual-P were sequentially extracted in samples from 0-5 and 5-10-cm soil depth intervals. Together, H_2O-Pi and $NaHCO_3$-Pi accounted on average for only 4% of soil total P in the cultivated soils. HClconc.-Pi ranged from 142.8 to 372.4 mg kg^{-1} being the predominant Pi fraction. The organic-Po pool accounted for 26 and 22% of soil total P in the cultivated soils at 0-5 and 5-10 cm layers, respectively. The AGF systems promoted an increment of 8% in the $NaHCO_3$-Po fraction in relation to the FSC systems in the upper soil layer. The FSC systems presented 43 and 21% more NaOH-Po than the AGF systems in Divino and Araponga(I), probably due to a larger fertilizer application. The AGF systems increased HClconc.-Po pool in relation to the FSC systems in Divino and Araponga(I), suggesting that agroforestry is an important management strategy to increase bioavailable P and for the maintenance of organic-P pool. The AGF systems showed higher potential of P to be biologically mineralized in AGF compared to the FSC systems. The distribution of inorganic and organic P pools varied among the different study sites, suggesting that P cycling depends on the inherent characteristic of each agroecosystem. The dynamics of P fractions in agroforestry systems seems depend on the organic-P pool.

Key words: P mineralization; biological cycle; On-farm experiment; Tiessen and Moir

1. Introduction

Phosphorus (P) is a critical macronutrient for plant growth that acts in various basic cellular functions (e.g. biosynthesis of adenosine triphosphate – ATP), in the activation of metabolic intermediates, as a component in signal transduction cascades and post-translational regulation of enzymes, and as a structural element in nucleic acid and phospholipids (Bucher, 2006). However, plant growth is commonly limited due to poor availability and low mobility of P in the soil. Thus, P deficiency represents a significant global concern to crop production (Chen et al., 2008).

Although most soils in the world contain a significant amount of P, around 200 – 3000 mg P per kg of soil (Richardson et al., 2005), only a small proportion of this (generally less than 1%) is immediately available to plants due to its physicochemical behavior and interaction with the soil chemistry (Stewart and Tiessen, 1987). In highly weathered soils, such as tropical Oxisols, P deficiency is mainly attributed to the strong adsorption of phosphate by Al- and Fe-(hydr) oxides through a mechanism not completely elucidated (Fontes and Weed, 1996). Plants possess a number of physiological adaptations that enhance P acquisition under conditions of low P availability. These included strategies that preserve internal P or those that increase the availability of P through the modification in root structure or function (Rausch and Bucher, 2002; Richardson et al., 2005) or even making a symbiotic association with specific microorganisms such as mycorrhizae (Shibata and Yano, 2003).

The forms of P in soils and sediments can be operationally defined by chemical extraction schemes (Cross and Schlesinger, 1995). Briefly, they assumed that the major inorganic P components are: i) adsorbed by exchange sites; ii) associated to complexes of Fe- and Al-oxides; iii) associated with calcium or carbonates; or iv) stabilized in a crystalline mineral. The organic P fraction in turn can be associated to: i) labile organic matter; ii) humic substances; iii) acid-soluble organic components; or iv) residual or refractory phosphate esters and phosphonates (Hedley et al., 1982; McKelvie, 2005).

The estimation of the various P pools in the soil is usually carried out by sequential P fractionation, which includes the use of increasingly aggressive reagents. One of the fractionation procedures often used is that of Hedley (Hedley et al., 1982) further modified by Tiessen and Moir (1993). The later comprises the sequential extraction of inorganic (Pi) and organic P (Po) forms by using reagents with different power of extraction, resulting in the fragmentation of P fractions, taking into account their different degree of lability. H_2O-Pi and $NaHCO_3$-Pi and -Po are considered the most labile P pool; NaOH-Pi and -Po and diluted HCl-Pi as moderately labile P; and hot concentrated HCl-Pi and -Po and residual-P as non-labile P pool (Tiessen and Moir, 1993; Guo et al., 2000). Although there is not a consensus about the definition of ‘labile P pool’ in literature (Cross and Schlesinger, 1995), we assumed as labile the extracted P pools considered available for the domesticated plants (Novais and Smyth, 1999).

The interrelations among the various P fractions in soil are complex. However, information about these fractions can increase our understanding about sinks and sources of P in the soil and is essential for an efficient P management programme (Verma et al., 2005). Soil P transformations are primarily mediated by microbial activity, which is in turn influenced by a combination of factors that can affect the P dynamics in the soil, including plant species, environmental conditions, soil type and soil management (Chen et al., 2008; Wright, 2009). The challenge for soils with low P availability, such as Oxisols, is to develop strategies of management that can enhance the P acquisition by plants. One of these important strategies is intercropping with tree species as in agroforestry systems (Cardoso et al., 2003). Agroforestry systems have been pointed out as a major opportunity to reclaim agricultural degraded lands (Cardoso et al., 2001; Mendonça et al., 2001; Mendonça and Stott, 2003). Agroforestry systems can enhance nutrient-use efficiency in tropical soils, including P, by: i) increasing the cycling of nutrients from tree litter and prunings; and ii) reducing losses by erosion (Young, 1997).

We hypothesized that the trees can enhance the efficiency of P use in agroforestry systems because some species are able to acquire P from different forms (labile and non-labile), modifying the distribution of soil P among the various pools. Hence, our objectives were: (i) to characterize the inorganic and organic P pools in three coffee cultivation fields managed under either agroforestry or full-sun cultivation systems; and (ii) to evaluate the effect of diversity and quality of organic residues derived from trees on the dynamics of different P fractions

2. Materials and methods

2.1. General description of study area

The study was carried out in the Zona da Mata (about 36,000 km^2), located in the Atlantic Coastal Rainforest biome of the state of Minas Gerais, Brazil (Figure 1). The region is characterized by a tropical highland climate (average temperature and precipitation of 18 °C and 1500 mm, respectively, with 2 to 4 months of dry period), steep slopes (20 to 45%) and altitudes ranging from 200 to

1800 m (Cardoso, 2002). The parental rock is gneiss and the dominant soil types are deep and well drained Oxisols, which are acid and poor in nutrients (Ker, 1995; Mendonça and Stott, 2003). More detailed information on pedology, agriculture and sociology of the Zona da Mata region was previously published by Cardoso et al. (2001).

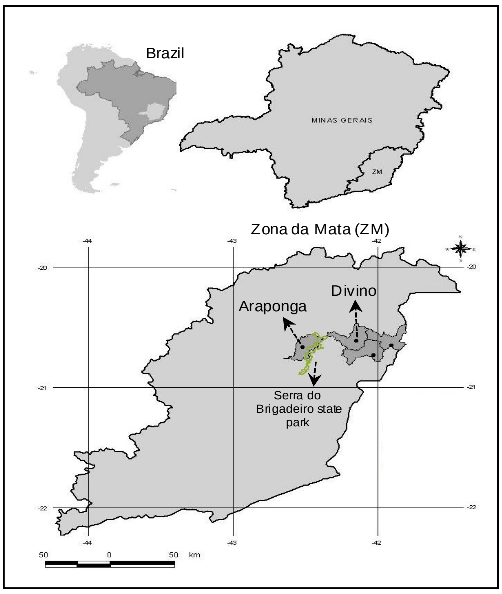

Figure 1. Localization of the municipalities of the study sites in the Zona da Mata (ZM), state of Minas Gerais.

2.2. Specific study sites and soil sampling

Three smallholder agroforestry coffee (*Coffea arabica* L.) systems (AGF) and three full sun coffee (FSC) systems fields with approximately 1.5 hectares and over 12 years of age were studied. These areas were situated at the municipalities of Divino and Araponga (Figure 1), managed by smallholding farmers. More detailed information about the historical land-use and management of the studied systems are presented in Box 1.

Box 1. Historical of land use and management of selected sites

Divino (coordinate: 20º33'S, 42º11'W; altitude: 1,160 m)
Agroforestry-coffee system: Prior cultivation this area was deforested and use as pasture, cultivated with *Melinis minutiflora* P. Beauv. (common name: Capim gordura). Some tree species of *Piptadenia gonoacantha* J.F. Macbr. (Jacaré) spontaneously grew in the pasture area. The intensive use of soil with pasture for several years (exact time unknown) declined the soil quality. Agroforestry-coffee system was implemented in 1994. The study was concentrated in an area of approximately 3,150 m^2 with 600 coffee-trees (*Coffea Arabica* L.) spaced in 3.5 m x 1.5 m. Native tree species were intercropped with coffee. The main tree species is *Luehea grandiflora* Mart (Açoita-cavalo), although other species such as *Aegiphila sellowiana* Cham. (Papagaio), *Erythrina verna* Vell (Mulungu), *Musa sp.* L. (Banana) and *Zeyheria tuberculosa* (Vell.) Bur. (Ipê-preto) can be found. Fertilizers and limestone were not applied during the two first years of the establishment of agroforestry systems. After this period, 3 Mg of limestone were applied in the projection of coffee-tree canopy. From 1999 to 2002, 50 g per plant of a mixture of ammonium sulfate, potassium chloride and monocalcium phosphate in a proportion of 3-1-1 was applied in a rate of 4 applications per year, totalizing 200 g per plant. In 2000, the trees species intercropped with coffee were drastically pruned, and the residues were left on the soil surface between the coffee rows. From 2003 to 2006 the farmer started the transition to organic coffee and stopped the inorganic fertilization. During this period, cow manure, castor bean cake, residues of leguminous species, supermagro[/3] and cattle urine were applied (Table 1). The productivity during organic cultivation was approximately 1.5 kg of coffee (pulp removed) per plant. In 2007, the organic coffee production was interrupted. Since this year, 100 g per plant of N-P-K fertilizer (20-5-20) has been applied twice a year (Table 1). The lower branches of the trees are pruned every 2 years and the residues are left on the soil surface, between coffee rows. Sporadically, jackbean, pumpkin and castor bean are cultivated between coffee rows. The mean annual productivity in 2007, 2008 and 2009 were about 0.90, 0.72 and 0.60 kg of coffee per plant. Full sun coffee system: the historical of land use is identical to the previous described site. The forest was converted in pasture for several years (exact time unknown) and further in coffee cultivation. The area has approximately 2,000 m^2 with 1,000 coffee trees spaced in 2 m x 1 m. There are no trees intercropped with coffee. Soil liming is not performed and there is no application of organic manure. Chemical fertilization of soil in 2007, 2008 and 2009 was done by applying 300, 200 and 150 g per plant of N-P-K (20-5-20). The mean annual productivity in 2007, 2008 and 2009 were 0.93, 1.2 and 0.06 kg of coffee per plant, respectively.

Araponga(I) (coordinate: 20º48'S, 42º32'W; altitude: 1,040 m)
Agroforestry-coffee system: In the past this area was deforested and used as pasture for several years (exact time is unknown). Then, coffee was cultivated under conventional management during 15 years, which resulted in severe reduction of soil fertility mainly caused by soil erosion. In 1995, agroforestry-coffee system was implemented in an area of approximately 5,040 m^2 with 1,200 coffee-trees spaced in 3 m x 1.2 m. The system was established in the highest slope area of the farm. The main tree species intercropped with coffee is *Persea americana* Mill. (Abacate). Soil is limed once a year, and there is no chemical fertilizer application. Chicken manure was used in the organic fertilization in 2001. Cow manure is applied annually and foliar fertilization is done by using supermagro twice a year (Table 1). Spontaneous vegetation is slashed 1- or 2-times per year and the residues are kept on the soil. Bean straw is applied annually on the rows. The lower branches of the tree-canopy are pruned during the dry season (June-July), after coffee harvesting. The residues of prune are kept on the soil surface avoiding soil erosion. The annual productivity is around 0.62 kg of coffee per plant. Full sun coffee system: the historical of land use is identical to the previous described site. The area has approximately 4,000 m^2 with 2,000 coffee trees spaced in 2 m x 1 m. The system was implanted in the lowest slope position, immediately below of the agroforestry-coffee area. There are no trees intercropped with coffee, but corn and beans had been planted between coffee rows. Soil liming and N-P-K fertilizer (20-5-20) applications are performed annually (Table 1) and there is no organic fertilization. The annual coffee productivity is approximately 0.79 kg of coffee per plant.

Araponga(II) (coordinate: 20º41'S, 42º31'W; altitude: 1,040 m)
Agroforestry-coffee system: In the past this area was deforested and used as pasture for several years (exact time is unknown). Further, it was burned and cultivated with rice during 7 years. During rice cultivation the soil was usually plowed by animal traction. Rice cultivation caused severe soil erosion leading to a decline of soil quality. After rice the area was cultivated with corn and beans, and finally, it was converted in pasture for 3 years when soil achieved its lowest level of fertility. In order to reclaim the land, in 1994 *Pennisetum purpureum* Schum. cv. Napier (capim-napier) and trees species such as, *Colubrina glandulosa* Perkins (sobrasil), *Hovenia dulcis* Thunb. (uva-do-japão), *Inga sessilis* Mart. and *Inga subnuda* subsp. *luschnathiana* (Benth.) T.D. Penn. were planted. The Inga species were introduced later on and the other tree species were removed. In 1998, Agroforestry-coffee was implemented. Soil liming was done in 1999, 2001, 2004 and 2006 by adding 200 g of limestone per m^2. The coffee field which includes the area covered by Inga species has approximately 1,500 m^2 with 500 coffee-trees spaced in 3 m x 1 m. At the beginning, corn and beans was usually intercropped between coffee rows, but since four years ago such inter-cropping is not performed. In the cultivation of corn and/or beans, N-P-K fertilizer (4-18-8) was applied on a rate of 30 g per m^2. Trees are not pruned but the herbaceous spontaneous vegetation is slashed three times per year. The residues of slashing are kept on the soil surface. N-P-K (20-5-20) and foliar fertilizer are applied annually (Table 1). There is no organic fertilization. The mean of coffee productivity in 2007 was 0.36 kg of coffee per plant. Full sun coffee system: the historical of land use is identical of the previous described site. This area corresponds to the other part in which Inga species were not planted. It has approximately 7,500 m^2 with 2,500 coffee trees spaced in 3 m x 1 m. The main difference in relation to agroforestry-coffee is the absence of trees. The mean of coffee productivity in 2007 was 0.45 kg of coffee per plant. Other information about chemical fertilization is presented in Table 1.

[/3] Liquid biofertilizer for foliar application prepared from fresh manure diluted in water and enriched with bone meal, blood, fish scraps (the latter two contributing minerals), and unrefined sugar and milk to stimulate fermentation. This mix is fermented anaerobically for about 1.5 months. Other organic liquid fertilizers include fermented, cattle urine and an infusion prepared from manure (Velásquez, 2002).

In each selected site, areas under natural forest fragments (NF) were sampled and used to represent the native or steady state condition of the soil. In all cases, NF fragments were at the same position on the landscape of the coffee-cultivated areas.

The more detailed characterization of the studied sites is presented in Table 1.

Table 1. Characterization of the agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino and Araponga.

	Divino		Araponga(I)		Araponga(II)	
Item	**AGF**	**FSC**	**AGF**	**FSC**	**AGF**	**FSC**
Area size, m^2	3,150	2,000	5,040	4,000	1,500	7,500
Number of coffee trees	600	1,000	1,200	2,000	500	2,500
Spacing of coffee trees, m	3.5 x 1.5	2 x 1	3 x 1.2	2 x 1	3 x 1	3 x 1
Number of trees per ha	150 - 200	-	200	-	~150	-
Fertilizer N-P-K (20-5-20), g/plant	100[b]	150[c]	na	180	200[d]	200[d]
Cow manure, kg	10,000[e]	na	2,880	na	na	na
Castor bean residue, kg	600[e]	na	na	na	na	na
Compost, kg	5,000[e]	na	na	na	na	na
Limestone, g/m^2	950[f]	na	20[g]	40[g]	200[h]	200[h]
Foliar fertilization (supermagro)	yes	na	yes	na	na	na
Biomass production[a] (litter)						
Coffee trees, kg/year	720	890	1,440	1,780	600	2,225
Trees, kg/year	2,398	-	2,004	-	4,331	-

[a] Coffee trees: estimated from Campanha et al. (2007) where litter production (dry matter) in agroforestry is 50.7 g m^{-2} month^{-1} and sun coffee system is around 37.2 g m^{-2} month^{-1}; Other trees: measured by Duarte (2007);

[b] From 2006 to 2009, applied twice a year; From 1999 to 2002: 200 g plant^{-1} year^{-1} of a mixture of ammonium sulfate, potassium chloride and monocalcium phosphate in a proportion of 3-1-1;

[c] Performed in 2008; In 2006 and 2007, N-P-K (20-5-20) was applied on a rate of 150 and 100 g per plant, respectively, twice a year;

[d] applied once a year;

[e] Total applied during organic cultivation from 2003 to 2006; supermagro applied twice a year;

na: not applied;

[f] applied in 1997;

[g] applied annually;

[h] total applied in 1999, 2001, 2004 and 2006.

The chemical composition of senescent leaves of the main trees species used in the agroforestry systems was previously measured by Duarte (2007) and a summary is presented in Table 2.

Table 2. Chemical composition and C:N, LG:N, LG:PP and LG+PP:N ratios of senescent leaves of the main tree species in areas under agroforestry-coffee systems at three municipalities of Zona da Mata, Minas Gerais state

Site/ species	Chemical composition[a]							Ratio			
	C	N	P	LG	HC	CL	PP	C:N	LG:N	LG:PP	LG+PP:N
	%										
Divino											
Luechea grandiflora	65.8	2.02	0.119	13.6	19.2	17.2	8.3	32.6	6.7	1.6	10.8
Araponga(I)											
Persea americana	60.7	2.05	0.163	21.0	13.4	12.8	7.3	29.6	10.2	2.9	13.8
Araponga(II)											
Inga subnuda	54.6	3.17	0.141	27.3	23.9	21.3	4.8	17.2	8.6	5.7	10.1

[a] C:carbon; N: nitrogen; P: phosphorus; LG: lignin; HC: Hemicellulose; CL: Cellulose; PP: total polyphenols. Adapted from Duarte (2007).

The soil samples were collected at intervals of 0-5, 5-10, 10-20 and 20-40 cm of depth from December 2006 to March 2007 (rainy season). In order to guarantee a representative sampling procedure, four sub-samples randomly distributed between coffee rows were taken from each site, and then combined to form one replicate. Four replicates were collected. Before the samples were taken, the litter layer was removed. Immediately after sampling, approximately 300 grams of soil from 0-5 and 5-10 cm layers were separated and frozen to perform a further microbiological analysis. Once in the laboratory, the moist soil was air-dried, sieved through a 2-mm sieve and stored at room temperature.

2.2. Soil physical and chemical analysis

The soil particle sized fractions (clay, silt and sand) were determined by the pipette method (Day, 1965). The total organic C was quantified by wet combustion with a mixture of potassium dichromate and sulfuric acid (Yeomans and Bremner, 1988). The soil pH was determined in water (1: 2.5, soil:water ratio). The exchangeable cations (Ca^{2+}, Mg^{2+}) were quantified by using 1*M* KCl as extractor, whereas K^+ and P were extracted by Mehlich-1 (EMBRAPA, 1997).

The cation exchange capacity (CEC) and base saturation (%) were estimated by means of calculations using the concentrations of the exchangeable cations.

2.3. Soil P fractionation

A modification in the Tiessen and Moir method (1993) was adopted to extract different pools of soil P. The sequential P fractionation followed the flow diagram of Figure 2. Briefly, a 0.5-g (air-dried and sieved at 2-mm) soil sample was placed in a 50-mL centrifuge tube and was sequentially extracted with 30 mL each of deionized water, 0.5 *M* $NaHCO_3$ (pH=8,5), 0.1*M* NaOH and 1*M* HCl. Each extraction was performed for 16 h by using a horizontal shaker followed by centrifugation at 1,282 *g* for 15 min. at room temperature. After 1*M* HCl extraction, the samples were treated with 15-mL of concentrated HCl at 80ºC for 10 min. After the final extraction, the residual-P was determined in the soil material left in centrifuge tubes by extraction with H_2SO_4–H_2O_2 at 360ºC (Tiessen and Moir, 1993). The total P (Pt) in the $NaHCO_3$, NaOH and concentrated HCl extracts were determined by digesting aliquots using an acidic mixture of HNO_3/$HClO_4$ (3:1, v:v) under heating. In the initial aliquot, the inorganic P (Pi) was measured without any digestion. Orthophosphate P initial and digests of each soil extract was determined colorimetrically with the molybdate-ascorbic acid procedure (Murphy and Riley, 1962) after pH adjustment using *p*-nitrophenol as indicator. The absorbance was determined at a wavelength of 712 nm. The organic P (Po) was calculated as the difference between Pt and Pi.

