UNIVERSIDADE ESTADUAL DE LONDRINA

THADEU RODRIGUES DE MELO

ESTRUTURA DO SOLO:

DINÂMICA E SUGESTÃO METODOLÓGICA

Londrina
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Tese apresentada ao Programa de Pós-graduação em Agronomia da Universidade Estadual de Londrina, como requisito à obtenção do título de Doutor em Agronomia.

Orientador: Dr. João Tavares Filho

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“Where all think alike, no one thinks very much”

“Onde todos pensam igual, ninguém pensa muito”
(Walter Lippmann)

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RESUMO

A avaliação da estabilidade dos agregados do solo é mandatória para seu manejo adequado. Nesse sentido, o aprimoramento de métodos existentes e a compreensão dos processos relacionados possibilitam a avaliação mais acurada dos efeitos do uso antrópico do solo e suas relações com o meio ambiente. Aqui, busquei preencher algumas lacunas acerca da estabilidade de microagregados de solo, especificamente na análise de argila mecanicamente dispersável em água. No primeiro estudo, a influência de dejetos sobre o tipo de agregação do solo e suas consequências nos atributos químicos e físicos foram investigadas. No segundo estudo, buscamos entender a relação da estabilização de macroagregados com a capacidade da argila em reflocular, quando esses agregados são rompidos mecanicamente. No terceiro e último estudo, propusemos um procedimento adicional ao método de argila dispersável em água, para permitir o detalhamento das classes de argila quanto ao comportamento estrutural.

Palavras-chave: Análise física de solo. Grau de dispersão. Grau de floculação. Argila dispersa em água. Potencial zeta. Balanço de cargas.

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ABSTRACT

The evaluation of the stability of soil aggregates is mandatory for its adequate management. In this sense, the improvement of the existing methods and the comprehension of the related processes allow a more accurate evaluation of the effects of the anthropic use of the soil and its relationships with the environment. Here, I aimed to fill some gaps regarding the stability of soil microaggregates, specifically on the mechanically water-dispersible clay analysis. In the first study, the influence of manures on the aggregation type and its consequences on chemical and physical attributes were investigated. In the second study, we sought to understand the relationship between macroaggregates stabilization and the capacity of the clay to re-flocculate, when these aggregates are mechanically disrupted. In the third and last study, we proposed an additional procedure to the water-dispersible clay analysis, to allow the detailing of the clay classes regarding the structural behavior.

Key words: Soil physical analysis. Dispersion degree. Flocculation degree. Water-dispersible clay. Zeta potential. Charges balance.

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1 INTRODUÇÃO

A qualidade estrutural dos solos é mandatória para o seu adequado funcionamento e conservação. Com a conversão de sistemas nativos para antrópicos, a degradação da estrutura do solo é comumente observada, sendo a redução na estabilidade em água dos agregados responsável pelo aumento de sua susceptibilidade à erosão hídrica e contaminação de corpos d'água. Dada sua importância, diversos métodos são empregados para o seu monitoramento.

A dispersão da fração argila é um indicador da estabilidade dos microagregados do solo. Quando sua quantificação é precedida pela ruptura mecânica dos agregados em laboratório, os resultados fazem inferência à susceptibilidade do solo à dispersão após o efeito de agentes disruptivos, potencialmente presentes nas condições de campo. Na presente tese, busquei preencher algumas lacunas que identifiquei no estado da arte acerca das metodologias existentes e dos processos relacionados à dispersão de argila em solos.

No primeiro estudo, investigamos se a melhoria dos atributos físicos e químicos do solo é intensificada pela agregação biogênica. Para isso, avaliamos um experimento de longa duração com aplicação de cama de frango e dejeto líquido de suínos. Adicionalmente, testamos se o aumento de frações mais estáveis da matéria orgânica, em razão da adição dos estercos e da agregação biogênica, aumenta a resistência dos microagregados à ruptura mecânica.

No segundo estudo, buscamos entender se a refloculação da fração argila é possível após a quebra de macroagregados estáveis em água. É conhecido na literatura que i) a matéria orgânica eleva a proporção de macroagregados estáveis em água e que ii) a matéria orgânica inibe a refloculação da fração argila por elevar a proporção de cargas negativas em sua superfície. Logo, espera-se que a refloculação da fração argila seja inibida, após liberadas de agregados ricos em matéria orgânica.

No terceiro estudo, propusemos um método para permitir a quantificação dos compartimentos refloculável e não dispersável da fração argila. Atualmente, estudos realizados em todo o mundo separam a fração argila em duas classes, quanto ao comportamento estrutural: dispersa e floculada (ou agregada). Discussões acerca das limitações da quantificação da argila floculada e o procedimento para quantificar as referidas classes da fração argila são apresentadas nesse estudo.

2 REVISÃO DE LITERATURA

2.1 TERMINOLOGIA

Manuais metodológicos de análises de solo, publicados em português, utilizam o termo “argila dispersa em água” quando se referem à análise que quantifica a fração argila que permanece em suspensão após desprendimento por agitação mecânica aplicada em laboratório. É o caso, por exemplo, dos manuais produzidos pela Empresa Brasileira de Pesquisa Agropecuária (CLAESSEN et al., 1997; DONAGEMA et al., 2011; TEIXEIRA et al., 2017) e pelo Instituto Agronômico de Campinas (CAMARGO et al., 2009). Como reflexo, é comum o uso desse mesmo termo em estudos publicados em português (FREITAS, 2011; VICENTE et al., 2012; PAES et al., 2013; ALVES et al., 2015; MOTA; ALENCAR; ASSIS JÚNIOR, 2015).