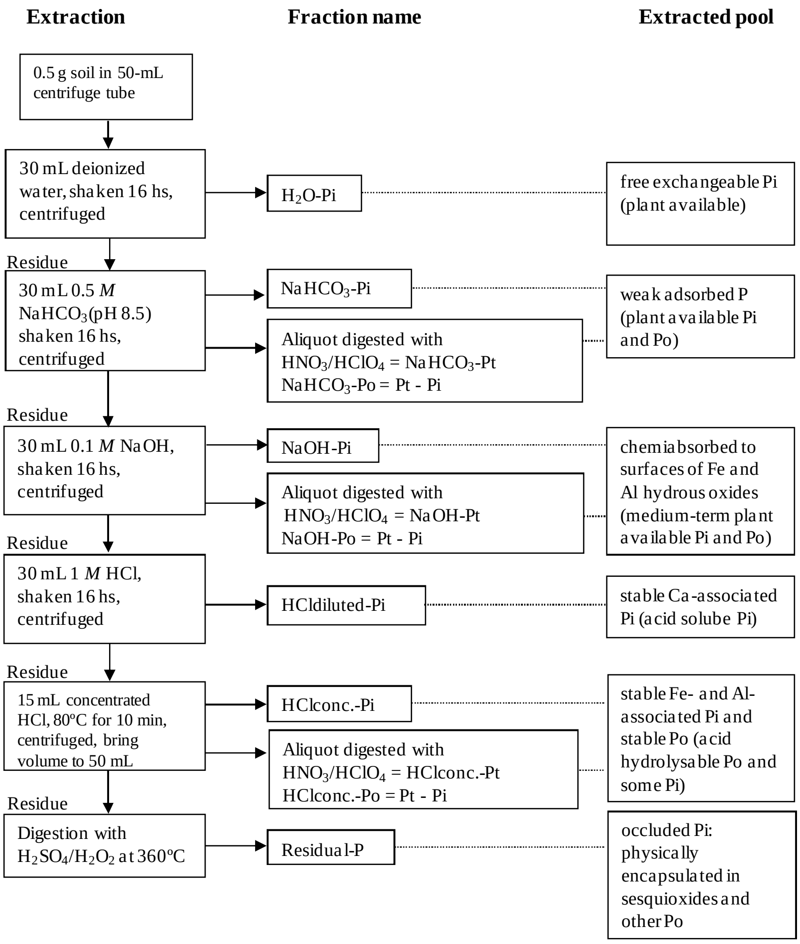

Figure 2. Flow diagram of the P fractionation method as developed by Tiessen and Moir (1993) and modified by Sui et al. (1999) and Lilienfein et al. (2000).

Our procedure differed from the standard Tiessen and Moir (1993) by using H_2O as the first extractant instead of equilibrating the soil sample with an anion-exchange resin (Sui et al., 1999; Verma et al., 2005). This P fraction is intended to represent the most labile P in the soil, and it has been assumed that P in the H_2O extract would be more closely related to bioavailable P in surface runoff (Sui et al., 1999). Furthermore, the initial P fractions were obtained without filtering (pore size of 0.45µm) and ultra-centrifuge at 0°C. Finally, Pt contents in the $NaHCO_3$ and NaOH extracts were determined by digesting aliquots with $HNO_3/HClO_4$ mixture instead of digesting aliquots by using autoclave and acidified ammonium persulphate (Tiessen and Moir, 1993).

The data of soil physical and chemical properties and different soil P fractions were subjected to the standard ANOVA followed by a least significant difference (LSD) by the Tukey test (*P* < 0.05 and 0.10).

3. Results and discussion

3.1. Soil physical and chemical properties

The main physical and chemical characteristics of the soils are presented in Table 3, and can be interpreted according to the general criteria of Soil Fertility Committee of Minas Gerais State, Brasil (Alvarez et al., 1999).

Table 3. Selected physical and chemical properties of the soil in areas under native forest fragments (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at 0- to 10-cm layer in three municipalities of Zona da Mata, Minas Gerais

	Divino				Araponga(I)				Araponga(II)			
Soil properties	NF	AGF	FSC	LSD[1]	NF	AGF	FSC	LSD	NF	AGF	FSC	LSD
Particle size distribution (g kg^{-1})												
Clay	259	305	316	44	399	361	381	44	402	499	422	46
Silt	238	123	165	80	109	119	124	21	123	113	135	14
Sand	504	573	519	99	493	520	495	31	474	388	444	46
pH H_2O (1:2.5)	6.4	6.0	6.1	0.2	4.9	5.8	5.8	0.2	4.8	5.6	6.2	0.5
Organic C[a], g kg^{-1}	80.4	26.1	23.4	28.4	69.0	28.9	31.3	5.4	50.7	31.9	26.9	9.4
CEC, $cmol_c$ dm^{-3}	21.4	11.1	11.6	2.7	16.6	11.1	10.1	1.2	17.7	12.2	11.0	2.0
Base saturation, %	77	69	63	9	2	46	51	8	1	30	40	12

[a] Sulfur acid oxidation (Yeomans and Bremner, 1998); CEC = cation exchange capacity. [1] LSD = least significant difference by Tukey test at *P* < 0.05.

In general, the soils were clayey and the acidity varied from slight in Divino to high in Araponga(II). The total soil organic C levels ranged from 23.4 to 31.9 g kg^{-1} among the cultivated sites, being classified as good. The cation exchange capacity (CEC) averaged 11 $cmol_c$ dm^{-3}, within the adequate levels for Minas Gerais' soils (Alvarez et al., 1999). The CEC of these soils is mainly related to soil organic matter content at soil surface (Mendonça and Rowell, 1996). The base saturation percentage in the cultivated areas in Divino, Araponga(I) and Araponga(II) soils was considered as adequate, medium and low, respectively. A very low base saturation in the NF areas in Araponga(I) and Araponga(II) was attributed to the low concentration of base cations. In these soils, CEC was mainly related to total acidity.

3.2. Soil total Pi and Po

The sum of soil total P and inorganic- and organic-P fractions are shown in Table 4. The Sum-Pt ranged from 879.3 to 1361.3 mg kg^{-1} among all evaluated sites. Our results for soil total P are higher compared to other data found in tropical Oxisols (Cardoso et al., 2003, Araujo et al., 2004). The largest values of sum-Pt in cultivated sites occurred in Araponga(II). In cultivated areas, regardless of the soil management, sum-Pt was reduced in 7.68% in relation to the native forest. Sum-Pi accounted for 38% of soil total P in the cultivated sites.

Table 4. Sum of Pt, Pi and Po in soils under native forest (NF) agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at 0-5 and 5-10 cm layers in the municipalities of Divino, Araponga(I) and Araponga(II)

Soil total P	Layer	Divino			Araponga(I)			Araponga(II)		
(mg kg-1)	(cm)	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
Sum-Pt[/a]	0-5	1361.3	988.1	954.7	1084.3	1007.3	1077.2	900.7	1059.2	1171.5
	5-10	1206.3	900.6	900.7	1005.5	879.3	899.3	905.9	971.5	1125.3
Sum-Pi[/b]	0-5	351.2	291.9	263.6	387.7	341.6	436.9	427.1	478.5	585.9
	5-10	307.4	307.6	225.7	367.9	285.4	316.1	425.3	455.8	551.3
Sum-Po[/c]	0-5	562.1	204.6	239.4	279.9	255.9	231.5	197.2	214.2	203.0
	5-10	401.5	161.3	180.9	232.3	192.0	197.2	169.6	195.4	182.2

[/a] Sum-Pt = Sum-Pi + Sum-Po + Residual-P; [/b] Sum-Pi = sum of all Pi fractions; [/c] Sum-Po = sum of all Po fractions.

At 0-5 cm layer, sum-Pi was larger in FSC than in the AGF system in Araponga(I) and Araponga(II) soils (Table 4). A contrary pattern occurred in Divino, where AGF increased sum-Pi in relation the FSC system. Sum-Po represented 21% of soil total P in the cultivated areas. Soil cultivation reduced sum-Po in 33% in relation to the reference area. In Divino, sum-Po tended to be higher in FSC than in the AGF system at both soil layers, whereas the opposite occurred in Araponga(I) and Araponga(II) soils.

Figure 3 shows the distribution of soil P fractions in native forest and cultivated soils. In general, both native and cultivated sites showed a somewhat similar percentage of Pi in the different P fractions, accounting for 35% (NF) and 38%(Cultivated) of the soil total P. On the other hand, organic-P pool was consistently higher in native forest compared to the cultivated soils, showing a difference of 9% at topsoil and 7% in the 5-10 cm.

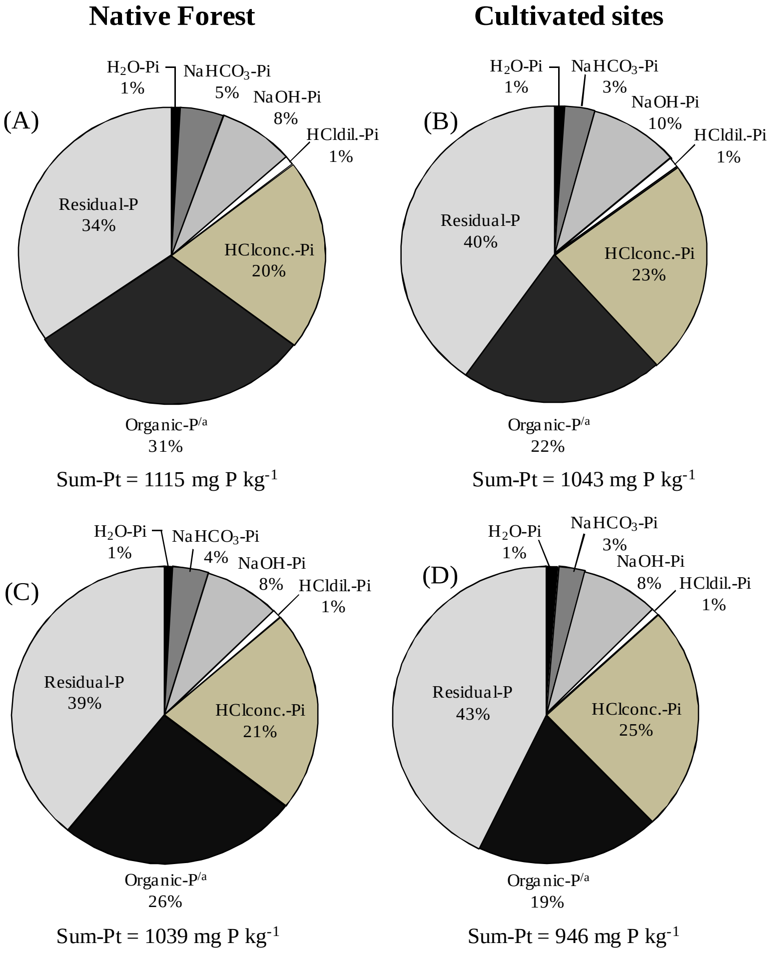

Figure 3. Distribution (%) of P fractions in native forest and cultivated soils in the 0-5 cm (A and B) and 5-10 cm (C and D) layers. [a] Organic P = $NaHCO_3$-Po + NaOH-Po + HClconc.-Po; Sum-Pt = sum of all P fractions.

Considering native forest as a steady state condition, these findings are important to emphasize that organic-P pool has a vital importance on the P cycling in the soil, especially for those with high P adsorption capacity, such as Oxisols. Such results suggest that the maintenance of organic-P pool is very important as inorganic-P in a soil management programme, mainly when most soil P is held as recalcitrant P forms.

3.3. Soil P fractionation

The distribution (%) of different soil P fractions in all evaluated sites is presented in Figure 4. In general, only few significant changes occurred in Pi fractions as a result of soil management. Since H_2O-Pi and $NaHCO_3$-Pi are considered the most labile P forms, these pools were analyzed together as being H_2O-Pi + $NaHCO_3$-Pi (Figure 4). This pool accounted for only 4% of soil total P. This is in agreement with other studies developed in Oxisols, which normally presented very low available P levels (Tiessen and Moir, 1993; Cross and Schlesinger, 1995; Lilienfein et al., 2000). There were no consistent changes on P concentration in the H_2O-Pi + $NaHCO_3$-Pi pool as a result of soil management, probably due to its intensive dynamics in the soil. Thereby, other evaluations on a scale of time are needed aiming at a better understanding about the effect of soil management on the dynamics of the most labile P forms. $NaHCO_3$-Pi amounts have been depleted in the AGF fields as a result of the fast turnover rate of this fraction by microbial biomass, which is in line with the greater microbial activity (higher C-CO2 emission) on these fields compared to the FSC systems (see Chapter 2). The microbial biomass can immobilize part of the available P in order to maintain the energy to mineralize the organic residues added to the soil. The P immobilization by microorganism, turnover of microbial P and mineralization of microbial by-products seem to be the major processes regulating P cycling and availability from organic material (Oberson and Joner, 2005).

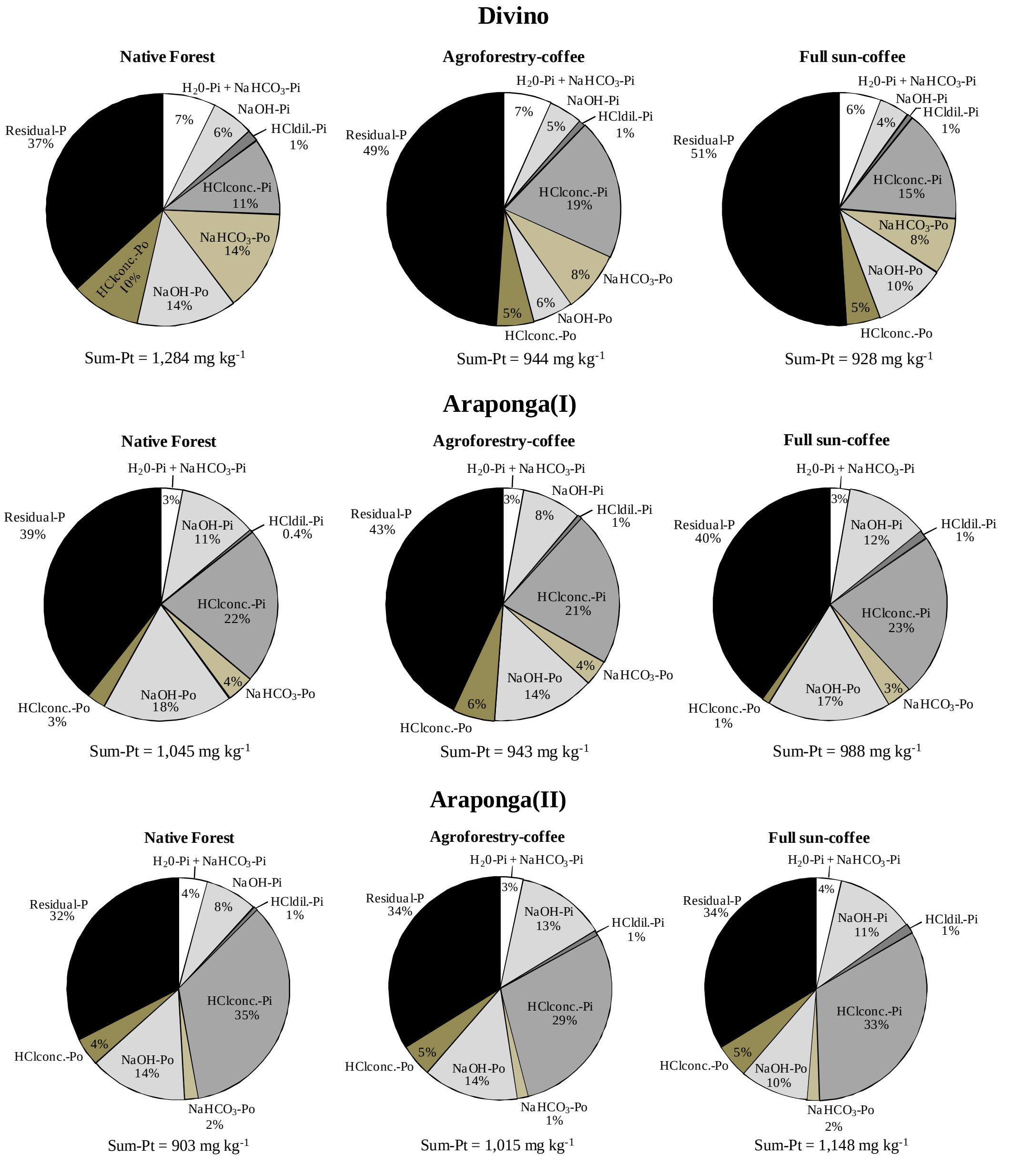

Figure 4. Relative distribution (%) of different P fractions in soils under native forest, agroforestry-coffee and full-sun coffee systems at 0-10 cm layer in the municipalities of Divino, Araponga(I) and Araponga(II). Sum-Pt = sum of all P fractions.

NaOH-Pi was the second most abundant Pi fraction, accounting on average for 9% of the soil total P. This fraction is held by chemisorption to Fe- and Al-complexes and is considered as a moderately labile P pool (Hedley et al., 1982). Indeed, $NaHCO_3$-Pi and NaOH-Pi are not completely separate pools, but represent a continuum of Fe- and Al-associated P extractable pool in acid soils (Tiessen and Moir, 1993). Significant changes in this fraction were registered in Araponga(I) where the FSC system presented higher NaOH-Pi content than the AGF system (Figure 4). This result might be attributed to fertilizer applications (Verma et al., 2005) or mineralization of NaOH-Po fraction (Cardoso et al., 2003) that was also higher in FSC compared to the AGF system.

HCldil-Pi was the smallest P fraction, accounting for only 1% of sum-Pt. This fraction is defined as Ca-associated P, and Pi contents are commonly low in high weathered soils (Cross and Schlesinger, 1995).

The hot concentrated HCl-Pi (HClconc.-Pi) was the most abundant Pi fraction in the cultivated soils, accounting for 24% of the soil total P. These results are consistent with other data for tropical Oxisols (Novais and Smyth 1999). This fraction is considered as a recalcitrant P pool, where Pi forms derive from stable residual pools associated to Fe and Al hydrous oxide complexes (Tiessen and Moir, 1993), thus few or none changes are expected to occur in this fraction as a result of land-use. Although Pi amounts in HClconc.-Pi extracts were consistently high, this Pi form is not effectively available for plants (Hedley et al., 1982). It suggests that soil management strategies need to prioritize the utilization of organic soil P pool by manipulation of plants and stimulation of microbial interactions on the P cycling processes (Cardoso et al., 2003; Richardson et al., 2005). In slightly weathered soils, the decline in HClconc.-Pi suggests the gradual conversion of this fraction into readily available P (Guo et al., 2000). However, such interpretation cannot be addressed to our study because there was no clear evidence of changes in the most labile P pool as a result of changes on the HClconc.-Pi fraction. Thereby, the mechanisms that could explain the effect of soil management on the stable Fe- and Al-associated P remain unknown.

The organic-P pool was comprised by the sum of $NaHCO_3$-Po, NaOH-Po and HClconc.-Po fractions (Figure 4). This pool represented approximately 24% of the soil total P in the cultivated soils. $NaHCO_3$-Po, considered an easily mineralizable Po form (Oberson and Joner, 2005), represented on average 8, 4 and 1% of the sum-Pt in the cultivated soils in Divino, Araponga(I) and Araponga(II), respectively. In general, there was no significant effect of soil management on this P fraction.