O uso do adjetivo “dispersa” para qualificar a argila transmite a ideia de que os valores de dispersão obtidos refletem a condição do solo no presente (momento da coleta). Entretanto, essa análise faz inferência ao potencial de dispersão quando agentes mecânicos de desagregação agem sobre o solo (RENGASAMY, 2002). Nesse sentido, é mais adequado o uso do adjetivo “dispersável”, pois os adjetivos com sufixo -vel, formados a partir de verbos, indicam possibilidade de o sujeito sofrer determinada ação (ORSI; BERGAMINI, 2014). Em concordância com o exposto, o termo em inglês *water-dispersible clay* também transmite a ideia de possibilidade.

Alguns estudos publicados em português utilizam o termo “argila dispersível em água” para transmitir a noção de possibilidade (ALMEIDA NETO et al., 2009; FERRAZ et al., 2013). Entretanto, para formação de adjetivos com sufixo -vel a partir de verbos, a vogal temática do infinitivo do verbo deve ser utilizada (PEREIRA; SILVESTRE; VILLALVA, 2013). Nesse sentido, o verbo “dispersar” dá origem ao adjetivo “dispersável” ao invés de “dispersível”.

Como a dispersão da fração argila também pode ocorrer por agentes químicos (CZYZ; DEXTER, 2015), como o pH e os cátions constituintes da dupla camada elétrica, é sensato indicar a natureza da dispersão causada em laboratório. No caso dos métodos mais utilizados no Brasil, com dispersão mecânica da amostra, o termo que optei por aqui utilizar foi “argila mecanicamente dispersável em água”.

2.2 SISTEMAS COLOIDAIS

Um coloide pode ser definido como uma entidade que possui uma de suas dimensões entre a escala do nanômetro e do micrômetro, ou seja, que varie de 10^{-9} a 10^{-6} m (SHAW, 1992). Pode ser líquido, sólido ou gasoso e, dentro de um sistema coloidal, se encontra em um meio de dispersão, que também pode possuir qualquer um dos três estados da matéria supracitados (SHAW, 1992).

Na ciência do solo, a principal aplicação da ciência coloidal é relacionada ao comportamento e aos fenômenos oriundos das partículas sólidas na fração argila, quando imersas em água. Esse tipo de sistema coloidal, sólido disperso em líquido, é denominado “sol”. O termo “pasta” também é utilizado quando a concentração de sólidos é elevada. Nesses sistemas, a região de transição da fase dispersa para o meio de dispersão é denominada interface (MYERS, 1999).

Segundo Sposito (2008), os coloides do solo abrangem sólidos orgânicos e minerais que possuem baixa solubilidade em água e com uma de suas dimensões entre 10^{-8} e 10^{-5} m. A fração argila dos solos possui elevada área superficial por unidade de massa (m^2 g^{-1}), ou área superficial específica, o que intensifica os fenômenos de superfície, como adsorção de íons e moléculas e o surgimento de dupla camada elétrica (LIMA, 2008), quando comparada às frações silte e areia.

Um sistema coloidal é dito estável quando a fase dispersa não tende a se agregar. A agregação leva ao ganho de massa das partículas e acelera sua sedimentação por ação mais intensa do campo gravitacional. Nesse último caso, a suspensão é dita instável. Em muitas aplicações, como na confecção de alimentos e medicamentos, é desejável que a suspensão seja estável (XU et al., 2018). Entretanto, em ciência do solo, é desejável que as partículas tendam a se agregar, dando origem à estrutura do solo ou, mais especificamente, aos microagregados (CARDOSO et al., 2013).

Para balancear as cargas na fração argila, íons de carga oposta, presentes na solução do solo, se aproximam da interface e são denominados contra-íons. Paralelamente, os íons de carga similar à fração argila são repelidos e denominados co-íons. O campo elétrico em torno da partícula influencia os íons até determinada distância, à partir da qual o efeito passa a ser desprezível. Nessa distância, a concentração de co-íons e de contra-íons se iguala e delimita o

complexo de troca do solo da solução do solo. O equilíbrio entre a solução e o complexo de troca é dinâmico e, nesse sentido, alterações na composição química da solução afetam os íons no complexo de troca em torno das partículas, alterando a magnitude e alcance do campo elétrico gerado.

Um sistema coloidal disperso é termodinamicamente instável e, para reduzir sua área interfacial, tende a formar agregados, levando à separação da fase dispersa com relação ao meio de dispersão (LEITE; RIBEIRO, 2012). Entretanto, quando os coloides apresentam cargas elétricas, as forças repulsivas oriundas da sobreposição de duplas-camadas elétricas, durante a aproximação das partículas, podem superar a tendência de agregação e manter a dispersão (LEITE; RIBEIRO, 2012). Esse comportamento é especialmente importante em ciência do solo, pois os minerais na fração argila apresentam cargas oriundas de substituição isomórfica e da descontinuidade estrutural, que gera cargas nos grupos funcionais das bordas expostas (TOMBÁCZ; SZEKERES, 2006). O baixo valor de pH para que as moléculas orgânicas do solo atinjam o ponto isoelétrico e o encapsulamento dos minerais por essas moléculas também favorece o aparecimento de cargas na fração argila do solo (LEE et al., 2012).

A estabilidade de um sistema coloidal pode ser compreendido em função da energia potencial total entre as partículas (V_T), descrita como (LEITE; RIBEIRO, 2012):

$$V_T = V_{vdW} + V_e + V_{estérico} + V_{estrutural} \quad \text{Eq. 1}$$

Em que: V_T – energia potencial total entre duas partículas adjacentes; V_{vdW} – energia potencial atrativa oriunda das interações de longa distância de van der Waals (que inclui a força de Keeson, força de Debye, força de interação dipolo-carga e forças de dispersão de London); V_e – energia potencial repulsiva entre partículas carregadas, devido à sobreposição de duplas camadas elétricas durante sua aproximação (BIKE; PRIEVE, 1990), sendo presente para sistemas com partículas eletricamente carregas, como o solo; $V_{estérico}$ – energia potencial repulsiva resultante da interação estérica entre partículas quando macromoléculas estão adsorvidas e impedem sua aproximação; $V_{estrutural}$ – energia potencial resultante de espécies não adsorvidas e que modificam a estabilidade do sistema.

Adicionalmente, forças repulsivas oriundas da solvatação dos coloides por moléculas de água (forças de hidratação) também podem dificultar sua

agregação ou levar à ruptura de agregados de solo quando umedecidos (HU et al., 2015). A presença de porções hidrofóbicas na matéria orgânica do solo (CHENU; LE BISSONNAIS; ARROUAYS, 2000) e em minerais, como na caulinita (JOHNSTON; TOMBÁCZ, 2002) pode, por outro lado, favorecer a atração desses coloides.

Apesar da existência de forças repulsivas oriundas da sobreposição das eletrosferas, em distâncias de separação das partículas muito pequenas a força atrativa é infinitamente intensa. À essa região de intensa atração, dá-se o nome de mínimo primário. Quando a curva total de interação dá origem à uma região de repulsão e, em distância maiores, há novamente tendência de atração, esta é denominada de mínimo secundário. Quando o mínimo primário é atingido, a agregação é dita irreversível e, quando o mínimo secundário é atingido, sem que a barreira repulsiva seja ultrapassada, a agregação é dita reversível e pode ser facilmente desfeita com a leve perturbação da suspensão (NG; KOH; WONG, 2012). No caso dos métodos que avaliam dispersão da fração argila de solos após desprendimento mecânico, a refloculação provavelmente ocorre pela aproximação das partículas até o mínimo secundário, uma vez que as suspensões são facilmente redispersas em laboratório após sua perturbação com uma haste.

A agregação da fração argila nos solos é, porém, mais complexa do que o comportamento de partículas coloidais em suspensões. Os ciclos de secagem e umedecimento do solo podem forçar as partículas a se aproximar, possivelmente até o mínimo primário ser alcançado. Adicionalmente, a matéria orgânica e os sesquióxidos metálicos atuam como agentes cimentantes e favorecem a formação de agregados que não se desmancham (estáveis) em água. Logo, em condições de campo, a fração argila pode permanecer agregada por forças que não são exclusivamente eletroestáticas (JOZEFACIUK; CZACHOR, 2014).

A presença de diferentes tipos de coloides no solo (macromoléculas orgânicas e diferentes tipos de minerais) faz com que as interações sejam complexas. A caulinita comumente é o mineral predominante na fração argila dos solos bem intemperizados. Nesse mineral, a presença de cargas positivas nos grupos aluminol, cargas negativas nos grupos silanol e carga neutra na superfície siloxana em uma ampla faixa de pH (TOMBÁCZ; SZEKERES, 2006) facilita a floculação do sistema (KRETZSCHMAR; HOLTHOFF; STICHER, 1998).

A presença considerável de sesquióxidos metálicos na fração argila de muitos desses solos também favorece sua floculação, pois esses minerais

possuem ponto isoelétrico em valores de pH elevados para solos tropicais (RIBEIRO et al., 2011). Essa característica faz com que esses minerais apresentem, predominantemente, cargas positivas. Sua coexistência com minerais e compostos orgânicos com ponto isoelétrico em valores baixos de pH (com predominância de cargas negativas), favorece sua aproximação. O fenômeno de união de partículas coloidais de diferentes naturezas é denominado “heteroagregação” (TREFALT; RUIZ-CABELLO; BORKOVEC, 2014) e provavelmente é o mecanismo predominante na maioria dos solos bem intemperizados.

A forte interação da matéria orgânica com os sesquióxidos de ferro e de alumínio (VENDRAME et al., 2011) favorece a formação de agregados estáveis, que são menos susceptíveis à ruptura (DUIKER et al., 2013). Entretanto, após o rompimento das pontes orgânicas entre as partículas, as moléculas orgânicas podem encapsular os minerais e favorecer a repulsão do sistema pela neutralização das cargas positivas dos minerais (LEE et al., 2012).

Cardoso et al. (2013) separam o processo de formação de agregados de solo em duas fases: a floculação, referente à formação de microagregados (< 250 μm) e a cimentação, referente à formação de macroagregados (> 250 μm). Entretanto, os flóculos formados pela atração coloidal em condições de laboratório são distintos dos microagregados de solo, pois, como mencionado anteriormente, os ciclos de secagem e umedecimento nas condições de campo favorecem sua estabilização (SINGER et al., 1992).

O teor de argila mecanicamente dispersável em água é um balanço entre a resistência dos agregados de solo à ruptura, quando submetidos à dispersão mecânica, e a tendência da fração argila em permanecer em suspensão, após liberada dos agregados. Os fatores que influenciam esses dois processos são discutidos nos próximos tópicos.