NaOH-Po was the most abundant Po fraction, accounting for 12% of the soil total P in the cultivated soils. Organic-P associated with humic and fulvic acids are mainly recovered in this fraction (Nziguheba and Bünemann, 2005). The FSC systems presented 39 and 21% more NaOH-Po than the AGF systems in Divino and Araponga(I), respectively (Figure 4). Such behavior can be attributed to the larger fertilizer applications in FSC compared to the AGF systems (Table 1), confirming the findings of Szott and Melendez (2001), who observed greater absolute amounts and proportions of P in the inorganic and organic NaOH-P pool in fertilized treatments, as compared to the forest area. The NaOH-P pool is actively involved in P cycling processes acting as a P sink when the system is fertilized, and as a source when the labile pool is being depleted (Beck and Sanchez, 1994). Contrary to Divino and Araponga(I) soils, in Araponga(II), the AGF system increased the NaOH-Po concentration in 20% in relation to the FSC system, despite of the application of fertilizer in the FSC. In such environmental conditions, it seems that this pool is likely acting as a P sink, which can be due to the slow decomposition rate of the litter (rich in lignin and polyphenols) in the AGF system, as reported by Duarte (2007). Despite the slow release of P into soil, the lowest lability of the organic residues in Araponga(II), in relation to other sites, plays a vital role in the protection of the soil surface against the erosive process, which benefits several soil functions.

HClconc.-Po accounted for 5% of the soil total P in the cultivated sites (Figure 4). In Araponga(I), the HClconc.-Po content was 82% higher in AGF than in the FSC system. Concentrate HCl acid recovers organic P from more stable pools, but it may also extract bioavailable organic P derived from particulate organic matter (Tiessen and Moir, 1993). These results are consistent with the previous data of higher free-particulate organic matter contents in the AGF system at this site (see Chapter 3). These findings support that agroforestry is an important management strategy to increase bioavailable P and maintain the organic-P pool.

The residual-P was the predominant soil P fraction, accounting on average for 42% of the soil total P (Figure 4). High residual-P concentrations were also reported by other studies developed in tropical Oxisols (Cross and Schlesinger, 1995; Araújo et al., 2004). In highly weathered soils, the residual P fraction appears to continue increasing over time (Guo et al., 2000). No significant effect of soil management was registered in this fraction. Since residual-P comprises a very stable P pool (Tiessen and Moir, 1993), differences on the absolute P concentrations between the AGF and FSC systems were not expected, although in other situations, such as exhaustive cropping systems, residual-P appeared to contribute to replenish the available-P (Zhang et al., 2006).

3.6. Relationship of soil P fractions

Readily labile P pool (Table 5) was comprised by H_2O-Pi + $NaHCO_3$-Pi + $NaHCO_3$-Po, representing the most available P forms for plants. In Divino, this pool was 11% higher in AGF compared to FSC system. Such difference was mainly related with the increase of $NaHCO_3$-Po, indicating that, in the AGF system, the available soil P is maintained at expense of organic P cycling.

Table 5. Soil P pools and ratios at 0-10 cm layer in areas under native forest (NF), agroforestry-coffee (AGF) and full sun-coffee (FSC) systems in the municipalities of Divino, Araponga(I) and Araponga(II)

	Divino			Araponga(I)			Araponga(II)		
Soil P	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
P pools[/a] (mg kg^{-1})									
Readily labile-P	275.6	142.8	126.9	71.5	61.2	61.4	55.5	49.8	63.3
Labile-Pi	169.7	106.4	92.7	145.8	105.6	140.7	107.0	165.2	174.0
Labile-Po	358.6	133.2	166.1	229.0	169.2	204.4	145.9	156.7	135.5
Moderately labile-Po	176.8	53.4	93.5	189.4	135.3	170.5	128.5	140.2	114.8
Mineralizable-Po	305.0	129.6	116.7	66.7	88.7	43.9	54.9	64.7	77.9
Ratios									
Readily labile-P/sum-Pi	0.84	0.48	0.52	0.19	0.20	0.16	0.13	0.11	0.11
Labile-Pi/sum-Pi	0.52	0.35	0.38	0.39	0.34	0.37	0.25	0.35	0.31
Labile-Po/sum-Pt	0.28	0.14	0.18	0.22	0.18	0.21	0.16	0.15	0.12
Moderately labile-Po/sum-Po	0.37	0.29	0.44	0.74	0.60	0.80	0.70	0.68	0.60
Mineralizable-Po/sum-Po	0.63	0.71	0.56	0.26	0.40	0.20	0.30	0.32	0.40

[/a] Readily labile-P: H_2O-Pi + $NaHCO_3$-Pi + $NaHCO_3$-Po; Labile-Pi: H_2O-Pi + $NaHCO_3$-Pi + NaOH-Pi; Labile-Po: $NaHCO_3$-Po + NaOH-Po; Moderately labile-Po: NaOH-Po; Mineralizable-Po: $NaHCO_3$-Po + concentrate HCl-Po; sum-Pi: sum of all Pi fractions; sum-Po: sum of all Po fractions.

The moderately labile Po pool (NaOH-Po) was 18% higher in the AGF than FSC system in Araponga(II). At this site, such pool represented 68 and 60% of the sum-Po in the AGF and FSC systems, respectively (Table 4). The proportional increase of this P fraction in the AGF system is an important factor in the replenishment of available P on medium-term (Zhang et al., 2006), which could affect the reduction of the use of P fertilizers. The mineralizable-Po was comprised by $NaHCO_3$-Po + HClconc.-Po fractions. In Divino, the mineralizable-Po pool accounted for 71 and 56% of the sum-Po in the AGF and FSC systems, respectively. In Araponga(I), it represented 40 and 20% of the sum-Po in the AGF and FSC systems, respectively. Such results suggest that the agroforestry management favored the increase of the organic P pool, which can be used by microorganisms as an available P source of energy.

Figure 5 shows an index of the P portion that may be easily mineralized through biological processes (Cross and Schlesinger, 1995).

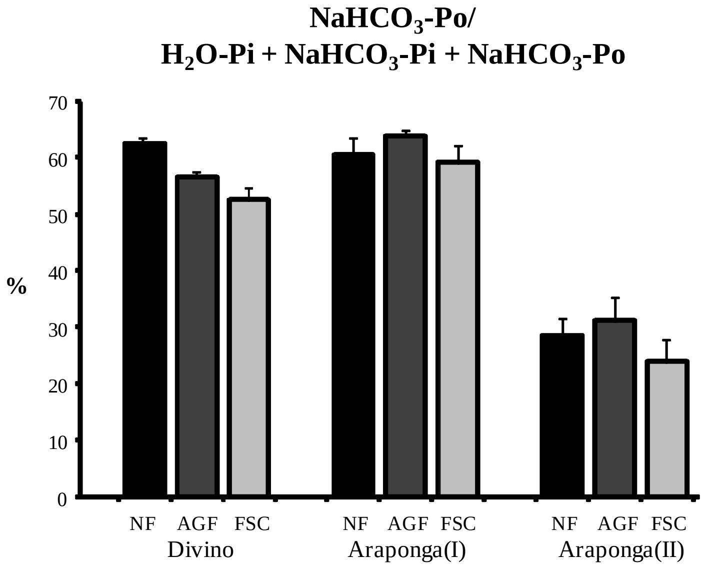

Figure 5. Bicarbonate Po as a percentage of the readily available P pool in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino, Araponga(I) and Araponga(II).

There was a similar pattern of higher potential of P to be biologically mineralized in the AGF system in comparison to FSC. Although such differences could not be marked, they point out to a recovery of P availability with the adoption of the AGF systems in these sites. This fact reinforces the importance of organic-P as a source of plant-available P in highly weathered soils (Nziguheba and Bünemann, 2005) and suggests that agroforestry is an attractive soil management strategy to increase the microbial activity on the P cycling processes.

Proportionally, Divino and Araponga(I) soils presented more easily mineralized P contents than Araponga(II), which can be associated with the lowest quality of organic residues in Araponga(II) or even to differences in the activity of the microbial community (see Chapter 2).

Our results should be interpreted with caution, since the separation of soil P into 'pools' that differ in the degree of their lability is a relative concept that depends on the characteristic of the environment (Zhang et al., 2006). Furthermore, some P pools have been assumed not to be really completely separated (Tiessen and Moir, 1993) and the inter-relationship among them seems not be completely accessed by fractionation techniques. Other imminent limitation lies on the fact that organic P can be overestimated, since it is calculated by the difference between Pt and Pi in each extract. Cardoso et al. (2003) highlighted that the rate and impacts of changes on P cycling by agroforestry systems in long-term need more detailed investigations aiming a full evaluation of the importance of agroforestry in soil P utilization.

4. Conclusions

The distribution of inorganic and organic P pools varied among the different studied sites, suggesting that P cycling depends on the inherent characteristic of each agro-ecosystem. The dynamics of P fractions in agroforestry systems seems to be dependent on the organic P pool. Agroforestry systems affected organic P pools differently in the evaluated sites. In Divino and Araponga(I), agroforestry increased the proportion of mineralizable Po ($NaHCO_3$-

Po + HClconc.-Po), which can favor biological processes on the P cycling. In Araponga(II), the agroforestry system increased moderately the labile Po pool, suggesting that P cycling occur on a medium-term scale, since such pool has been considered as a source of P when most labile P fractions are depleted.

The transformations of P fractions in the studied agroforestry systems can be directly related to the decomposition rate of organic residues that, in turn, are associated to their quality. Hence, the effect of the agroforestry management on P dynamics and the role of organic P in P cycling need to be stressed by more detailed studies, also taking into account the role of microorganisms in the inter-relationship among the different P pools.

The soil P fractionation approach has been useful to point out the potentiality of the mineralization of different P forms. However, the interpretation of the results has to take into account that it is a static tool to study P transformations in the soil. Thus, firm conclusions on the P dynamics regarding the effect of soil management cannot be addressed.

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CHAPTER 5

Structural features of soil humic substances as affect by agroforestry- and full sun-coffee management in the Atlantic Coastal Forest Biome, Brazil

Abstract – The studies on soil humic substances dynamics in the tropics have been traditionally focused on its quantification rather than the monitoring of their chemical characteristics and structural changes as influenced by land use. The aim of this study was to identify the qualitative changes of soil humic and fulvic acids (HAs and FAs) as influenced by agroforestry (AGF) and full-sun coffee (FSC) systems in areas under coffee production in the Atlantic Coastal Forest biome in the state of Minas Gerais, Brazil. Soil was collected from three smallholding coffee production areas under AGF and FSC systems which were situated at the municipalities of Divino and Araponga. Soil HAs and FAs extracted from 0-5 and 5-10 cm layers were characterized comparatively by using chemical and spectroscopic techniques including: elemental and functional group analysis, thermogravimetry (TG), Fourier transform infra-red (FTIR) and solid-state ^{13}C nuclear magnetic resonance (^{13}C CP-MAS/NMR). Soil depth and the quality of the organic residues incorporated into the soil appeared to be the main factors controlling the characteristics of soil humic substances. At soil surface, HAs from AGF presented higher H/C and lower O/C ratio than FSC system at Divino, suggesting that AGF management favored the genesis of HAs with less aromatic and oxidative character. However, opposite trend occurred at Araponga(II), characterized by different soil and climate characteristics. The patterns of elemental composition were supported by the findings of TG analysis and FTIR. Solid-state ^{13}C NMR spectroscopy also confirmed the data from the previous analysis in which HAs from AGF system at Divino and Araponga(I) are less humified than in FSC system, whereas at Araponga(II) this clear evidence was not verified. In all sites ^{13}C NMR assignment of HAs were dominated by the *O*-alkyl C resonance in the both soil layers followed by a resonance line assigned to alkyl C, reflecting the incorporation of plant biomacromolecules into the humic structure. Conclusively, the chemical changes on the structure of HAs and FAs as influenced by agroforestry management depend on inherent characteristics of environment on which it is developed. Thus, the effect of this type of land use on the structural characteristics of humic substances in comparison to a monoculture system should not be broadly generalized.

Key words: Spectroscopy; Tropical soil; Organic matter; Humification degree

1. Introduction

Soil organic matter (SOM) has been recognized as a major factor controlling the capacity of soil to deliver agricultural and environmental services and also to sustain human societies at both local (e.g. maintaining soil fertility) and global (e.g. increasing of C sequestration) scale (Manlay *et al.*, 2007).

The levels of SOM depend on different factors such as climate, vegetation, topography and inherent soil characteristics (Feller & Beare, 1997). However, C dynamics and the rate of SOM accumulation and losses are strongly affected by land use and management practices (Carvalho *et al.*, 2009). The replacement of natural ecosystems by agricultural lands usually promotes a substantial decline on the soil C stocks. Since SOM is considered one of most important attribute of soil quality, the loss of SOM leads to a decline of important soil functions.

The deforestation of Atlantic Coastal Forest biome in the state of Minas Gerais, one of most important biome of Brazilian vegetation, and further expansion of coffee cultivation (*Coffea arabica* L.) during the mid-19th century caused severe ecosystem damage which has lead to land degradation (Valverde, 1958). In this region, coffee is normally cultivated on hills, representing a favorable environmental condition for soil erosion and other soil degradation processes. On this context, agroforestry systems, a land-use system in which agricultural practices are combined spatially with trees, have been pointed out as a major opportunity to deal with the problems related to land-use in this region (Cardoso *et al.*, 2001; Mendonça *et al.*, 2001; Mendonça & Stott, 2003).

Agroforestry systems have been shown to enhance the SOM levels, compared to monoculture agricultural systems (Mendonça *et al.*, 2001; Maia *et al.*, 2007). However, only few studies have been devoted to the qualitative changes of SOM as a result of different management practices. In Brazil, some of these reports corresponded to soils under no-tillage management (Bayer *et al.*, 2002; González Pérez *et al.*, 2004; Dieckow *et al.*, 2005), however information on the chemical characterization of SOM in areas under agroforestry management remains scarce.

Humic substances comprise the most important fraction of SOM from a quantitative and qualitative point of view. Humic substances have been traditionally studied due to its important functions in the soil, such as the improvement of soil structure, the capacity to interact with metal ions, the ability to buffer pH, and the ability to act as a potential source of nutrients for plants (Stevenson, 1994). Most studies addressed to soil humic substances dynamics in the tropics have focused mainly on its quantification rather than monitoring of their chemical characteristics and structural changes caused by different soil management practices.

Besides the most traditional techniques used for characterization of humic substances, such as elemental composition, thermogravimetry, etc, recent advances on the spectroscopic techniques applied to soil science have emerged as a useful tool for characterizing the chemical nature of SOM (Kogël-Knabner, 1997; Gerzabek *et al.*, 2006). The attempts are focused in the identification of functional groups and molecular structures providing a better understanding of decomposition pathways of organic matter and qualitative alterations induced by management (Helfrich *et al.*, 2006; Muñoz *et al.*, 2008). Among these techniques the combined application of Fourier transformed infra-red (FTIR) and solid-state ^{13}C nuclear magnetic resonance with cross-polarization and magic angle spinning

(^{13}C NMR/CP-MAS) can provide a suitable background on the qualitative aspect of the structure of SOM.

The constant input and quality of organic residues derived from tree-component in agroforestry systems, in contrast to monoculture systems, is expected to have an important effect on the humification processes and consequently on the chemical and structural features of soil humic substances. Hence, the aim of this research was to identify the qualitative changes of soil humic and fulvic acids as influenced by agroforestry and full sun coffee systems in areas under coffee production in the Atlantic Forest biome in the state of Minas Gerais, Brazil.

2. Materials and methods

2.1. General description of study area

The study was carried out in the Zona da Mata (about 36,000 km^2), located in the Atlantic Coastal Rainforest biome of the state of Minas Gerais, Brazil (Figure 1). The region is characterized by a tropical highland climate (average temperature and precipitation of 18 °C and 1500 mm, respectively, with 2 to 4 months of dry period), steep slopes (20 to 45%) and altitudes ranging from 200 to 1800 m (Cardoso, 2002). The parental rock is gneiss and the dominant soil types are deep and well drained Oxisols, which are acid and poor in available nutrients (Ker, 1995; Mendonça and Stott, 2003). More detailed information on pedology, agriculture and sociology of Zona da Mata region was previously published by Cardoso et al. (2001).

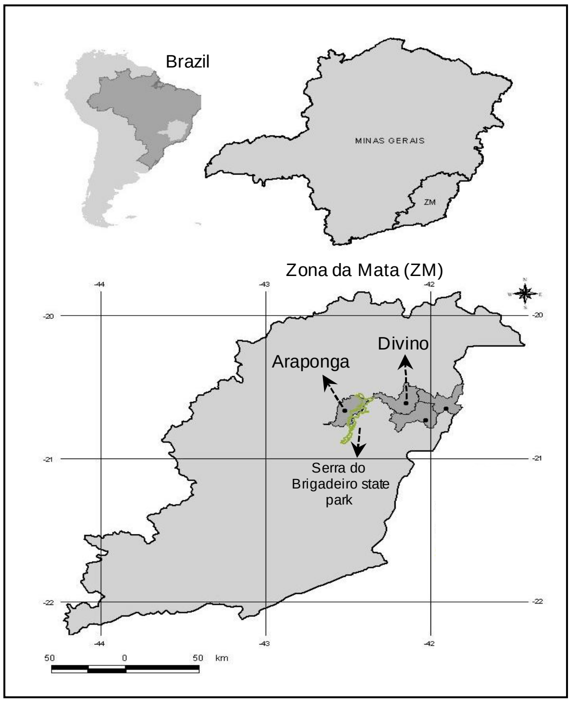

Figure 1. Localization of the municipalities of the study sites in the Zona da Mata (ZM), state of Minas Gerais.

2.2. Specific study sites and soil sampling

Three smallholder agroforestry coffee (*Coffea arabica* L.) systems (AGF) and three full sun coffee (FSC) systems fields with approximately 1.5 hectares and more than 12 years-old were studied. These areas were situated at the municipalities of Divino and Araponga (Figure 1), managed by smallholding farmers. More detailed information about the historical of land-use, management and fertilization of the studied sites are presented in Box 1 and Table 1.

In each selected site, areas under natural forest fragments (NF) were selected and used to represent the native or steady state condition of soil. In all cases NF fragments were situated at the same position on the landscape of the coffee-cultivated areas.

Box 1. Historical of land use and management of selected sites

Divino (coordinate: 20º33’S, 42º11’W; altitude: 1,160 m)
Agroforestry-coffee system: Prior cultivation this area was deforested and use as pasture, cultivated with *Melinis minutiflora* P. Beauv. (common name: Capim gordura). Some tree species of *Piptadenia gonoacantha* J.F. Macbr. (Jacaré) spontaneously grew in the pasture area. The intensive use of soil with pasture for several years (exact time unknown) declined the soil quality. Agroforestry-coffee system was implemented in 1994. The study was concentrated in an area of approximately 3,150 m^2 with 600 coffee-trees (*Coffea Arabica* L.) spaced in 3.5 m x 1.5 m. Native tree species were intercropped with coffee. The main tree species is *Luehea grandiflora* Mart (Açoita-cavalo), although other species such as *Aegiphila sellowiana* Cham. (Papagaio), *Erythrina verna* Vell (Mulungu), *Musa sp.* L. (Banana) and *Zeyheria tuberculosa* (Vell.) Bur. (Ipê-preto) can be found. Fertilizers and limestone were not applied during the two first years of the establishment of agroforestry systems. After this period, 3 Mg of limestone were applied in the projection of coffee-tree canopy. From 1999 to 2002, 50 g per plant of a mixture of ammonium sulfate, potassium chloride and monocalcium phosphate in a proportion of 3-1-1 was applied in a rate of 4 applications per year, totalizing 200 g per plant. In 2000, the trees species intercropped with coffee were drastically pruned, and the residues were left on the soil surface between the coffee rows. From 2003 to 2006 the farmer started the transition to organic coffee and stopped the inorganic fertilization. During this period, cow manure, castor bean cake, residues of leguminous species, supermagro[/4] and cattle urine were applied (Table 1). The productivity during organic cultivation was approximately 1.5 kg of coffee (pulp removed) per plant. In 2007, the organic coffee production was interrupted. Since this year, 100 g per plant of N-P-K fertilizer (20-5-20) has been applied twice a year (Table 1). The lower branches of the trees are pruned every 2 years and the residues are left on the soil surface, between coffee rows. Sporadically, jackbean, pumpkin and castor bean are cultivated between coffee rows. The mean annual productivity in 2007, 2008 and 2009 were about 0.90, 0.72 and 0.60 kg of coffee per plant. Full sun coffee system: the historical of land use is identical to the previous described site. The forest was converted in pasture for several years (exact time unknown) and further in coffee cultivation. The area has approximately 2,000 m^2 with 1,000 coffee trees spaced in 2 m x 1 m. There are no trees intercropped with coffee. Soil liming is not performed and there is no application of organic manure. Chemical fertilization of soil in 2007, 2008 and 2009 was done by applying 300, 200 and 150 g per plant of N-P-K (20-5-20). The mean annual productivity in 2007, 2008 and 2009 were 0.93, 1.2 and 0.06 kg of coffee per plant, respectively.