2.2.1 Resistência dos Agregados de Solo à Ruptura Mecânica

Um dos principais fatores que afeta a resistência de agregados de solo à ruptura mecânica é seu tamanho. Quanto maior o agregado, maior a probabilidade da existência de regiões de baixa resistência e, consequentemente, maior a probabilidade de ruptura (NIMMO, 2004). Consequentemente,

microagregados (< 250 µm) são significativamente mais resistentes à ruptura mecânica do que macroagregados. Essa característica explica o motivo de, em áreas sob intenso revolvimento mecânico, a dispersão completa do solo não ser atingida e os microagregados predominarem (TISDALL; OADES, 1982).

Muitos dos fatores que afetam a resistência dos agregados à ruptura mecânica podem favorecer determinadas classes de tamanho em detrimento de outras. Os ciclos de secagem e umedecimento, por exemplo, podem reduzir a proporção de agregados maiores (HU et al., 2018), mas tendem a reduzir a dispersão da fração argila e formar microagregados estáveis (SINGER et al., 1992; BAKTI; KIRCHHOF; SO, 2010). Xu, Tang e Zhou (2017) observaram que os ciclos de secagem e umedecimento reduziram a proporção de agregados maiores que 2 mm, porém os agregados remanescentes se tornam mais resistentes à hidratação.

A presença de sesquióxidos metálicos, sobretudo os de baixa cristalinidade, tendem a favorecer a resistência de microagregados à ruptura mecânica (IGWE; ZAREI; STAHR, 2009; PENG, 2015), principalmente em solos bem intemperizados (SIX et al., 2002). IGWE, ZAREI e STAHR (2009) observaram um aumento expressivo na agregação das frações argila e silte em diferentes solos da Nigéria, em função do aumento do conteúdo de minerais amorfos de ferro. O mesmo comportamento foi observado por Goldberg, Kapoor e Rhoades (1990), que observaram aumento na dispersão de argila após a remoção dos sesquióxidos metálicos de baixa cristalinidade. O sinergismo entre os sesquióxidos metálicos e a matéria orgânica induz a formação e estabilização dos agregados do solo (ZHAO et al., 2017).

Moléculas orgânicas de elevado peso molecular podem favorecer a formação de pontes entre as partículas minerais, enquanto moléculas orgânicas leves favorecem o desbalanço de cargas e a repulsão eletroestática (LEE et al., 2012; NGUYEN et al., 2013; HU et al., 2015). Nesse sentido, espera-se que solos com maiores teores de frações estáveis da matéria orgânica possuam agregados mais resistentes à ruptura mecânica. Nelson et al. (1999) observaram que a fração argila mais facilmente dispersa dos agregados continha menor teor total de carbono, porém com maior proporção de amino ácidos e proteínas, enquanto na fração argila dificilmente dispersável, predominava compostos orgânicos alifáticos (amostras de superfície) ou carboidratos (amostras de profundidade). Melo et al. (2018) observaram que, após a aplicação de vinhaça em um Cambissolo, o aumento do

conteúdo de matéria orgânica reduziu a dispersão de argila e se sobrepôs ao efeito dispersivo do aumento de K^+.

2.2.2 Estabilidade das Suspensões de Argila de Solos

Após dispersa dos agregados, a fração argila pode permanecer em suspensão ou reflocular e, consequentemente, sedimentar. O aumento do desbalanço de cargas nessa fração favorece sua repulsão eletroestática pelo aumento da espessura da dupla camada elétrica. O desbalanço de cargas, porém, não ocorre apenas em função da densidade de cargas, mas também pela natureza dos grupos funcionais, área superficial específica e condições do meio (SHAINBERG; LEVY, 2005).

Alguns grupos funcionais de superfície, como o aluminol (Al–OH) e o ferrol (Fe–OH) apresentam ponto isoelétrico em valores elevados de pH, enquanto grupos silanol (Si–OH) e grupos da matéria orgânica possuem ponto isoelétrico em valores baixos de pH (TOMBÁCZ; SZEKERES, 2006; PLAZA et al., 2015). Nesse sentido, a presença de partículas de diferentes composições ou de partículas que possuam vários grupos funcionais pode reduzir a estabilidade das suspensões de argila (TOMBÁCZ; SZEKERES, 2006). Além dos grupos funcionais de superfície, o excesso de cargas permanentes dentro da estrutura cristalina dos minerais também intensifica o campo elétrico, que gera desbalanço de cargas e induz a estabilidade do sistema (SHAINBERG; LEVY, 2005).

Apesar da matéria orgânica permitir a formação de pontes entre as partículas, o que pode dificultar sua dispersão, quando expostas a agentes desagregantes, as moléculas orgânicas podem encapsular as partículas, elevando o desbalanço de cargas (LEE et al., 2012; NGUYEN et al., 2013; PLAZA et al., 2015). De modo semelhante, a aplicação de fosfato e sua consequente adsorção aos minerais neutraliza os sítios de predomínio de cargas positivas, intensificando a eletronegatividade das partículas (RIBEIRO et al., 2011; VENDRAME et al., 2011; JOZEFACIUK; CZACHOR, 2014). Entretanto, regiões hidrofóbicas da matéria orgânica podem interagir com a porção siloxana da caulinita (MOYO et al., 2014), que também é hidrofóbica devido à estabilização eletrônica dos oxigênios pelos átomos de silício e pela ausência de substituições isomórficas, favorecendo sua

atração.