Araponga(I) (coordinate: 20º48’S, 42º32’W; altitude: 1,040 m)
Agroforestry-coffee system: In the past this area was deforested and used as pasture for several years (exact time is unknown). Then, coffee was cultivated under conventional management during 15 years, which resulted in severe reduction of soil fertility mainly caused by soil erosion. In 1995, agroforestry-coffee system was implemented in an area of approximately 5,040 m^2 with 1,200 coffee-trees spaced in 3 m x 1.2 m. The system was established in the highest slope area of the farm. The main tree species intercropped with coffee is *Persea americana* Mill. (Abacate). Soil is limed once a year, and there is no chemical fertilizer application. Chicken manure was used in the organic fertilization in 2001. Cow manure is applied annually and foliar fertilization is done by using supermagro twice a year (Table 1). Spontaneous vegetation is slashed 1- or 2-times per year and the residues are kept on the soil. Bean straw is applied annually on the rows. The lower branches of the tree-canopy are pruned during the dry season (June-July), after coffee harvesting. The residues of prune are kept on the soil surface avoiding soil erosion. The annual productivity is around 0.62 kg of coffee per plant. Full sun coffee system: the historical of land use is identical to the previous described site. The area has approximately 4,000 m^2 with 2,000 coffee trees spaced in 2 m x 1 m. The system was implanted in the lowest slope position, immediately below of the agroforestry-coffee area. There are no trees intercropped with coffee, but corn and beans had been planted between coffee rows. Soil liming and N-P-K fertilizer (20-5-20) applications are performed annually (Table 1) and there is no organic fertilization. The annual coffee productivity is approximately 0.79 kg of coffee per plant.

Araponga(II) (coordinate: 20º41’S, 42º31’W; altitude: 1,040 m)
Agroforestry-coffee system: In the past this area was deforested and used as pasture for several years (exact time is unknown). Further, it was burned and cultivated with rice during 7 years. During rice cultivation the soil was usually plowed by animal traction. Rice cultivation caused severe soil erosion leading to a decline of soil quality. After rice the area was cultivated with corn and beans, and finally, it was converted in pasture for 3 years when soil achieved its lowest level of fertility. In order to reclaim the land, in 1994 *Pennisetum purpureum* Schum. cv. Napier (capim-napier) and trees species such as, *Colubrina glandulosa* Perkins (sobrasil), *Hovenia dulcis* Thunb. (uva-do-japão), *Inga sessilis* Mart. and *Inga subnuda* subsp. *luschnathiana* (Benth.) T.D. Penn. were planted. The Inga species were introduced later on and the other tree species were removed. In 1998, Agroforestry-coffee was implemented. Soil liming was done in 1999, 2001, 2004 and 2006 by adding 200 g of limestone per m^2. The coffee field which includes the area covered by Inga species has approximately 1,500 m^2 with 500 coffee-trees spaced in 3 m x 1 m. At the beginning, corn and beans was usually intercropped between coffee rows, but since four years ago such inter-cropping is not performed. In the cultivation of corn and/or beans, N-P-K fertilizer (4-18-8) was applied on a rate of 30 g per m^2. Trees are not pruned but the herbaceous spontaneous vegetation is slashed three times per year. The residues of slashing are kept on the soil surface. N-P-K (20-5-20) and foliar fertilizer are applied annually (Table 1). There is no organic fertilization. The mean of coffee productivity in 2007 was 0.36 kg of coffee per plant. Full sun coffee system: the historical of land use is identical of the previous described site. This area corresponds to the other part in which Inga species were not planted. It has approximately 7,500 m^2 with 2,500 coffee trees spaced in 3 m x 1 m. The main difference in relation to agroforestry-coffee is the absence of trees. The mean of coffee productivity in 2007 was 0.45 kg of coffee per plant. Other information about chemical fertilization is presented in Table 1.

[/4] Liquid biofertilizer for foliar application prepared from fresh manure diluted in water and enriched with bone meal, blood, fish scraps (the latter two contributing minerals), and unrefined sugar and milk to stimulate fermentation. This mix is fermented anaerobically for about 1.5 months. Other organic liquid fertilizers include fermented, cattle urine and an infusion prepared from manure (Velásquez, 2002).

Table 1. Characterization of the agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino and Araponga.

	Divino		Araponga(I)		Araponga(II)	
Item	**AGF**	**FSC**	**AGF**	**FSC**	**AGF**	**FSC**
Area size, m^2	3,150	2,000	5,040	4,000	1,500	7,500
Number of coffee trees	600	1,000	1,200	2,000	500	2,500
Spacing of coffee trees, m	3.5 x 1.5	2 x 1	3 x 1.2	2 x 1	3 x 1	3 x 1
Number of trees per ha	150 - 200	-	200	-	~150	-
Fertilizer N-P-K (20-5-20), g/plant	100[/b]	150[/c]	na	180	200[/d]	200[/d]
Cow manure, kg	10,000[/e]	na	2,880	na	na	na
Castor bean residue, kg	600[/e]	na	na	na	na	na
Compost, kg	5,000[/e]	na	na	na	na	na
Limestone, g/m^2	950[/f]	na	20[/g]	40[/g]	200[/h]	200[/h]
Foliar fertilization (supermagro)	yes	na	yes	na	na	na
Biomass production[/a] (litter)						
Coffee trees, kg/year	720	890	1,440	1,780	600	2,225
Trees, kg/year	2,398	-	2,004	-	4,331	-

[/a] Coffee trees: estimated from Campanha et al. (2007) where litter production (dry matter) in agroforestry is 50.7 g m^{-2} $month^{-1}$ and sun coffee system is around 37.2 g m^{-2} $month^{-1}$; Other trees: measured by Duarte (2007);

[/b] From 2006 to 2009, applied twice a year; From 1999 to 2002: 200 g $plant^{-1}$ $year^{-1}$ of a mixture of ammonium sulfate, potassium chloride and monocalcium phosphate in a proportion of 3-1-1;

[/c] Performed in 2008; In 2006 and 2007, N-P-K (20-5-20) was applied on a rate of 150 and 100 g per plant, respectively, twice a year;

[/d] applied once a year;

[/e] Total applied during organic cultivation from 2003 to 2006; supermagro applied twice a year; na: not applied;

[/f] applied in 1997;

[/g] applied annually;

[/h] total applied in 1999, 2001, 2004 and 2006.

The chemical composition of senescent leaves of the main trees species used in the agroforestry systems was previously measured by Duarte (2007) and a summary is presented in Table 2.

Table 2. Chemical composition and C:N, LG:N, LG:PP and LG+PP:N ratios of senescent leaves of the main tree species in areas under agroforestry-coffee systems at three municipalities of Zona da Mata, Minas Gerais state

	Chemical composition[/a]							Ratio			
Site/ species	C	N	P	LG	HC	CL	PP	C:N	LG:N	LG:PP	LG+PP:N
	---------------------------- % ----------------------------										
Divino											
Luechea grandiflora	65.8	2.02	0.119	13.6	19.2	17.2	8.3	32.6	6.7	1.6	10.8
Araponga(I)											
Persea americana	60.7	2.05	0.163	21.0	13.4	12.8	7.3	29.6	10.2	2.9	13.8
Araponga(II)											
Inga subnuda	54.6	3.17	0.141	27.3	23.9	21.3	4.8	17.2	8.6	5.7	10.1

[/a] C:carbon; N: nitrogen; P: phosphorus; LG: lignin; HC: Hemicellulose; CL: Cellulose; PP: total polyphenols. Adapted from Duarte (2007).

Soil samples were collected at 0-5 and 5-10 cm depths, during the period from December of 2006 to March of 2007 (rainy season). In order to guarantee a representative sampling procedure, four sub-samples randomly distributed between coffee rows were taken at each site, and then combined to form one replicate. Four replicates were collected. Before the samples were taken, the litter layer was removed. Once in the laboratory, the remained moist soil was gently broken, air dried, sieved through a 2-mm sieve and stored at room temperature. Selected physical and chemical soil properties are shown in Table 3.

Table 3. Values of particle sized fractions, pH (H_20), cation exchange capacity (CEC) and base saturation of soils under native forest (NF), agroforestry coffee (AGF) and full sun coffee (FSC) systems at 0-10 cm layer in the municipalities of Divino, Araponga(I) and Araponga(II)

	Divino			Araponga(I)			Araponga(II)		
Soil characteristic	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
Particle size, g kg^{-1}									
Sand	504	573	519	493	520	495	474	388	444
Silt	237	122	165	108	119	124	124	113	134
Clay	259	305	316	399	361	381	402	499	422
pH H_2O (1:2.5)	6.4	6.0	6.1	4.9	5.8	5.8	4.8	5.6	6.2
CEC, $cmol_c$ dm^{-3}	21.4	11.1	11.6	16.6	11.1	10.1	17.7	12.2	11.0
Base saturation, %	77.0	69.0	63.0	2.0	46.0	51.0	1.0	30.0	40.0

2.2. Humic substances extraction and purification

The extraction and isolation of soil humic acids (HA) and fulvic acids (FA) was performed according to the International Humic Substances Society (IHSS) methodology (Swift, 1996). FA and HA were extracted and separated by the use of 0.1 *M* NaOH solution with a soil:solvent ratio of 1:10 under N_2 gas atmosphere, and then precipitated with 6 *M* HCl added to the extract until a pH of 2.0 was reached. The precipitates were allowed to coagulate for 24 hours at 4°C and were then separated by centrifugation (3,000 *g* for 20 minutes). The precipitated HAs were then purified by successive washes of a solution of 10% HF + 0.1 *M* HCl by shaking the suspension in 100-ml plastic bottles for 24 hours in order to reduce the ash content and the influence of paramagnetic ions (Gonçalves et al., 2003). After shaking, the samples were centrifuged at 10,000 *g* for 20 minutes and the supernatant was discarded. This procedure was carried out three times, and at the end of the third cycle, the samples were dialyzed by using cellulose membranes (Visking dialysis tubing 36/32) until free of chlorine and then freeze-dried. The pretreatment for FAs was performed by passing approximately 1 L of sample through a column of Amberlite XAD-8 resin. The percolated was discarded and the adsorbed amount of FA onto XAD-8 resin was eluted in reverse direction with 0.1 *M* NaOH. The total eluated was immediately brought to pH 2 and further passed through a column of Amberlite 120^+ resin to remove excess of salt and then was freeze-dried to a low-ash form.

2.3. Elemental analysis

The elemental composition (C, H, N and S contents) of freeze-dried solid HA and FA were measured by dry combustion using a Carlo Erba EA1108 CNHS Elemental Analyzer. The oxygen content was determined by the difference from 100%.

2.4. Thermogravimetry analysis (TG)

Thermal analysis of the solid freeze-dried HA and FA was measured using a SDT-2960 simultaneous DSC-TGA thermal analyzer (TA instruments). The experimental conditions for TG were done under static air atmosphere as following: a temperature equilibrating at 30ºC followed by a linear heating rate of 5ºC min^{-1} from 30 to 105ºC (that was used for calculating the moisture content of the HA and FA). At this point it was done an isotherm for 10 min and then continued ramping of 5ºC min^{-1} from 105 to 680ºC. The ash content in the solid HA and FA samples were calculated from the inorganic residue remaining at the end of the ramp. Based on the thermal behavior of thermograms, and considering that main weight losses occurred at 110-350ºC and 350-550ºC ranges, it was calculated two zones of mass loss as following:

$$\text{Zone I} = \frac{\text{mass loss at } 110 - 350^{\circ}\,\text{C}}{\text{total mass loss at } 110 - 550^{\circ}\,\text{C}}$$ and

$$\text{Zone II} = \frac{\text{mass loss at } 350 - 550^{\circ}\,\text{C}}{\text{total mass loss at } 110 - 550^{\circ}\,\text{C}}.$$

The relationship between two zones was accessed by the ratio Zone II/Zone I which was used as an index of thermal lability of humic structures.

2.5. Acidic functional groups

Total acidity and carboxyl groups of HA were measured using the barium hydroxide and the calcium acetate methods, respectively (Perdue, 1985). Phenolic groups were calculated as the difference between total acidity and carboxyl groups. Chemical analysis was done in duplicate.

2.6. Fourier-transformed infrared spectroscopy (FTIR)

Infrared spectra were recorded on a FTIR Perkin Elmer, Spectrum 1000 apparatus using the KBr pellet technique. The KBr pellets were prepared by grounding and mixing thoroughly a portion of 1.5 mg for HAs or 1 mg for FAs with 400 mg KBr (both dried at 60°C for 24 h) and pressing under vacuum at 10.000 kg cm^{-2} for 10 min. Spectra were recorded over the range of 4000 and 400 cm^{-1} wavenumbers at 4 cm^{-1} resolution. In all cases, 20 scans were averaged to reduce noise and corrected against the spectrum for ambient air as background.

The interpretation of the FTIR spectra was based on several data published by Stevenson (1994), Hsu and Lo (1999), Sánchez-Monedero et al. (2002), González Pérez et al. (2004) and Ellerbrock and Kaiser (2005).

2.7. Solid-state ^{13}C CPMAS/NMR spectroscopy

The solid-state ^{13}C NMR spectra of freeze-dried HAs were obtained using a Varian Unity 300 spectrometer operating at a ^{13}C resonance frequency of 75.42 MHz and a ^{1}H frequency of 300 MHz. The experiments were performed using cross-polarization with magic angle spinning (CP-MAS) technique applied with a spectral width of 50 kHz with 90º pulse of 6.7 ms, contact time of 1.5 ms, spinning speed of 4 kHz, a pulse delay of 4 s and acquisition time of 35 ms. For all samples it was performed 20,000 scans. The total signal intensity and the proportions that contributed to each carbon type were determined by integration of the spectral regions, with spectra being divided into four main regions: (i) alkyl C (0-45 ppm), (ii) *O*–alkyl C (45-92 ppm), (iii) aromatic C (92-150 ppm) and (iv) carbonyl C (150-215 ppm) (Dieckow et al., 2005b).

An index of the extent of decomposition was obtained by the ratio between alkyl C to *O*-alkyl C regions (A/*O*-A) and was used to indicate substrate quality as a resource for soil microorganisms (Baldock et al., 1997; Webster et al., 2001).

The aromaticity index was calculated as: [aromatic C (92-150 ppm)]/[alkyl C + *O*-alkyl C (0-92 ppm) + aromatic C] *100. This index was used to characterize the extent of humification of HA (Hatcher et al., 1981). Carbonyl C resonance (–COOH groups) was omitted from the aromaticity calculation, because it is not known how many –COOH groups are bonded to aromatic or to aliphatic structures (Schnitzer, 1991).

2.8. Statistical analysis

Experimental data were subjected to ANOVA to determine the effect of land use and soil depth on the composition and structure of soil HA and FA. Multiple mean separations were performed using Tukey´s multiple range test at $P < 0.05$. Student's *t*-test was applied to access differences among estimated means at $P < 0.05$.

3. Results and discussion

3.1. Chemical analysis

The elemental composition of soil HA was significantly affected by the land use and soil depth (Table 4). The C concentration of HA ranged from 491.4 to 519.8 g kg^{-1} at 0-5 cm and from 513.6 to 603.9 g kg^{-1} at 5-10 cm layers. In general, the elemental composition of HA was consistent with values proposed by Stevenson (1994) for tropical soils as well as by Nascimento *et al.* (1992) and González Pérez *et al*. (2004) for Brazilian soils.

The elemental composition of the HA extracted from upper soil layer (0-5 cm), was characterized by low C concentrations, being in the lower limit of the range proposed by Stevenson (1994), and rich in N and O compounds. These results were similar to the humic-like substances extracted from rich organic matrices such as composts (Sánchez-Monedero *et al*, 2002), indicating that the formation of HA in the soil surface may have been affected by the input of plant residues or organic amendments (Table 2). This pattern was confirmed by the atomic ratios H/C and O/C, which showed significantly decreased ($P > 0.01$) with soil depth, indicating that HA extracted from the soil surface (0-5 cm) had a less aromatic structure, typical of humic acids extracted from organic matrices.

Table 4. Elemental composition of the humic acids extracted from soils at 0-5 and 5-10 cm layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in three municipalities of Zona da Mata, Minas Gerais

		Elemental composition[a] (g kg^{-1})				Atomic ratio		
Sites	Land use	C	H	N	O[b]	H/C	O/C	N/C[c]
					0-5 cm			
Divino	NF	505.1	45.7	50.3	398.9	1.09	0.59	8.54
	AGF	510.1	51.4	46.6	392.0	1.21	0.58	7.83
	FSC	504.6	43.3	49.5	402.6	1.03	0.60	8.41
	SE[d]	7.0	1.4	1.0	9.2	0.04	0.01	0.20
Araponga(I)	NF	511.4	46.5	47.3	394.7	1.09	0.58	7.93
	AGF	511.8	45.3	48.8	394.2	1.06	0.58	8.17
	FSC	491.4	46.8	43.4	418.4	1.14	0.64	7.57
	SE	2.5	2.2	0.5	4.7	0.05	0.01	0.09
Araponga(II)	NF	519.8	45.9	47.0	387.3	1.06	0.56	7.75
	AGF	492.7	44.7	46.9	415.7	1.09	0.63	8.16
	FSC	508.9	49.2	49.5	392.5	1.16	0.58	8.34
	SE	1.9	2.1	2.7	3.3	0.05	0.01	0.45
					5-10 cm			
Divino	NF	561.4	49.8	60.1	328.7	1.06	0.44	9.18
	AGF	563.5	53.0	54.1	329.3	1.13	0.44	8.23
	FSC	543.6	47.6	56.8	352.0	1.05	0.49	8.96
	SE	2.1	0.8	1.1	2.3	0.02	0.004	0.17
Araponga(I)	NF	553.4	47.2	53.6	345.8	1.02	0.47	8.30
	AGF	569.8	48.4	55.9	325.9	1.02	0.43	8.41
	FSC	572.1	47.5	53.3	327.1	1.00	0.43	7.99
	SE	1.9	0.9	0.5	2.1	0.02	0.003	0.08
Araponga(II)	NF	603.9	53.5	59.4	283.2	1.06	0.35	8.43
	AGF	542.5	47.2	48.4	361.9	1.04	0.50	7.65
	FSC	561.1	47.5	54.7	336.7	1.02	0.45	8.36
	SE	2.2	1.2	1.0	2.2	0.03	0.01	0.19
Effect of depth		**	**	**	**	**	**	*
Usual range for humic acids[e]		538-587	32-62	8-43	328-383	~1.0	~0.5	-

[a] on an oven dry ash-free basis; [b] calculated by difference; [c] expressed as: atomic ratio x 100; [d] pooled standard error (SE) of the chemical analysis; [e] Stevenson (1994); *, **: significant at 0.05 and 0.01, respectively, by least significant difference test.

There were no definitive trends regarding the effect of land use on the elemental composition of HA. At soil surface HA from AGF soil showed higher C contents compared to FSC system at Araponga(I). However, the opposite occurred at Araponga(II) (Table 4). In the deepest soil layer, higher C contents were registered in HA from FSC than in AGF system, exception to Divino. C, H and N contents of HA increased significantly from upper to deeper soil layer, probably as a result of lower influence of the oxidation process at the soil subsurface. This finding was supported by the significant decrease of O/C ratio with increase of soil depth. The N/C ratio of HA at Divino and Araponga(I) was higher in AGF than FSC system, suggesting that the biomass input derived from trees in the AGF management drives the N cycling in the humic structure. The contrary trend for land-use was verified at Araponga(II), where higher N/C ratio occurred in FSC in comparison to AGF system.

A graphical method to study the coalification process in which the atomic H/C ratio is plotted as a function of the atomic O/C ratio was developed by van Krevelen (1961). This ratio, commonly known as van Krevelen diagrams, has been used to illustrate compositional differences between humic and fulvic acids, and also to show variations in humic substances as a function of source (Rice and MacCarthy, 1991; Barančíková et al., 1997). The van Krevelen diagrams of HA from different land use are shown in Figure 2.

In Divino soils, the higher position of HA from AGF system compared to FSC in the diagram indicates the dominance of the processes of hydrogenation and methylation, which is related to the incorporation of aliphatic fractions into the humic structures as a consequence of the incorporation of organic residues. HA extracted from soils under FSC, due to lower organic residue addition, are expected to be more stable, representing a higher degree of humification (Barančíková *et al.*, 1997).

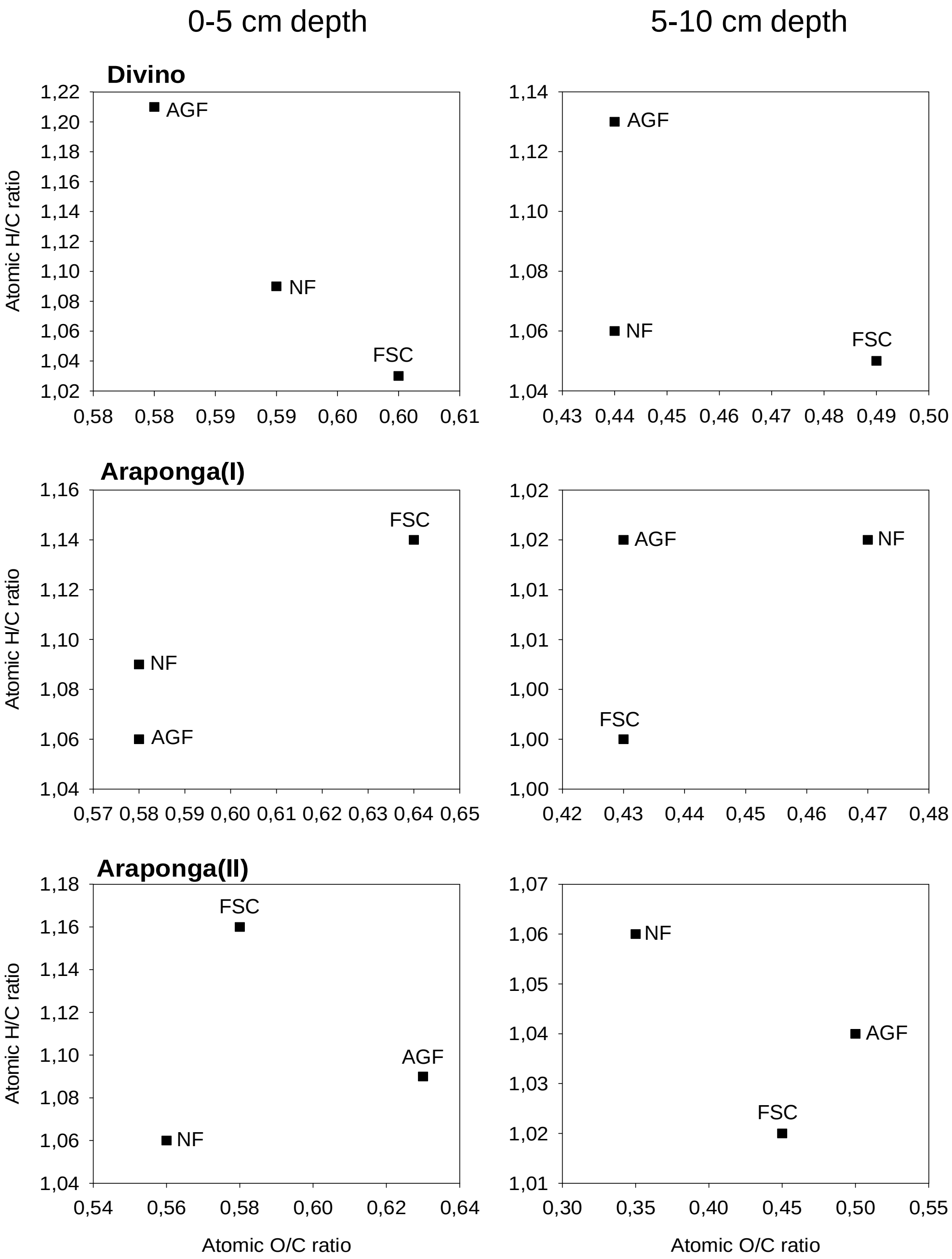

Figure 2. H/C versus O/C diagrams for humic acids extracted from 0- to 5- and 5- to 10-cm soil layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in the municipalities of Divino, Araponga(I) and Araponga(II).

In Araponga(II), HA from the upper soil layer in the AGF system presented lower position in the diagram compared to FSC (Figure 2), indicating that, at this site, AGF management favored the formation of HA with higher degree of humification. This behavior was contrary to that found at Divino, which suggests that the effect of agroforestry management is directly influenced by characteristics of the environment, such as soil properties and quality of residues. At this site, the quality of organic residues appear to be the main factor affecting SOM dynamics. In a previous study performed in Araponga(II) site, Duarte (2007) found that the residues of the main tree-component (*Inga* sp.) in the AGF system presented the highest content of lignin (27.3%), hemicellulose (23.9%) and cellulose (21.3 %) and showed slower decomposition rate compared to other sites, thus implying in a slow turnover organic residues.

In general, FA presented lower C and N and higher O contents than HA (data not shown). The ranges of C, H, N and O contents were in line to the usual range for FA proposed by Stevenson (1994). The differences on the elemental composition between HA and FA are well refereed in the literature. For instance, higher H/C ratio of FA compared to HA is probably due to the larger amount of acidic functional groups, particularly COOH, in the FA (Stevenson, 1994). On the other hand, the opposite occurred in the O/C and N/C ratios showing the greater aromatic character of HA compared to FA. Few changes in the elemental composition of soil FA were registered as a function of land use.

The concentration of acidic carboxylic groups (COOH) of HA is shown in Figure 3. The content of the COOH groups has been used as a valuable index of humification, so that the highest values suggest an increase in the degree of humification of humic molecules (Barančíková et al., 1997; Cunha et al., 2007).

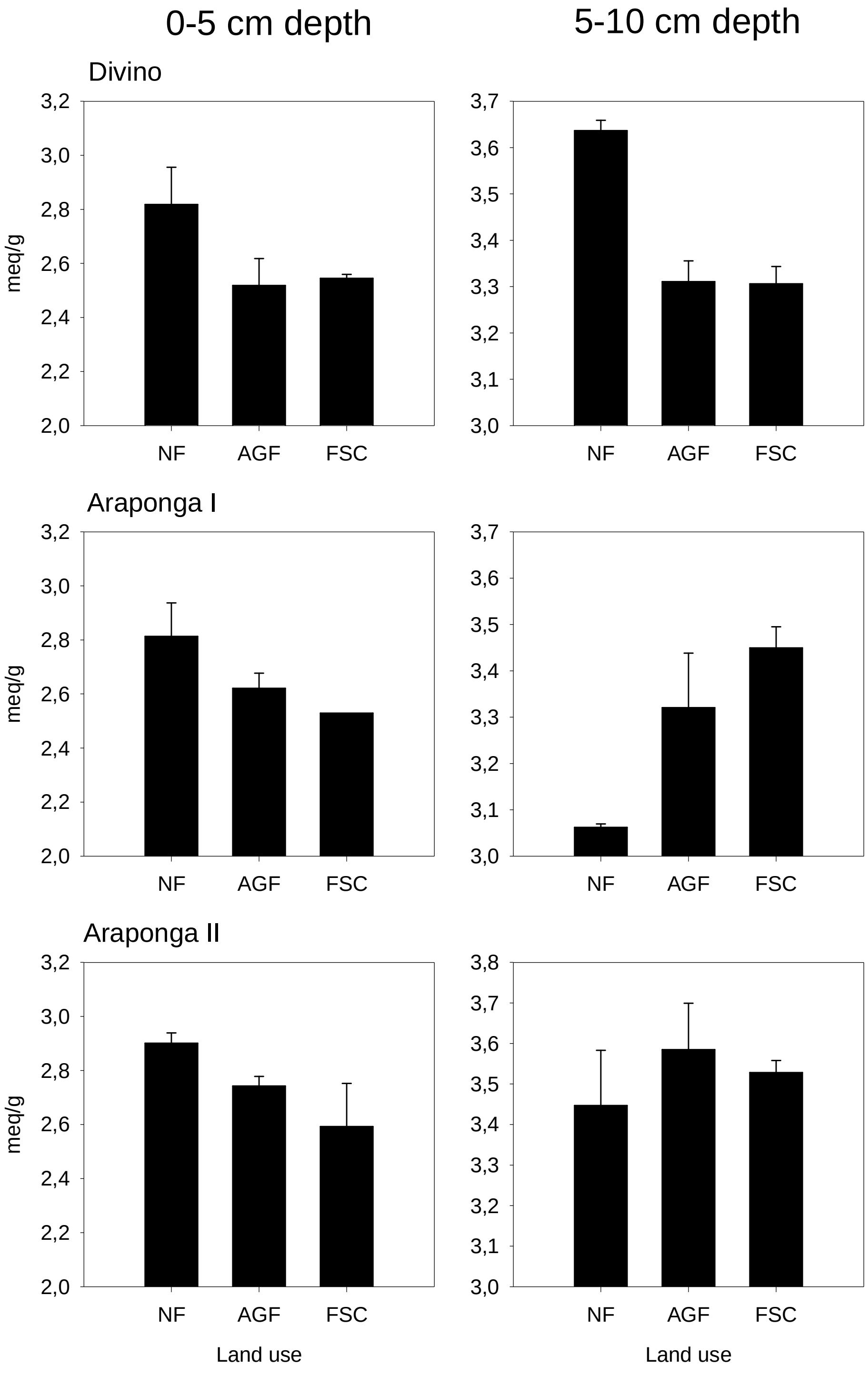

Figure 3. Carboxylic group acidity (COOH) content of humic acids extracted from 0-5 and 5-10 cm soil layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in different municipalities of Zona da Mata, Minas Gerais state. Bars represent mean ± standard error.

In Divino, HA from the AGF and FSC systems presented similar content of COOH in both soil layers, suggesting a similar degree of humification. This result contrasts with the elemental analysis which showed a lower degree of humification of HAs from AGF compared to the FSC system. Carboxyl contents of humic substances can be overestimated by the calcium acetate method. This problem has been attributed to the failure in removing all of the humic substance from the equilibrated reaction mixture (Perdue et al., 1980). The content of the carboxylic groups can be estimated also from ^{13}C NMR spectra (Fründ et al., 1989; Barančíková et al., 1997). In general, the values of COOH acidity obtained from ^{13}C NMR are substantially higher than those determined by titration (Ritchie and Perdue, 2008). Regardless of such differences, when we evaluated the COOH acidity by ^{13}C NMR in Divino soils (Table 7), FSC presented higher COOH content than the AGF system, supporting the previous findings of the elemental analysis.

In Araponga(II) the higher COOH acidity content in AGF than in FSC system (Figure 3) was confirmed by the lowest position of HA from AGF system in the van Krevelen diagram (Figure 2), thus implying in a greater degree of humification, specially for HA from the upper soil layer.

Briefly, the elemental composition and the carboxylic functional groups indicate that the effect of AGF management on the structure of HA and FA depends on the inherent characteristics of the study site, especially with regard to the quality of the organic residues.

3.3. Thermogravimetry analysis

The thermal behavior of soil HA and FA was characterized by an initial weight loss at 101 to 102ºC, followed by a shoulder between 150 and 350ºC and an intense exotherm around 400ºC (thermograms not shown). Few or any change in the thermal behavior occurred in temperatures above 550ºC. In general, for HA a sharply peak of mass loss occurred at high range of temperature (350 to 550ºC) which is attributed to the loss of more aromatic structures (Dell'Abate *et al.*, 2002; Trompowsky *et al.*, 2005). Weight losses at the range from 110 to 350ºC were constant with increasing the temperature and did not show a characteristic peak on the DSG curve. Losses at this range are mainly related to the elimination of aliphatic structures in the functional groups (Plante *et al.*, 2005). The greatest mass loss of FA occurred at 110 to 350ºC range in all sites and soil depths, followed by lowest losses at the 350 to 550ºC. Such pattern may be related to the higher amount of functional groups of FA compared to HA as also reported elsewhere (Fründ *et al.*, 1989; Mendonça *et al.*, 2006; Ritchie & Perdue, 2008).

The most important mass loss events of soil HA and FA are summarized in Table 5. Two zones of mass loss were defined in function to the total of losses occurred between 110 and 550ºC. The zone I represented relative losses occurring between 110 and 350ºC, whereas zone II depicted relative mass losses between 350 and 550ºC. The zone I accounted in average for 36 and 55% of total mass loss of HA and FA, respectively. There was a slight trend of higher proportion of mass loss at this zone in AGF than in FSC system, especially for HA. The mass losses in the zone II represented 64 and 44% of total for HA and FA, respectively. In general, the differences on the proportion of mass losses at this zone between FSC and AGF systems were less expressive than in zone I.

Table 5. Thermogravimetry: mass loss in function of different ranges of temperature of solid-state humic acids and fulvic acids (in parenthesis) extracted from soils at 0-5 and 5-10 cm layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in three municipalities of Zona da Mata, Minas Gerais state

		TG relative mass losses[/a]		Ratio
Sites	Land use	Zone I	Zone II	Zone II:Zone I
			0-5 cm	
Divino	NF	0.35(0.59)	0.65(0.41)	1.86(0.69)
	AGF	0.33(0.51)	0.67(0.49)	2.03(0.96)
	FSC	0.31(0.51)	0.69(0.49)	2.23(0.96)
Araponga(I)	NF	0.31(0.55)	0.69(0.45)	2.23(0.81)
	AGF	0.33(0.52)	0.67(0.48)	2.03(0.92)
	FSC	0.29(0.55)	0.71(0.45)	2.45(0.82)
Araponga(II)	NF	0.34(0.56)	0.66(0.44)	1.94(0.79)
	AGF	0.40(0.50)	0.60(0.50)	1.50(1.00)
	FSC	0.37(0.54)	0.63(0.46)	1.70(0.85)
			5-10 cm	
Divino	NF	0.39(0.51)	0.61(0.49)	1.56(0.96)
	AGF	0.44(0.59)	0.56(0.41)	1.27(0.69)
	FSC	0.38(0.55)	0.62(0.45)	1.63(0.82)
Araponga(I)	NF	0.37(0.58)	0.63(0.42)	1.70(0.72)
	AGF	0.37(0.64)	0.63(0.36)	1.70(0.56)
	FSC	0.36(0.56)	0.64(0.44)	1.78(0.79)
Araponga(II)	NF	0.37(0.61)	0.63(0.39)	1.70(0.64)
	AGF	0.36(0.59)	0.64(0.41)	1.78(0.69)
	FSC	0.35(0.53)	0.65(0.47)	1.86(0.89)

[/a] Zone I defined as: [mass loss at 110-350ºC]/[total mass loss at 110-550ºC]; Zone II defined as: [mass loss at 350-550ºC]/[total mass loss at 110-550ºC].

The relationship between two mass loss zones, expressed by the ratio zone II/zone I, is presented in Table 5. This ratio was used to access the thermal lability of humic substances and can depict the extent of humification of its structure. HA from soils under AGF systems presented lower values of the ratio in practically all sites and soil layers when compared to FSC systems, and were close to the values of the reference areas. It suggests that HA from AGF soils were less aromatic than those from FSC systems, supporting our previous findings. Similar pattern was registered to FA extracted from 5-10 cm layer. In general, the values of zoneII:zone I ratios were larger in HA from soil surface, indicating the greater aromatic character compared to HA from deepest soil layer.

The thermal behavior revealed that FSC systems seems to favor the formation of HA with more thermally stable structures, whereas in AGF systems HA are richer in aliphatic chains, which may imply the presence of less stabilized humic substances in the soil (Dell'Abate *et al.*, 2002).

3.4. Infrared spectra (FTIR)

The infrared (FTIR) behavior of the spectra of soil HA and FA isolated from different land use showed similar pattern on the spectral signature. Some differences occurred in the intensity of certain bands (spectra not shown). The interpretation of the spectra was based on several works (Stevenson, 1994; Hsu and Lo, 1999; González-Pérez et al., 2004; Gerzabek et al., 2006) and the proposed assignments of the main spectra bands are listed in Table 6.

Table 6. Assignment of Fourier transformed infrared (FTIR) spectral peaks indicating the main functional groups of humic and fulvic acids extracted from soil in areas under native forest, agroforestry-coffee and full-sun coffee systems

Wavenumber, cm^{-1}	Proposed assignments
3430 – 3410	O–H stretching of OH groups of phenols, water, alcohol, carboxylic, N–H stretching of amine.
2923 – 2848	Asymmetric and symmetric aliphatic C–H stretching vibrations of CH_3 and CH_2 groups (e.g. fatty acids, waxes and other aliphatics).
1717 – 1712	C=O stretching of COOH, ketones and aldehydes.
1630 – 1625	C=O stretching of amide group (amide I), quinine and/or conjugated ketones; C–O of COO^- (antisymmetric); aromatic C=C, strongly H-bonded C=O of conjugated ketones.
1457 – 1384	Aliphatic C–H vibrations; OH deformation and C–O stretching of phenolic OH; C–H deformation of CH_2 and CH_3 groups; COO^- antisymmetric stretching.
1261 – 1233	C–O stretching and OH deformation of COOH; C–O stretching of aryl ethers and phenols.
1116 – 1029	C–O stretching of C–O–C groups (polysaccharides); Si–O stretching of silicate impurities.

Broadly bands in HA occurred around wavenumber 3450, 1630, 1235 and 1030 cm^{-1}. In Divino, the main changes between both coffee-cultivated areas were an increase of peaks in the aliphatic region at 2923-2848 cm^{-1} in AGF followed by a slightly increase of peak in the aromatic region at 1630-1625 cm^{-1} in the FSC system. Such behavior suggests that AGF favored the increase of the components most easily degraded in the HA, which can represent an available source of energy for soil microbes (Jouraiphy et al., 2005), whereas the increase of the aromatic structure in FSC indicates a decline in the quality of the resource as a substrate (Mathers et al., 2003).

No substantial differences were registered in the absorption ratios of FTIR peaks 2924/1629 (C–H aliphatic/C=C aromatic) and 2924/1721 (C–H aliphatic/ C=O of COOH) of HA when comparing the AGF and FSC systems, exception to HA from Araponga(I) soils, which showed a slight increase in the 2924/1721 ratio in AGF (1.22) compared to FSC (1.09). Such result indicates the higher aromatic character of HA from the FSC system, confirming our previous results.

Features of FTIR spectra of FA showed more defined peaks when compared to HA (spectra not shown). Although both HA and FA presented somewhat similar spectra, the main differences was noted in the intensity of the peaks. A clear change in the FTIR spectra between HA and FA was attributed to the increase of peak around 1717 cm^{-1} in FA, followed by a decrease of peak at 1630 cm^{-1}. This behavior can be explained by the higher content of acidic functional groups of FA in comparison to HA, mainly related to COOH, which has an assignment close to 1700 cm^{-1} (Stevenson, 1994). None or few substantial changes could be observed in the FTIR assignments of FA as a result of land use.

A great similarity could be seen in the general appearance of all FTIR spectra. This technique provided only few detailed information about chemical or structural changes in HAs and FAs derived from soil management. This fact is in accordance with the findings of González-Pérez et al. (2004) in a study on humic acids from a Brazilian Oxisol under different tillage management. They stated that, although FTIR can be used for the identification of functional groups and the determination of their relative distribution, the technique failed to provide more detailed information about the structural changes of HAs influenced by the tillage management.