O pH pode alterar a estabilidade do sistema por causar a protonação ou desprotonação dos grupos funcionais, alterando o balanço de cargas. Quanto mais afastado o pH estiver do ponto isoelétrico médio dos coloides, maior a dispersão (CHOROM; RENGASAMY, 1995). Em solos, a dispersão comumente ocorre quando o pH está acima do ponto isoelétrico médio, pois quando o pH está abaixo desse valor, a forma trivalente do alumínio (Al^{3+}) pode predominar, favorecendo a floculação.

Como a maioria dos solos são eletronegativos, mesmo em camadas em que o conteúdo de matéria orgânica é baixo, os contra-íons (atraídos pelas partículas) são cátions e os co-íons (repelidos pelas partículas) são ânions (SHAINBERG; LEVY, 2005). Nesse sentido, a concentração e natureza dos cátions na solução do solo possuem influência mais marcante na estabilidade dos sistemas coloidais do que os ânions adsorvidos por forças eletroestáticas (SPARKS, 2003). O efeito dos cátions nas forças repulsivas entre partículas pode ser entendido em função da alteração da espessura da dupla camada elétrica. Quanto maior sua espessura, maior a sobreposição das duplas camadas elétricas e, consequentemente, maior é a barreira a ser superada durante a aproximação das partículas (SHAINBERG; LEVY, 2005).

Cátions de maior valência, como o Al^{3+}, são atraídos à superfície dos minerais com mais força do que os cátions de menor valência. Logo, a espessura da dupla camada elétrica é inversamente proporcional à valencia do cátions no complexo de troca (SHAINBERG; LEVY, 2005; MAHANTA, MISHRA, KANSAL, 2014). Melo, Machado e Tavares Filho (2020) introduziram o conceito de esparsidade de cargas dos cátions para explicar o efeito diferenciado de cátions de mesma valência sobre a dispersão de argila em solos. Segundo esses autores, a capacidade do cátion em neutralizar o campo elétrico das partículas se dá pela razão de seu raio iônico hidratado e valência.

Independente das características dos cátions, quando a solução atinge a concentração eletrolítica crítica, denominada “valor de floculação” ou “concentração crítica de coagulação/floculação”, a compressão da dupla camada elétrica é intensa e o sistema disperso se desestabiliza (SHAINBERG; LEVY, 2005; NG; KOH; WONG, 2012). Porém, quanto menor a esparsidade de cargas do cátion, maior a concentração necessária para que o valor de floculação seja atingido.

Um bom indicador do comportamento de sistemas coloidais em suspensão é o potencial zeta (ζ), ou potencial eletrocinético, definido como o potencial elétrico no plano de cisalhamento da dupla camada elétrica (HONG, 2006). Esse plano delimita a nuvem de contra-íons que acompanha a partícula enquanto a mesma se move aleatoriamente na suspensão (movimento Browniano). O potencial zeta expressa, portanto, o resultado líquido de todos os processos supracitados, que interferem na estabilidade dos sistemas coloidais e se associa ao seu comportamento de modo mais acurado do que a densidade de cargas e o potencial elétrico superficial, por também considerar os contra-íons presentes (MCCLEMENTS, 2015).

Independente das características dos coloides e das condições do meio, a concentração de partículas coloidais em suspensão altera significativamente a taxa de floculação e sedimentação. Quanto menor a concentração, maior a distância média entre as partículas e menor a frequência de colisões pelo movimento Browniano (NG; KOH; WONG, 2012) e, consequentemente, maior a estabilidade do sistema (TREFALT; RUIZ-CABELLO; BORKOVEC, 2014). Adicionalmente, menor concentração de partículas implica em suspensões com menor concentração de íons, o que favorece a expansão da dupla camada elétrica e intensifica a repulsão do sistema (SHAINBERG; LEVY, 2005).

2.3 Métodos para Avaliação da Dispersão da Fração Argila

Os métodos de análise que visam a quantificação da dispersão de argila objetivam, de modo geral, inferir sobre a estabilidade dos microagregados (0,053 – 0,250 mm) do solo (IGWE; OBALUM, 2013). Esses protocolos possuem algumas diferenças práticas, que não devem influenciar significativamente nos resultados encontrados. Por exemplo, a quantificação da concentração de argila dispersa na suspensão pode ser realizada por gravimetria, densimetria, espectrofotometria ou turbidimetria (RENGASAMY, 2002; CZYZ; DEXTER, 2015; RENGASAMY; TAVAKKOLI; MCDONALD, 2016; TEIXEIRA et al., 2017). Entretanto, o aspecto mais relevante para diferenciar os métodos existentes se dá em função da ausência ou presença de energia mecânica para a ruptura dos agregados e, no último caso, da intensidade da energia empregada.

Os métodos para avaliação da dispersão da fração argila foram aqui separadas em dois grupos, com base em Rengasamy (2002): a argila espontaneamente dispersa em água e a argila mecanicamente dispersável em água. As principais características de cada método são descritas nos próximos tópicos.

2.3.1 Argila Espontaneamente Dispersa em Água

A argila espontaneamente dispersa em água é aquela que se libera dos agregados mesmo sem a aplicação de energia mecânica externa (CZYZ; DEXTER, 2015), ou seja, apenas com o umedecimento do solo (AMEZKETA et al., 2003). A análise para sua quantificação é baseada na ausência de perturbação mecânica da amostra e, normalmente, é indicativo dos efeitos danosos causados pela sodicidade em solos (RENGASAMY, 2002). Entretanto, qualquer alteração nas condições do solo que favoreça as forças repulsivas entre as partículas, desde que suficientemente intensas, pode causar a dispersão espontânea da fração argila.