3.5. Solid-state ^{13}C CPMAS/NMR

The ^{13}C NMR signatures of HAs from all sites were quite similar in peak position and intensity (Figure 4). The similarity of the ^{13}C NMR spectra of soil HA under different land use was also reported elsewhere (González-Pérez et al., 2004; Dou et al., 2008). The ^{13}C NMR spectra were subdivided into four regions: (i) aliphatic or alkyl-C (0–45 ppm) from lipids, fatty acids and plant aliphatic polymers; (ii) *O*-alkyl-C (45–92 ppm) deriving primarily from polysaccharides (cellulose and hemicelluloses), but also from proteins and side chains of lignin; (iii) aromatic or aryl-C (92–150 ppm), derived from lignin and/or protein; and finally (iv) carbonyl-C (150–215 ppm) from aliphatic esters, carboxyl groups and amide carbonyls. The integration of the peaks within each of the chemical shift regions allowed the estimation of the relative ^{13}C contents expressed as percentages of the total area (Table 7).

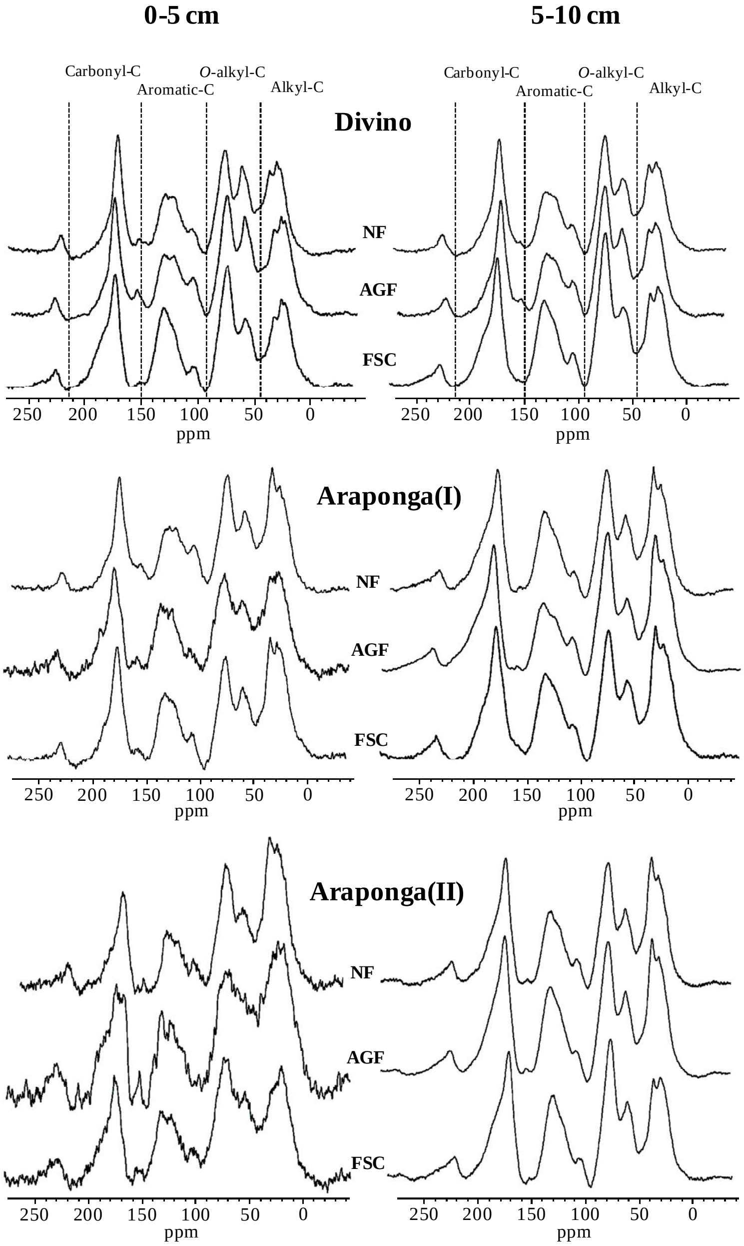

Figure 4. ^{13}C CP-MAS/NMR spectra of humic acids extracted from 0-5 and 5-10 cm soil layers in areas under native forest (NF), agroforestry-coffee (AGF) and full sun coffee (FSC) systems in the municipalities of Divino, Araponga(I) and Araponga(II). Vertical dotted bars indicate the respective ^{13}C assignments.

Table 7. Distribution of ^{13}C in soil humic acids from areas under native forest (NF), agroforestry system-coffee (AGF) and full-sun coffee (FSC) systems as determined by ^{13}C CP-MAS/NMR

Sites	Land use	Alkyl C 0-45 ppm	*O*-alkyl C 45-92 ppm	Aromatic C 92-150 ppm	Carbonyl C 150-215 ppm
		-------------------------------- % [/a]			--
			0-5 cm		
Divino	NF	26.4	30.9	21.3	21.4
	AGF	26.7	31.3	21.8	20.3
	FSC	23.6	29.8	22.5	24.1
Araponga(I)	NF	29.2	30.3	21.6	18.9
	AGF	31.6	32.1	18.3	18.0
	FSC	31.4	26.1	20.6	21.9
Araponga(II)	NF	36.1	30.2	15.9	17.8
	AGF	32.4	29.5	17.9	20.2
	FSC	28.3	36.6	19.0	16.1
			5-10 cm		
Divino	NF	27.6	33.1	19.3	20.0
	AGF	25.2	35.4	19.2	20.2
	FSC	23.4	33.9	21.2	21.5
Araponga(I)	NF	25.4	28.4	20.5	25.6
	AGF	26.9	28.4	19.2	25.5
	FSC	26.9	27.3	22.1	23.7
Araponga(II)	NF	27.3	28.0	19.6	25.1
	AGF	25.7	27.1	20.8	26.4
	FSC	23.5	29.4	21.0	26.1

[/a] values are expressed as percentage of the whole spectrum area.

In all sites, ^{13}C NMR assignment of HA were dominated by the *O*-alkyl C resonance (45-92 ppm) in both soil layers followed by a resonance line assigned to alkyl C (Figure 4). The relative intensity of the signals associated to aliphatic C (alkly C + *O*-alkyl C) indicate that aliphatic portions seem to be preserved and increased due to the incorporation of plant residues and as a result of the microbial activity, favoring the synthesis of dominantly alkyl- and *O*-alkyl C (Baldock et al., 1990; González-Pérez et al., 2004).

The chemical shift region of *O*-alkyl C had two distinct peaks: 45-70 ppm, mainly related to cellulose; 70-90 ppm, due to aliphatic side chains of lignin, hemicelluloses and others carbohydrates (Stevenson, 1994). The major signal in the alkyl C region was centered at 30 ppm, which can be assigned to C in longchain polymethylene ($(CH_2)n$) structures, such as surface waxes, lipids, cutin and resins, and is relatively stable against microbial attack (Quénéa et al., 2006). The aromatic C region (92-150 ppm) shows two fairly differentiated regions corresponding, respectively, to the region between 92 to 110 ppm, mainly produced by aromatic C linked to O or N, and that between 110 and 150 ppm for H-substituted and C-substituted aromatic carbons (Keeler et al., 2006). The phenolic C region displayed a weak signal at 153 ppm indicative of syringyl lignin. The carbonyl C region (150-215 ppm) in all the spectra displayed a broad peak centered at 173 ppm, originated from carboxyl, amide, aliphatic esters or carbonyl-C of lignin, hemicelluloses, lipids and proteins (Helfrich el at., 2006).

In Divino, the HA from the FSC system showed a decrease in the intensity of the peak centered at 56 ppm (methoxyl C), followed by a slight increase of the peak at 130 ppm in the aromatic C resonance, when compared to AGF. A similar pattern was confirmed by the FTIR analysis, suggesting that the FSC management seems to favor the intensification of the process of humification of HAs.

Figure 5 shows the ratio of alkyl C to *O*-alkyl C (A/*O*-A). This ratio has been used as an index of the degree of SOM decomposition (Baldock et al., 1997; Webster et al., 2001). Usually, during biodegradation of SOM, the relative amount of alkyl C increases while the amount of *O*-alkyl C decreases (Ussiri and Johnson, 2003). Therefore, as the A/*O*-A ratio increases, the quality of the resource as a substrate for soil microbes declines. In Divino, A/*O*-A ratios were quite similar between both coffee-cultivated areas. The major responses of the A/*O*-A ratio as a result of land use were registered in Araponga(I) and Araponga(II) soils, where opposite trends between the AGF and FSC systems were verified, mainly at the soil surface (Figure 5).

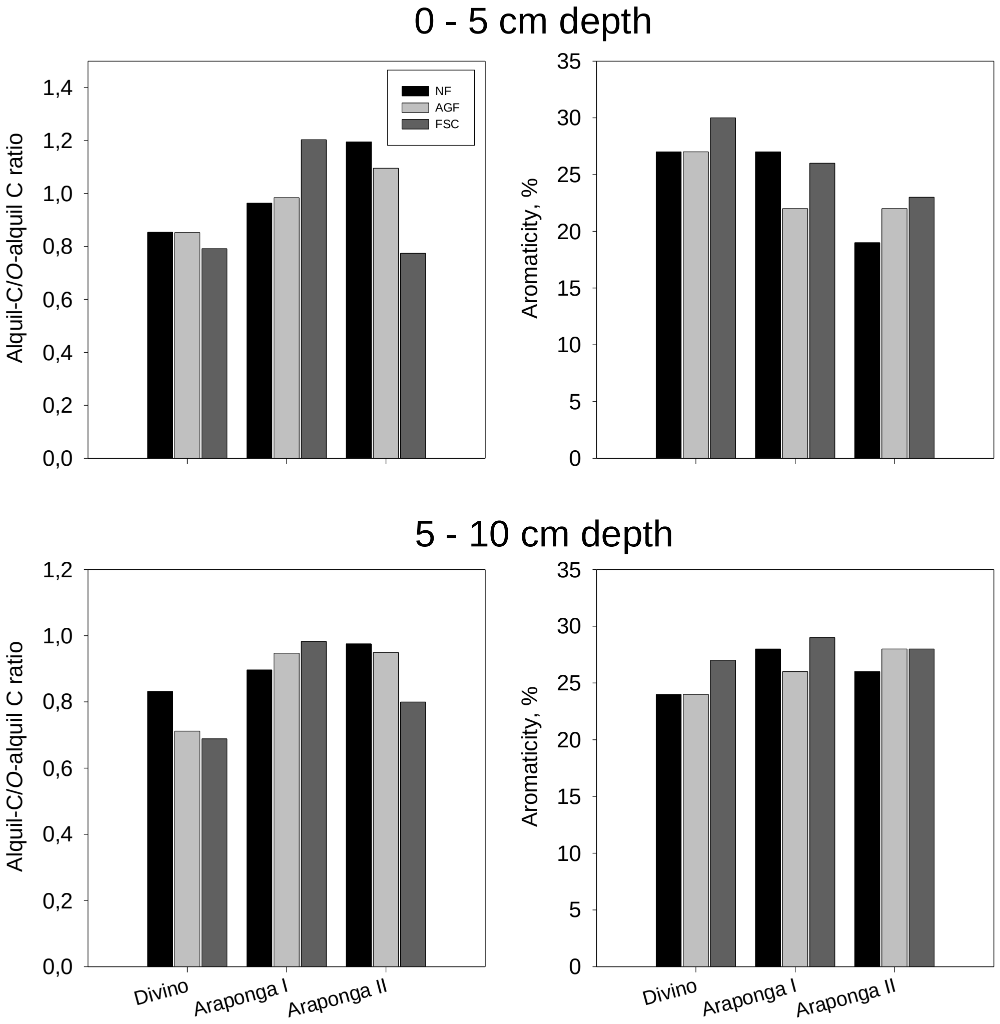

Figure 5. Alkyl C/*O*-alkyl C ratio and aromaticity index as determined by ^{13}C CP-MAS/NMR of soil humic acids extracted from 0-5 and 5-10 cm layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in three municipalities of the Zona da Mata, Minas Gerais state.

The higher aromaticity index of HA from FSC compared to the AGF system in Divino indicates a higher degree of humification of the structure, which is in line with previous findings of this work. In Araponga(I), the increase of A/*O*-A ratio in the FSC system was consistent with the increase of aromaticity index (Figure 5), confirming that HA becomes more stabilized when the FSC management is adopted.

By evaluating the A/*O*-A ratio, as occurred in Araponga(I), an increase in the aromaticity index should be expected in AGF in relation to FSC in Araponga(II). However, the aromaticity of HA was quite similar in both areas, contradicting the use of the A/*O*-A ratio as an indicator of the degree of decomposition of soil organic C. Mathers et al. (2003) also reported a somewhat similar trend, where the A/*O*-A ratio failed to indicate that SOM from no harvest residue treatments were more decomposed than from double harvest treatments in areas under *Eucalyptus globules* plantation. The authors stated that the use of the A/*O*-A ratio may be limited, since it is influenced by the nature of the original C input into the soil. The limitation on the interpretation of the A/*O*-A ratio is that the proportion of lignin is a determinant of the substrate quality for heterotrophic microbes, and the main substitutes for lignin can contribute to both *O*-alkyl and aromatic C resonance (Stevenson, 1994; Keeler et al., 2006). In Araponga(II), the lignin content (27.3%) of the organic residue of the main tree-component (*Inga subnuda*) in the AGF was substantially greater than residues from the other sites (Duarte, 2007). Therefore, the *O*-alkyl C resonance seems to be overestimated (Webster et al., 2001). In that case, due to the presence of lignin and other resistant plant biomacromolecules, the aromaticity index could represent a better estimate of the degree of humification (Mathers et al., 2003). In addition, the potential for the adsorption of highly decomposable materials and the impacts which such adsorption may have on bioavailability in mineral soils need to be considered when A/*O*-A ratio is used to assess the extent of decomposition of organic materials (Baldock et al., 1997).

In brief, the use of solid-state ^{13}C CPMAS/NMR spectroscopy confirmed the data from the previous analysis in which HA from the AGF management in

Divino and Araponga(I) are less humified than in FSC, whereas in Araponga(II), this clear evidence was not verified. At this site, the quality of organic residues, characterized by a high lignin content, is one of the most important factors controlling the dynamics of the transformations of humic substances.

4. Conclusions

The combination of both chemical and spectroscopic analyses represented a suitable approach for the structural characterization and the evaluation of the humification degree of soil HA and FA, as a consequence of different management system effects.

The humification parameters of HA and FA extracted from the agroforestry-coffee system in Divino revealed a lower degree of humification in relation to the full sun coffee system, indicating a greater SOM quality. A similar pattern occurred in Araponga(I). However, the opposite trend on the degree of humification of humic substances was observed in Araponga(II), suggesting a slower turnover of SOM in relation to the other sites. In this context, the agroforestry-coffee system seem to be a more attractive management option to protect soil against erosion, since a significant amount of organic residues is kept under soil surface. It can also reflect in the maintenance of soil humidity and suggests a great potential for C sequestration.

Higher-humified HAs with a high content of carboxylic groups in the agroforestry-coffee systems, such as found in Araponga(II), could imply in a higher binding capacity to interact with organic and inorganic ions in the soil, thus enhancing the nutrient cycling mechanism.

The effect of agroforestry management under the chemical structure of HA and FA depends on inherent characteristics of environment on which it is developed. These findings supported that this type of land use can favor as well the formation of humic substances less humified, as found in Divino soils, as more humified structures such as occurred in Araponga(II). In this aspect, the quality of organic residues on each individual condition appears to be the main factor controlling SOM dynamics; thereby the effect of agroforestry systems on the structural characteristics of humic substances should not be broadly generalized.

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CHAPTER 6

SUMMARY AND FINAL REMARKS

In Brazil, around 2.7 millions hectares are cropped under coffee (Embrapa, 2009). The amount of coffee produced in the country accounts for one quarter of the global coffee production, ranking the Brazil on top of production and exportation of this commodity in the world (FAO, 2009). The state of Minas Gerais is the main producer of coffee in Brazil, with approximately one million hectares cropped.

In the state of Minas Gerais, the Zona da Mata – a region situated in the domain of the Atlantic Coastal Rainforest biome – is considered an important zone of coffee production. Nevertheless, the most agro-ecosystems in the Zona da Mata are inserted in a process of decreasing productivity as a result of the intensive soil cultivation without the adoption of adequate management practices. In this region, coffee is cultivated on hills, normally with steep slopes ranging from 20 to 45%. These scenarios can intensify land degradation whether inappropriate management practices are adopted.

In 1993, a joint effort involving farmers and researchers was launched in the Zona da Mata aiming to discuss and point out sustainable alternatives for coffee production in this region (Carvalho, 2005). In this context, the agroforestry system was considered a good option to cope with the environmental problems in the Zona da Mata. During the debate, it was stated that the main goals involving agroforestry were: i) land regeneration and conservation; ii) decrease of external input to agriculture; iii) increase or maintenance of production level; and iv) improvement of productivity (Cardoso, 2002).

The general agroforestry hypothesis related to the soil environment states that appropriate agroforestry systems potentially control runoff and erosion, maintain SOM and physical properties, and promote nutrient cycling and efficient nutrient use (Young, 1997). However, this is a highly generalized statement that needs to be confronted to particular conditions of specific environments. A grouping of 12 specific hypotheses regarding the main aspects of agroforestry in soil management was postulated by Young (1997). Among these, I studied more deeply the third hypothesis, which states that *"Agroforestry systems can maintain soil organic matter and biological activity at levels satisfactory for soil fertility"*. It is assumed that the effects of organic matter on the properties fall into three groups: on soil physical properties, nutrient availability and biological activity.

In this study, not only quantitative but also qualitative aspects of SOM could be accessed. In a general view, I found that the effect of the agroforestry system on the SOM dynamics depended on environmental characteristics (including soil, climate and topography), diversity and quality of the residues under soil surface, and biomass management. Therefore, a general statement regarding the effects of agroforestry on SOM could not be generalized to any system in the Zona da Mata. This is an important finding since a conceptual model of agro-ecosystem could not be drawn in terms of organic matter, forcing farmers and researchers to prioritize the particularities of the environment and the goals on which agroforestry is adopted.

In chapter 2, no clear evidences were found indicating that agroforestry systems increased the stocks of total soil organic C, N and P when compared to a full sun coffee system (FSC). Such behavior is in disagreement with other studies showing the greater potential of agroforestry to increase C sequestration in comparison to monoculture systems in a global scale (Montagnini et al., 2004; Schoeneberger, 2009). Hereafter, some considerations have to be made, taking our findings into account. In some situations, such as in Araponga(II) soils, other soil characteristics were directly associated to the behavior of organic C stocks. At this site, the similar soil organic C stock in the FSC system compared to agroforestry was mainly attributed to the increase of soil bulk density. The calculation of organic C stocks considers the current values of density of each specific soil layer. It is worthy to note that this result represents a real field condition, not achieved if evaluated only in terms of C contents. Furthermore, other previous works performed in different agroforestry experiments in the Zona da Mata reported an increase in the organic C contents in comparison to conventional systems (Mendonça et al., 2001; Perez et al., 2004). Even in Araponga(I), it has been registered higher C contents in the agroforestry-coffee system compared to the FSC system (Aguiar, 2008). In addition, it is important to highlight that the FSC systems used to compare the effects of agroforestry are not considered as a model of intensive coffee cultivation in the region of the Zona da Mata. Agroecological practices or reduced tillage are normally adopted in these areas. This fact can partially explain the similarities found between both evaluated crop systems. Finally, the total amount of C sequestered in the live-biomass of tree-components has not been counted in the potential of agroforestry in sequestering C, but it should be considered at least as an important environmental service of agroforestry.

Besides the quantitative aspects, SOM was also investigated in a qualitative point of view in chapter 2. We found that agroforestry systems tended to increase the amounts of easily oxidizable C. Such increases were fundamentally important to the increase of the Carbon Management Index (CMI), used as a sensitive indicator of recent changes in the SOM levels as a result of soil management. The highest CMI values in agroforestry-coffee systems suggest the rehabilitation of SOM. The results of CMI confirmed agroforestry as an attractive option of management to restore SOM.

In chapter 3, I investigated the influence of agroforestry on soil aggregation, including the study of C and N dynamics in different aggregate-sized fractions. In general, the effects of agroforestry were not similar among the different tested systems. The agroforestry-coffee systems increased the amount of macroaggregates in Araponga(I), compared to the FSC system. It was attributed to the increase in organic residues under soil surface. As a result, the agroforestry-coffee system in Araponga(I) showed a better indication of soil aggregation as evaluated by the increase of the mean weight diameter of aggregates. The small macroaggregates (250–2000 μm) was the most important fraction for soil aggregation. The major part of soil organic C was found in this aggregate-sized fraction. In Divino and Araponga(I), organic C in macroaggregate was increased in agroforestry compared to the FSC system. It suggests that the study of the organic C dynamics, when performed in a fractionated soil, seems to be a more sensitive approach to evaluate the effect of soil management. Due to the importance of small macroaggregates on the soil aggregation, we also investigated the behavior of free- and intra-particulate organic matter (free-POM and iPOM, respectively) in this aggregate-sized fraction. Once again, it was noted that such specific fractions were sensitive to the recent changes in the SOM caused by soil management. The free-POM was increased in agroforestry-coffee systems mainly in Divino and Araponga(I) soils, as a consequence of organic residue input under soil surface. Free-POM is considered an important pool to the stabilization of soil aggregates (Six et al., 2000) and represents a source of substrate to the soil microbiota (Oades, 1984). The dynamics of POM varied among the studied sites. For instance, in the agroforestry-coffee system in Divino, the cycling of free-POM into coarse and fine iPOM seems to be faster than in Araponga(I) and Araponga(II) soils. Such pattern has been attributed to the differences in the quality of the organic residues in each particular condition. In addition, we found that higher iPOM-C contents occurred in Araponga(I) and Araponga(II) soils, compared to the Divino soils, indicating a higher SOM protection. The relatively higher clay contents in Araponga soils, in comparison to the soils in Divino, can be considered the most important factor contributing to the mechanism of SOM protection. In conclusion, we stated that the long-term stability of SOM in the soils of this study is directly dependent on the maintenance of small macroaggregates which, in turn, are favored by agroforestry management. Thus, long-term stability of soil organic C and N is likely dependent on the continuation of agroforestry.

One of most important concerns in food production in cultivated lands under highly weathered tropical soils, such as Oxisols, is phosphorus (P) deficiency. In chapter 4, the influence of agroforestry under different P forms, including inorganic and organic P, was investigated. A previous work performed by Cardoso (2002) in environmental conditions similar to those of the present study represents an important contribution to a better understanding about the effect of agroforestry systems on P cycling. In general, few changes among the different soil P fractions occurred as a result of soil management, even in the most labile P forms. Non-labile P pool accounted for 73% of total soil P in almost all evaluated sites, whereas most labile P pool represented only 5% of the total P. The moderately labile P pool seems to be preferentially depleted in agroforestry-coffee systems than in the FSC systems in Divino and Araponga(I), suggesting that such pool plays an important role in the maintenance of the levels of available P for plant nutrition. In Araponga(I) and Araponga(II) soils, agroforestry systems tended to increase the proportion of P that can be biologically mineralized in relation to the FSC systems. Although the differences were not marked, they point out that agroforestry-coffee systems favor the maintenance of the biological cycle on the P transformation in the soil. Actually, the study of soil P by adopting the sequential fractionation approach is limited as well under a conceptual sphere as a methodological consensus. Thus, all statements raised in this study need to be interpreted with caution and must not be generalized to other environments. The approach used to access the different soil P forms does not seem to be enough to elucidate completely the effect of soil management on P dynamics. However, it was important to indicate that agroforestry favored the mechanism involved with the biological cycle of P.

Chapters 2 and 3 showed that the effect of agroforestry management on the behavior of SOM seems to be strongly related to the quality of the organic residues in each particular site. In these studies, the focus of the objectives was mainly on quantitative aspects of SOM. In chapter 5, however, I evaluated the effects of soil management on the quality of the very important SOM pool, comprised by humic substances. The investigations involving qualitative aspects consider the analysis of the chemical composition and structure of humic and fulvic acids extracted from soils under both agroforestry-coffee and FSC systems. In this study, the use of spectroscopic techniques was fundamental to achieve a better insight of the chemical features of humic substances. Once again, I found that the answers considering the adopting of agroforestry could not be generalized. Humic substances from agroforestry-coffee systems may have a more aliphatic character, such as in Divino soils, or present greater amounts of aromatic structures, as found in Araponga(II). The diversity and chemical compositions of the organic residues derived from tree-components have been considered important factors governing the structural characteristics of humic substances in each individual site. The sites in which the organic residues were more diversified and have lower content of lignin and/or polyphenols seem to favor humic substances with lower degree of humification compared to sites with opposite conditions. Thus, in agroforestry, the adoption of a specific tree-component needs to consider its effects on the SOM quality in order to achieve the main goal in the implementation of agroforestry as an option of soil management. Further research is needed for a better understanding of the effects of agroforestry on the chemical characteristics of soil humic substances in different environments.

Future research in agroforestry

The biological cycle of C, N and P has an important role in the dynamics and distribution of these nutrients in the ecosystem. By adopting agroforestry, the action of soil microbial biomass is intensively stimulated in order to mineralize organic components. To understand more deeply the mechanism of the soil microbial biomass in the cycle of C, N and P in areas under agroforestry systems, it is essential to construct a sustainable management programme. For instance, the role of specific communities in the release and availability of nutrients, likewise mycorrhiza, needs to be more investigated.

SOM is only one of the components in the evaluation of soil quality. Studies that interact aspects related to SOM with other studies on soil physics, mineralogy, fertility, etc., are equally necessary, aiming at a complete evaluation of agroforestry as an attractive management option. Physical, chemical and biological indicators of soil quality are likely a better way to contrast agroforestry with conventional soil management. A new research programme considering such indicators in the evaluation of soil quality is necessary.

Studies involving the modeling of SOM in agroforestry are scarce. This approach is urgent to sustain the debate about the development of more sustainable agro-ecosystems in the Zona da Mata. The construction of the scenarios by modeling can be an important tool to calculate the costs for the payment of the environmental services brought by agroforestry, especially in smallholding farms in the region.

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APPENDIX

Agro-ecosystems – Divino

Figure 1A. General view of the studied agro-ecosystems at Divino. (A), (B) and (C) agroforestry-coffee systems; (D) full-sun coffee system.

Agro-ecosystems – Araponga(I)

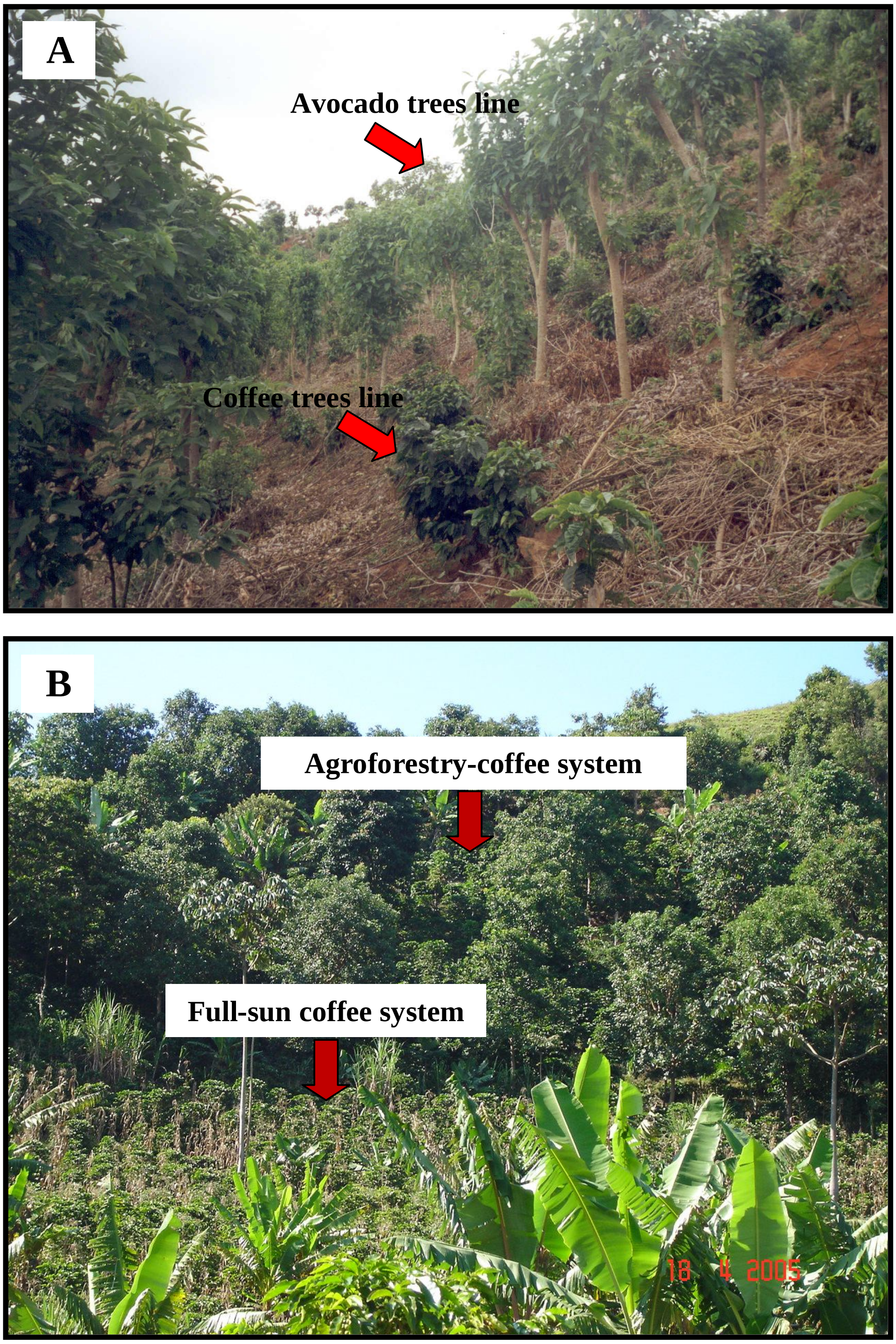

Figure 2A. General view of the studied agro-ecosystems at Araponga(I). (A) area at beginning of agroforestry implementation; (B) current stage of agroforestry. Full-sun coffe system is highlighted by a red-line circle.

Agro-ecosystems – Araponga(II)

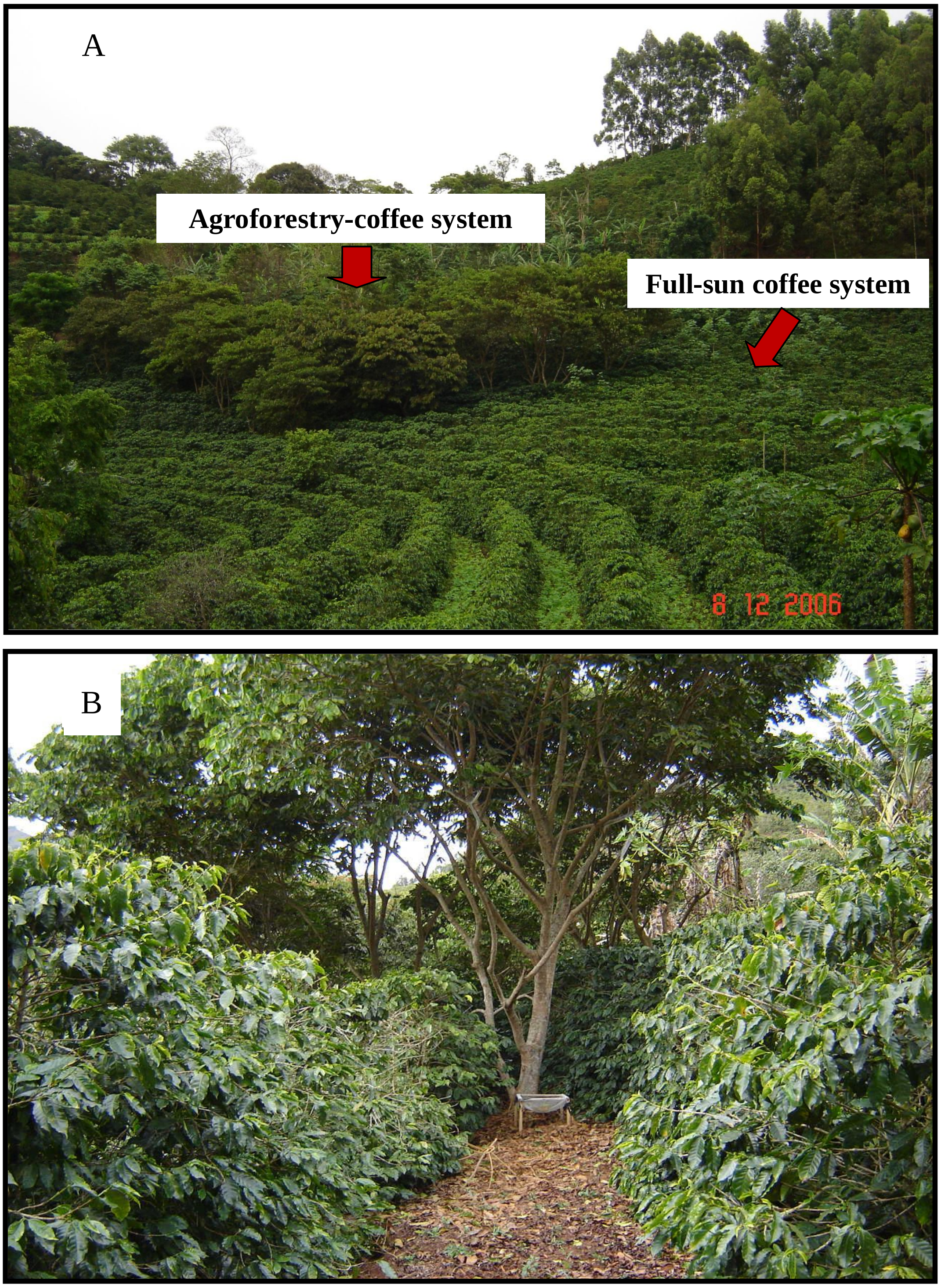

Figure 3A. General view of the studied agro-ecosystems at Araponga(II). (A) current stage of agroforestry. Full-sun coffe system is highlighted by a red-line circle; (B) Focus of the inside of agroforestry-coffee systems. Inga trees can be visualized.

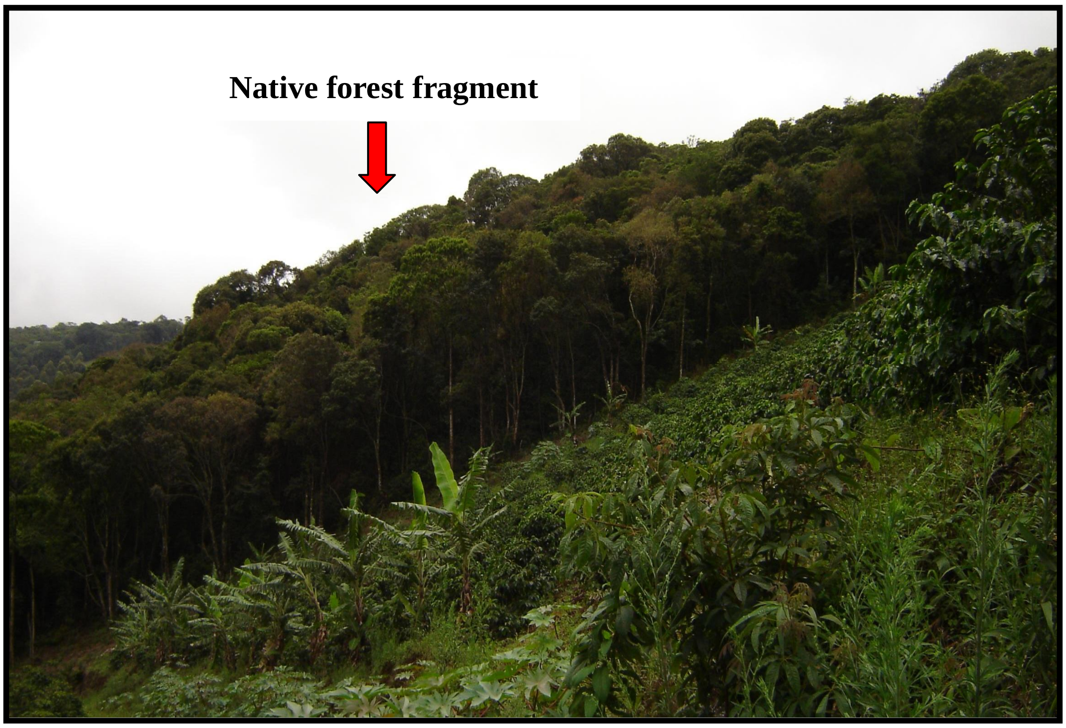

Figure 4A. Model of native forest fragment used as a reference in the comparative study with cultivated sites.

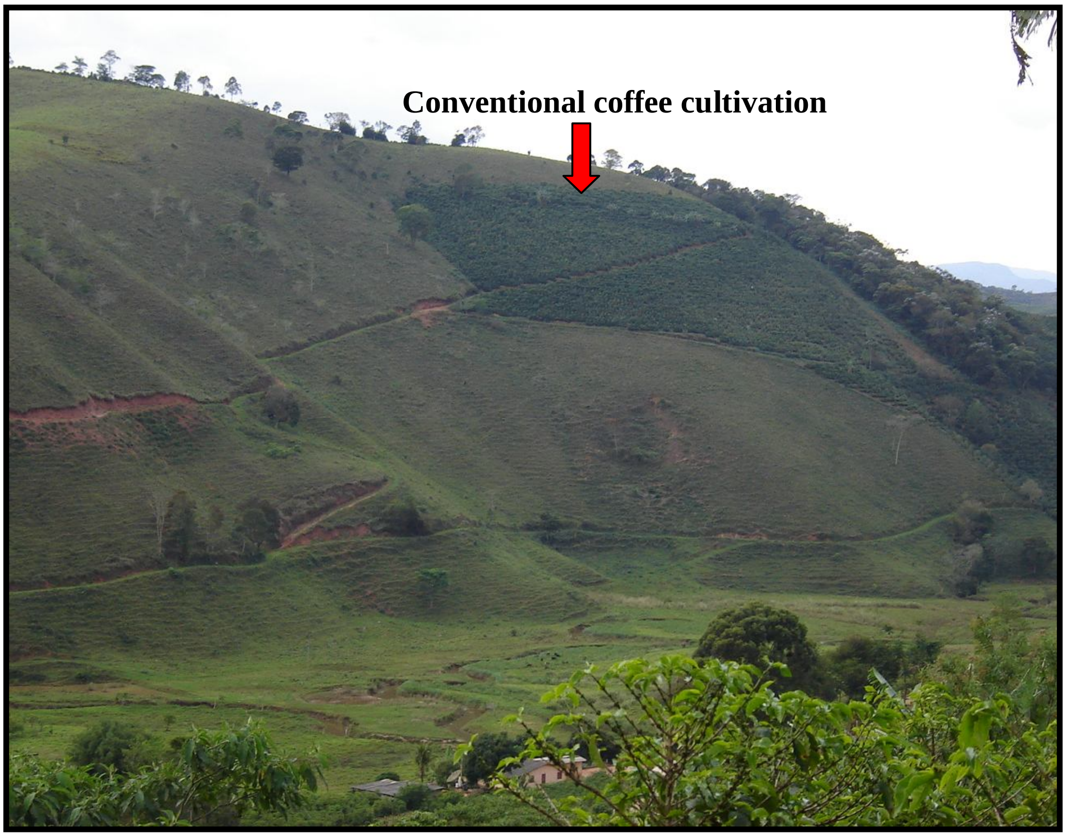

Figure 5A. Model of a conventional coffee cultivation system in the Zona da Mata.