2.3.2 Argila Mecanicamente Dispersável em Água

A argila mecanicamente dispersável em água é aquela que se libera dos agregados após aplicação de forças disruptivas (RENGASAMY, 2002). Para sua análise, as forças aplicadas podem variar desde o uso de agitadores mecânicos (TEIXEIRA et al., 2017) até o uso de ultrassom (RIBEIRO et al., 2013). O grau de rompimento dos agregados é diretamente proporcional à intensidade da força aplicada, o que torna os resultados dependentes do método (PARADELO; VAN OORT; CHENU, 2013). Segundo Rengasamy (2002), esse método indica a dispersão potencial que o solo pode atingir quando exposto à forças disruptivas nas condições de campo, como por exemplo o impacto de gotas de chuva ou o revolvimento do solo úmido. Entretanto, a relação direta entre as forças aplicadas em laboratório e as experenciadas em campo é difícil de ser mensurada.

3 ARTIGO A: BIOGENIC AGGREGATION INTENSIFIES SOIL IMPROVEMENT CAUSED BY MANURES

3.1 ABSTRACT

The use of manures as organic fertilizers commonly improves soil chemical and structural attributes. We investigated the effect of biogenic aggregation on the structural and chemical dynamics of a Rhodic Ferralsol after nine continuous years of chicken manure or swine liquid manure application. The biogenic aggregation increased nutrient availability, neutralized acidity, and increased organic matter content. Additionally, the proportion of pores with a diameter higher than 0.100 mm was increased by biogenic aggregation. The intensity of this improvement depended on the manure nutrient content, and the rate of biogenic aggregation depended on the carbon input provided by the manure. However, aggregates with higher base saturations were more susceptible to dispersion and such aggregates, therefore, need to be protected from mechanical disrupting agents.

Key words: Zeta potential. Soil structure. Nutrients availability.

AGREGAÇÃO BIOGÊNICA INTENSIFICA A MELHORIA DO SOLO CAUSADA PELO USO DE ESTERCOS

3.2 RESUMO

O uso de estercos como fertilizantes orgânicos comumente melhora os atributos químicos e estruturais do solo. Nós investigamos o efeito da agregação biogênica na dinâmica química e estrutural de um Latossolo Vermelho após nove anos contínuos de aplicação de cama de frango e de dejeto líquido de suínos. A agregação biogênica elevou a disponibilidade de nutrientes, neutralizou a acidez e elevou o conteúdo de matéria orgânica. Adicionalmente, a proporção de poros com diâmetro maior que 0,100 mm foi aumentada pela agregação biogênica. A intensidade desse aumento dependeu do conteúdo de nutrientes no esterco e a taxa de agregação biogênica dependeu da entrada de carbono providenciada pelo esterco. Entretanto, os agregados com maior saturação por bases foram mais susceptíveis à dispersão e, consequentemente, precisam ser protegidos contra agentes disruptivos.

Palavras-chave: Potencial zeta. Estrutura do solo. Disponibilidade de nutrientes.

3.3 INTRODUCTION

Manures are used as a nutrient source in agriculture all over the world. Their adequate disposal in agricultural soils is advantageous, as it can reduce the environmental impact of meat production, improve soil quality, reduce costs, and reduce the need for inorganic fertilizers (HE; PAGLIARI; WALDRIP, 2016). Besides improving chemical and physical soil attributes (BARBOSA *et al.*, 2015; ANDRADE *et al.*, 2016), manure application stimulates biological activity, favoring biogenic aggregation and improving soil quality (LOSS *et al.*, 2017).

Biogenic aggregates are formed mainly by soil biota and root activity and are indicators of soil quality (SIX *et al.*, 2002). Biogenic aggregates are formed by the action of cementing agents, such as organic matter, roots, and microbial exudates, in addition to the compressive effect of roots and hyphae (CARDOSO *et al.*, 2013), and soil fauna activity. Biogenic aggregates can be physically and chemically distinct from the physicogenic aggregates (LOSS *et al.*, 2014; SILVA NETO *et al.*, 2016; LOSS *et al.*, 2017). Consequently, biological aggregation can have a crucial role in soil improvement when manure is applied.

The forces between primary particles can change concurrently with changes in soil attributes resulting from manure application and the aggregate formation pathway. Some studies have shown that clay dispersion can be favored by the presence of low-weight organic molecules (NGUYEN *et al.*, 2013), phosphorous adsorption (RIBEIRO *et al.*, 2011), increases in pH (CHOROM; RENGASAMY, 1995), and saturation by cations with less flocculant power (RENGASAMY; TAVAKKOLI; MCDONALD, 2016). However, the increment of stable organic matter molecules, promoted by manure application, can increase the resistance of aggregates to mechanical disruption and, consequently, reduce clay dispersion.

There is a lack of studies that associate soil chemical and physical attributes with the aggregate formation pathways induced by different manures. These associations could allow a better comprehension of the role of soil engineers in soil improvement caused by manure application. In addition, it is not clear if the increase in stable organic compounds inhibits clay dispersion when aggregates are exposed to disrupting forces.

Our hypothesis is that biogenic aggregation can intensify soil improvement caused by manure application, and that these changes can also affect

soil susceptibility to clay dispersion. Here, we tested if i) soil chemical and structural improvement is intensified by biogenic aggregation, and ii) the increase in stable organic matter content can inhibit clay dispersion after the mechanical rupture of aggregates.

3.4 Material and Methods

3.4.1 Site Description

The experiment was conducted in Londrina, Paraná State, Brazil (latitude -23,367°, longitude -51,167°, altitude: 585 m). According to Köppen's classification, the climate is Cfa–Humid subtropical with oceanic weather, without a dry season, and with hot summers (ALVARES *et al.*, 2013). The annual precipitation is 1634 mm and the average temperature is 21.1 °C.

The soil was classified as a Rhodic Ferralsol, according to the International System of Soil Classification (IUSS WORKING GROUP WRB, 2015) and as a *Latossolo Vermelho Distroférrico típico*, according to the Brazilian System of Soil Classification (SANTOS *et al.*, 2018). The soil is formed from basalt from the Serra Geral formation, and some selected attributes are presented in Table 3.1. Further information about Serra Geral formation can be found in CUNHA *et al.* (2019).

Table 3.1. Soil characterization (0–10 cm) in 2008, before the commencement of the experiment. The quantification of minerals was performed in 2017.

Attribute	Unit	Value
Clay[a]	g kg^{-1}	830.0
Silt[a]	g kg^{-1}	140.0
Sand[a]	g kg^{-1}	30.0
Kaolinite[b]	g kg^{-1}	566.0
Gibbsite[b]	g kg^{-1}	98.0
Fe_2O_3[c]	g kg^{-1}	156.0
C[d]	g kg^{-1}	17.8
P[e]	mg kg^{-1}	27.3
pH_{cacl2}[f]	-log[H^+]	5.1
CEC[g]	$cmol_c$ kg^{-1}	12.8
BS[h]	%	55.7
Al^{3+}[i]	$cmol_c$ kg^{-1}	0.7
Ca^{2+}[i]	$cmol_c$ kg^{-1}	4.0
Mg^{2+}[i]	$cmol_c$ kg^{-1}	2.4
K^+[j]	$cmol_c$ kg^{-1}	0.7
H+Al[k]	$cmol_c$ kg^{-1}	5.7

[a]Pipette method after dispersion with NaOH 0.1 mol l^{-1}. [b]Thermogravimetric analysis after sesquioxides removal by DCB-Na. [c]Atomic absorption spectroscopy after dissolution by DBC-Na. [d] Oxidation by $K_2Cr_2O_7$ in sulfuric medium. [e]Extracted with Mehlich-1. [f]$CaCl_2$ 0.01 mol l^{-1} soil:solution proportion 1:2.5 (m:v). [g]H+Al+Ca+Mg+K. [h]Base saturation: (Ca+Mg+K)×100/CEC. [i] Extracted with KCL 1 mol l^{-1}. [j]Flame photometry after extraction with Mehlich-1. [k]Estimated after equilibrium with SMP solution.

Before the start of the experiment in 2007, the area was ploughed twice per year to a depth of 0.3 m with posterior leveling of the soil to a depth of 0.15 m using a disc harrow. From 2008, the area was managed under no-tillage system, receiving 3.0 Mg ha^{-1} of limestone on the soil surface. Since the commencement of

the experiment in 2008, manures were applied twice per year. The application of manure is based on the crop's demand either for phosphorous (*Glycine* max L.) in the summer (60 kg ha^{-1}), or for nitrogen (*Zea mays* L., *Triticum aestivum* L., or *Avena sativa* L.) in the winter (150, 60 and 60 kg ha^{-1}, respectively). The characterization of the manures is presented in Table 3.2.

Table 3.2. Average attributes of the manures used since the beginning of the experiment.

Attribute	Unit	CM	SLM
pH	$-\log[H^+]$	8.58	7.90
C	g kg^{-1}	231.00	91.00
N	g kg^{-1}	24.40	24.90
P	g kg^{-1}	8.40	15.45
C:N	-----	9.47	3.65
C:P	-----	27.50	5.89
P:N	-----	0.34	0.62
Ca	g kg^{-1}	2.29	0.84
Mg	g kg^{-1}	0.69	0.38
K	g kg^{-1}	1.05	3.57
Na	g kg^{-1}	0.53	0.91

CM: chicken manure. SLM: swine liquid manure.

3.4.2 Experimental Design and Treatments

A randomized block design was used in a factorial scheme of 5 × 2 with four field replicates and with 5 × 10 m plots. The levels of the first factor are related to the field treatments: control, with no manure application (Contr.); application of chicken manure to supply nutrients equal to the crop's demand (CM1×); application of swine liquid manure to supply nutrients equal to the crop's demand (SLM1×); application of chicken manure to supply twice the amount of nutrients required to meet the crop's demand (CM2×); and application of swine liquid manure to supply twice the amount of the nutrients required to meet the crop's

demand (SLM2×). The levels of the second factor are related to the formation pathways of aggregates: biogenic (Biog.) or physicogenic (Physic.).