Table 1A. Annual aboveground biomass and organic C inputs from agroforestry systems at three municipalities of Zona da Mata, Minas Gerais state (values in parentheses are the total input for each specie)

Site/tree species	Tree structure	Annual senescent biomass input (kg ha^{-1} year^{-1})	Annual organic C input (kg C ha^{-1} year^{-1})
Divino	Leaves	1,205.3	793.1
Luechea grandiflora	Branches	692.7	397.6
	Flowers/Fruits	499.7	260.8
		(2,397.7)	(1,451.5)
Araponga(I)	Leaves	694.2	421.4
Persea americana	Branches	68.9	39.1
	Flowers/Fruits	1,241.4	701.4
		(2,004.5)	(1,161.9)
Araponga(II)	Leaves	3,278.8	1,790.2
Inga subnuda	Branches	435.5	239.5
	Flowers/Fruits	616.9	344.8
		(4,331.2)	(2,374.5)

Adapted from Duarte (2007).

Table 2A. Soil total organic C, N and P contents in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at 0-5, 5-10, 10-20 and 20-40 cm soil layers at Divino, Araponga(I) and Araponga(II) municipalities

	C (g kg^{-1})			N (g kg^{-1})			P (mg kg^{-1})		
	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
Divino									
0-5	97.02	26.59	24.48	10.12	2.43	2.52	748	719	416
5-10	63.86	25.70	22.50	7.42	2.20	2.45	858	627	621
10-20	53.34	18.21	18.33	6.21	1.65	1.93	757	443	291
20-40	44.21	15.30	13.36	4.82	1.20	1.27	621	312	400
Araponga(I)									
0-5	77.00	31.05	34.58	6.19	2.69	4.19	489	511	482
5-10	60.96	26.78	27.93	5.18	3.06	2.22	635	423	426
10-20	47.94	20.09	24.11	3.70	2.29	2.03	537	490	437
20-40	22.87	17.20	22.36	2.12	1.79	1.71	485	437	466
Araponga(II)									
0-5	55.06	29.62	29.05	4.25	3.18	3.12	656	785	841
5-10	46.32	26.33	24.68	3.31	2.33	2.12	748	774	566
10-20	33.68	16.90	15.27	3.13	2.10	1.72	583	640	660
20-40	30.77	17.91	13.65	2.15	1.99	1.42	536	585	526

Table 3.A. Total C, N and P contents in fulvic acids, humic acids and humin in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at 0-5, 5-10, 10-20 and 20-40 cm soil layers in the municipality of Divino

	C (g kg^{-1})			N (g kg^{-1})			P (mg kg^{-1})		
	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
Fulvic acids									
0-5	5.40	2.77	2.95	0.66	0.29	0.36	42	75	52
5-10	5.72	2.45	2.83	0.70	0.30	0.36	56	60	38
10-20	3.95	2.64	2.29	0.47	0.16	0.36	49	46	28
20-40	3.03	2.39	2.49	0.41	0.52	0.20	51	33	20
Humic acids									
0-5	15.35	6.89	7.05	2.04	0.59	1.05	96	119	66
5-10	13.16	5.45	6.61	1.45	0.71	0.98	112	112	69
10-20	14.47	4.97	5.78	2.19	1.07	0.93	157	107	79
20-40	12.16	4.78	5.36	1.84	0.62	0.68	199	105	63
Humin									
0-5	87.43	19.03	15.59	8.60	2.48	1.44	314	134	586
5-10	54.57	17.37	13.52	5.79	1.23	1.06	275	160	604
10-20	34.71	4.87	9.23	3.94	0.74	0.76	194	99	643
20-40	23.75	9.13	10.18	2.71	0.60	0.70	166	78	626

Table 4.A. Total C, N and P contents in fulvic acids, humic acids and humin in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at 0-5, 5-10, 10-20 and 20-40 cm soil layers in the municipality of Araponga(I)

	C (g kg^{-1})			N (g kg^{-1})			P (mg kg^{-1})		
	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
Fulvic acids									
0-5	7.23	6.01	4.07	0.37	1.11	1.80	34	18	79
5-10	8.21	5.77	3.76	0.29	1.08	0.55	36	14	46
10-20	7.05	6.01	4.02	0.31	1.19	1.11	21	11	37
20-40	5.54	5.49	3.61	0.35	1.09	0.60	17	11	25
Humic acids									
0-5	18.30	8.89	7.15	1.17	2.10	1.12	185	58	112
5-10	13.84	10.01	6.11	0.77	2.19	1.08	173	54	111
10-20	9.77	7.81	6.29	0.63	1.69	1.49	147	69	118
20-40	3.34	4.60	4.87	0.29	0.96	0.70	102	65	93
Humin									
0-5	62.92	11.17	16.80	1.61	4.26	0.73	nd	nd	353
5-10	55.12	8.10	12.45	1.14	3.91	0.36	nd	nd	304
10-20	22.39	7.57	11.67	0.93	3.70	0.55	nd	nd	229
20-40	12.12	5.33	9.59	0.46	3.07	0.51	nd	nd	225

nd: not determined.

Table 5.A. Total C, N and P contents in fulvic acids, humic acids and humin in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems at 0-5, 5-10, 10-20 and 20-40 cm soil layers in the municipality of Araponga(II)

	C (g kg^{-1})			N (g kg^{-1})			P (mg kg^{-1})		
	NF	AGF	FSC	NF	AGF	FSC	NF	AGF	FSC
Fulvic acids									
0-5	6.56	4.63	5.43	1.20	0.66	0.57	107	136	149
5-10	6.68	4.31	5.59	1.29	0.79	0.34	137	80	104
10-20	6.09	4.63	9.77	1.33	0.45	0.34	130	53	63
20-40	4.69	7.50	11.64	0.53	0.40	0.31	66	37	49
Humic acids									
0-5	14.15	7.56	5.93	1.73	1.07	0.57	195	107	107
5-10	8.47	6.80	6.89	1.62	1.02	0.71	156	89	201
10-20	6.30	6.49	4.41	1.35	0.93	0.73	206	68	158
20-40	3.78	4.57	2.12	1.01	0.74	0.26	149	47	58
Humin									
0-5	21.35	22.76	12.72	2.03	1.70	1.87	587	623	952
5-10	17.58	13.70	9.37	1.89	1.59	1.18	644	593	888
10-20	18.52	16.72	6.50	1.25	1.18	1.02	607	565	707
20-40	15.21	10.21	6.22	1.04	1.12	0.74	711	600	749

nd: not determined.

Table 6A. Elemental composition of the fulvic acids extracted from soils at 0-5 and 5-10 cm layers in areas under native forest (NF), agroforestry-coffee (AGF) and full-sun coffee (FSC) systems in three municipalities of Zona da Mata, Minas Gerais

		Elemental composition[/a] (g kg^{-1})				Atomic ratio		
Sites	Land use	C	H	N	O[/b]	H/C	O/C	N/C[/c]
0-5 cm								
	NF	473.1	46.5	36.4	444.1	1.18	0.70	6.59
Divino	AGF	449.1	43.3	27.7	479.9	1.16	0.80	5.29
	FSC	435.7	43.8	30.7	489.7	1.21	0.84	6.04
	SE[/d]	3.7	0.4	0.4	3.3	0.01	0.01	0.09
	NF	445.2	41.5	17.6	495.7	1.12	0.84	3.39
Araponga(I)	AGF	443.9	40.5	23.9	491.8	1.09	0.83	4.61
	FSC	454.5	41.4	25.0	479.1	1.09	0.79	4.71
	SE	1.8	0.3	0.1	2.1	0.01	0.005	0.02
	NF	459.9	41.7	20.5	477.9	1.09	0.78	3.81
Araponga(II)	AGF	462.6	42.0	23.8	471.6	1.09	0.76	4.41
	FSC	429.7	45.3	25.7	499.3	1.27	0.87	5.13
	SE	2.2	0.6	0.1	2.4	0.02	0.01	0.03
5-10 cm								
	NF	462.4	45.4	36.3	455.9	1.18	0.74	6.73
Divino	AGF	471.0	43.6	26.9	458.5	1.11	0.73	4.90
	FSC	391.3	39.7	25.7	543.3	1.22	1.04	5.63
	SE	1.5	0.4	0.1	2.0	0.01	0.004	0.02
	NF	467.4	42.8	17.2	472.5	1.10	0.76	3.15
Araponga(I)	AGF	452.8	41.2	22.9	483.1	1.09	0.80	4.33
	FSC	450.0	40.7	23.3	486.0	1.09	0.81	4.44
	SE	1.1	1.6	0.1	2.1	0.04	0.004	0.01
	NF	438.5	40.2	19.2	502.1	1.10	0.86	3.75
Araponga(II)	AGF	450.4	42.2	20.5	486.9	1.12	0.81	3.90
	FSC	448.9	40.3	25.4	485.4	1.08	0.81	4.85
	SE	2.0	0.7	0.1	1.9	0.02	0.01	0.03
Effect of depth		ns	ns	ns	ns	ns	ns	ns
Usual range for humic acids[/e]		407-506	38-70	9-33	397-498	~1.0	~0.7	

[/a] on an oven dry ash-free basis; [/b] calculated by difference; [/c] expressed as: atomic ratio x 100; [/d] pooled standard error (SE) of the chemical analysis; [/e] Stevenson (1994); *, **: significant at 0.05 and 0.01, respectively, by least significant difference test.

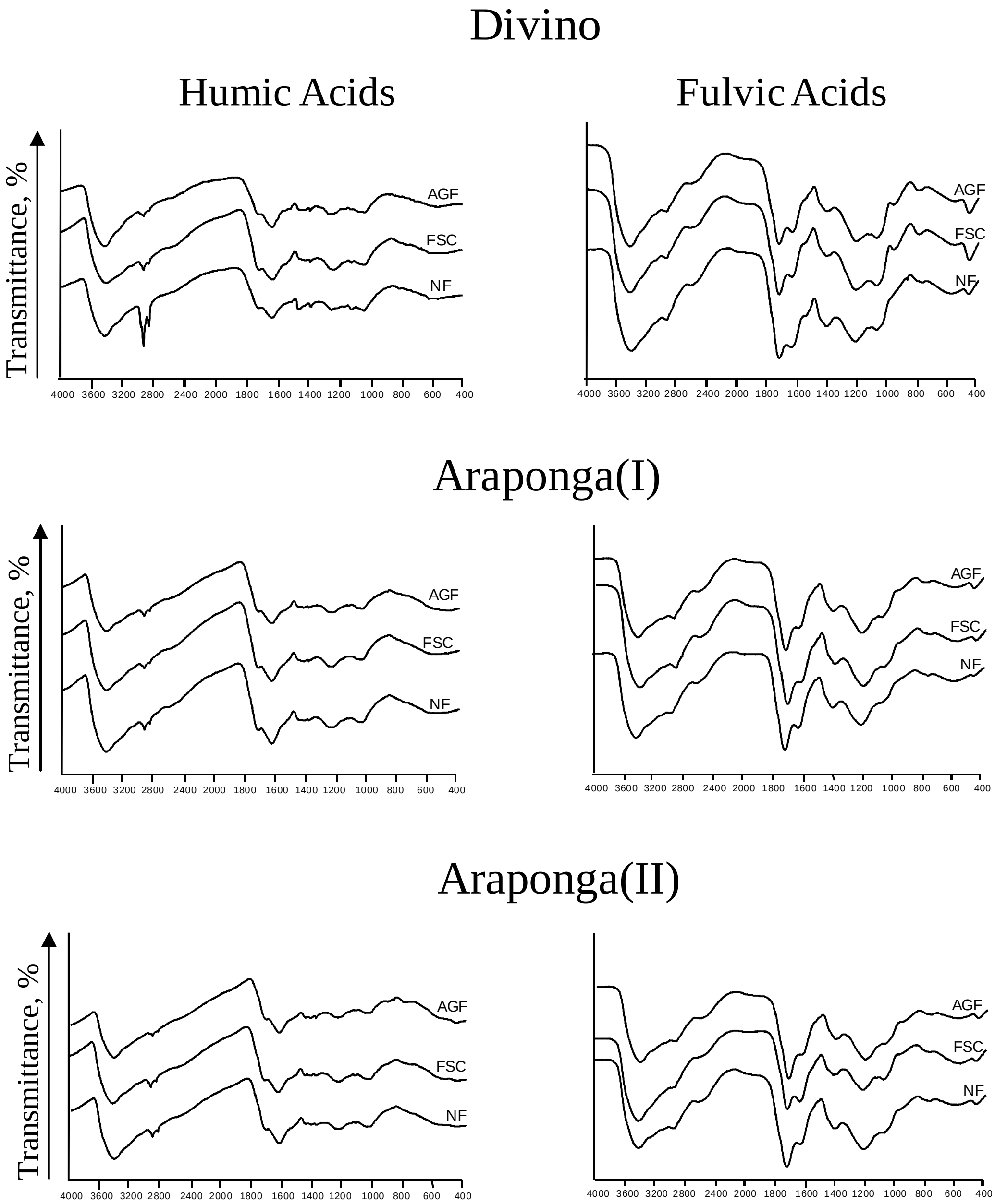

Figure 6A. FTIR signature of humic and fulvic acids extracted from 0-5 cm soil layer in areas under agroforestry-coffee (AGF), full-sun coffee (FSC) systems and native forest (NF) in the municipalities of Divino and Araponga.

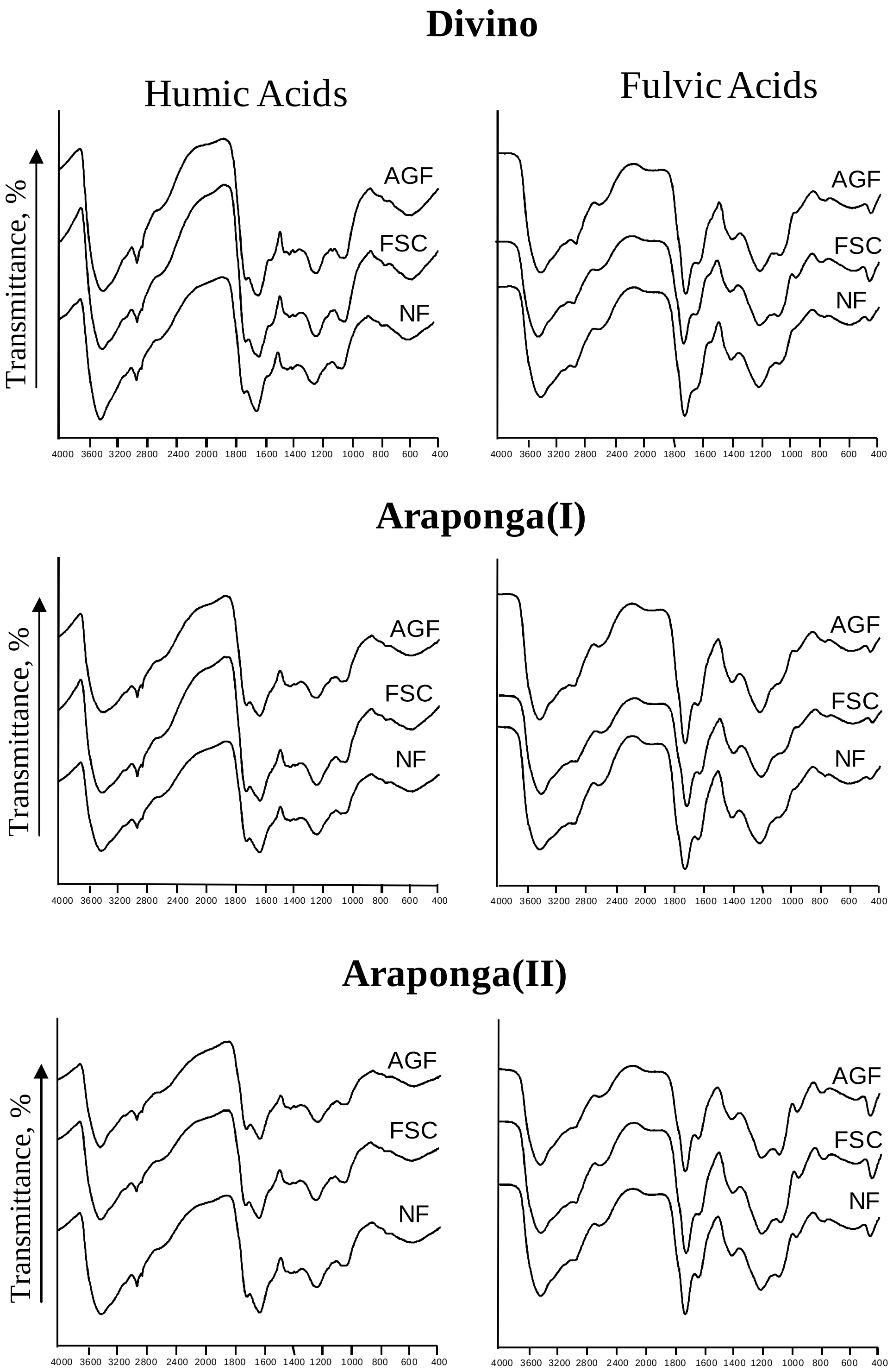

Figure 7A. FTIR signature of humic and fulvic acids extracted from 5-10 cm soil layer in areas under agroforestry-coffee (AGF), full-sun coffee (FSC) systems and native forest (NF) in the municipalities of Divino and Araponga.

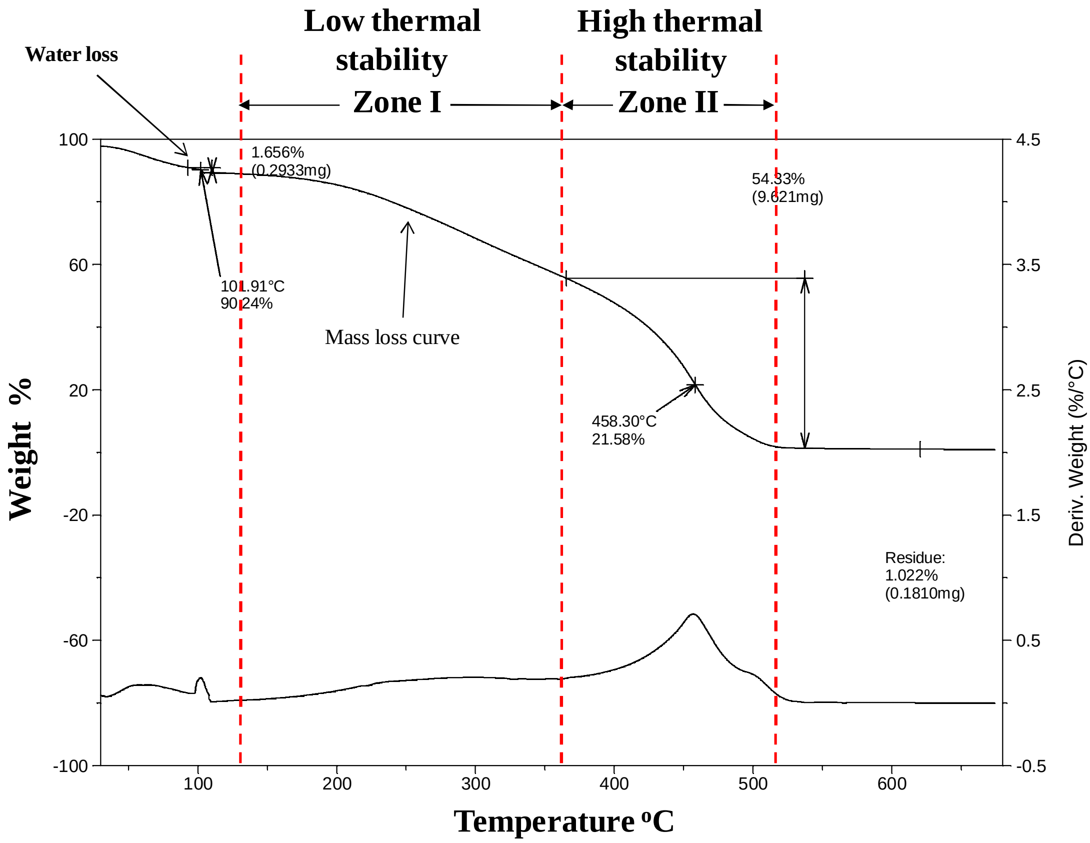

Figure 8A. Thermogravimetry: model of thermogram of humic acids indicating the mass losses in function to temperature. Two zones of thermal stability are shown by the dotted lines.