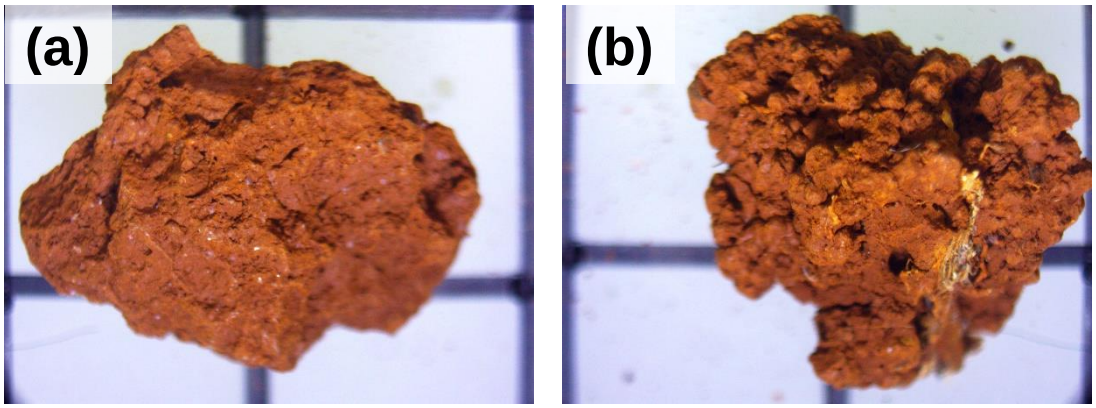
3.4.3 Soil Sampling and Preparation

Undisturbed soil samples were collected in a single spot for each field replication, from the 0.00–0.10 m layer in April, 2017, after a soybean harvest (nine years after the commencement of the experiment). The samples were transported in polystyrene containers. In the laboratory, the samples were air-dried and manually sieved. The aggregates between 19 and 8 mm were used in the present study because they consisted of more than 62 % of mass of the samples and because the error associated to the classification of the aggregation pathway is smaller for larger aggregates (JOUQUET *et al.*, 2009).

3.4.4 Aggregate Formation Pathways

Classification of the aggregate formation pathway was performed according to the morphological pattern (BULLOCK et al., 1985) in 200 g of sample, using a magnifying glass. The morphological patterns are physicogenic (Figure 3.1a): angular shapes, well defined edges, and apparent cementation; and biogenic (Figure 3.1b): rounded shapes, originating from the intestinal tract of soil fauna, mainly Oligochaeta. Aggregates with high root residues are also included in this class, although these were rarely found in the present study.

Figure 3.1. Morphological patterns of physicogenic (a) and biogenic (b) aggregates between 19 and 8 mm.



3.4.5 X-ray Computed Microtomography

The X-ray computed microtomography images were obtained with a microCT Skyscan 1173 from Bruker® with a voltage of 70 kV, current of 100 µA, exposition time of 700 ms in a spatial resolution of 10 µm. After obtention, the 2D images were reconstructed in the NRecon software (version 1.6.10.4) with smoothing, ring and bean hardening corrections. The segmentation of the samples was performed in the CTan software (version 1.15.4.0) using 3D space by the automatic Otsu method. After segmentation, the pore size distribution was quantified. One representative biogenic and physicogenic aggregate was taken from each sample, totaling 40 aggregates.

3.4.6 Particle Size Distribution, Zeta Potential, and Clay Dispersion

Preceding the analyses, soil aggregates were crushed until they could completely pass through a 2 mm sieve. The particle size distribution was performed using 20 g of soil shaken with 100 mL of 0.1 mol L^{-1} NaOH at 200 rpm for 16 h in an orbital horizontal shaker. Particle sedimentation velocity was calculated according to Stokes' law. Zeta potential was measured at different pH values in the clay fraction (Ø < 0.002 mm) extracted during the particles size analysis by electroacoustic spectroscopy in a Zeta-APS from Matec®. The mechanically water-dispersible clay was quantified from 20 g of soil shaken with 100 mL of distilled water at 200 rpm for 1 h in an orbital horizontal shaker. The dispersion degree was

calculated by the ratio between the mechanically water-dispersible clay and total clay.

3.4.7 Chemical Attributes

Preceding the analyses, air-dried soil aggregates were crushed until they could completely pass through a 2 mm sieve. pH was measured in a 0.01 mol L^{-1} $CaCl_2$ solution at a soil: solution ratio of 1:2.5 (mass: volume). Available phosphorous (P) and exchangeable potassium (K^+) were extracted with Mehlich-1 solution and quantified in a spectrophotometer and in a flame photometer, respectively. The exchangeable aluminum (Al^{3+}), calcium (Ca^{2+}), and magnesium (Mg^{2+}) were extracted with a 1 mol L^{-1} KCl solution and quantified by titration with NaOH (for Al^{3+}) and by atomic absorption spectrometry (for Ca^{2+} and Mg^{2+}). The potential acidity ($H+Al^{3+}$) was estimated by potentiometry after equilibration with SMP solution. Cation exchange capacity (CEC) was estimated by the sum of $H+Al^{3+}$, Ca^{2+}, Mg^{2+}, and K^+. The base saturation was calculated as the percentage of exchangeable bases (Ca^{2+}, Mg^{2+}, and K^+) in relation to the CEC. Amorphous forms of iron sesquioxides were extracted with oxalate solution at pH 3.00 in the dark and quantified by atomic absorption spectrometry. These procedures are presented in TEIXEIRA *et al.* (2017).

The humic substances fractionation (humin, humic acids, and fulvic acids) was performed by selective solubility according to Benites et al. (2003). Quantification of the carbon associated with these fractions and with the total organic matter was performed by oxidation with $K_2Cr_2O_7$ in a sulfuric medium, according to Yeomans and Bremner (1988).

3.4.8 Statistical Procedures

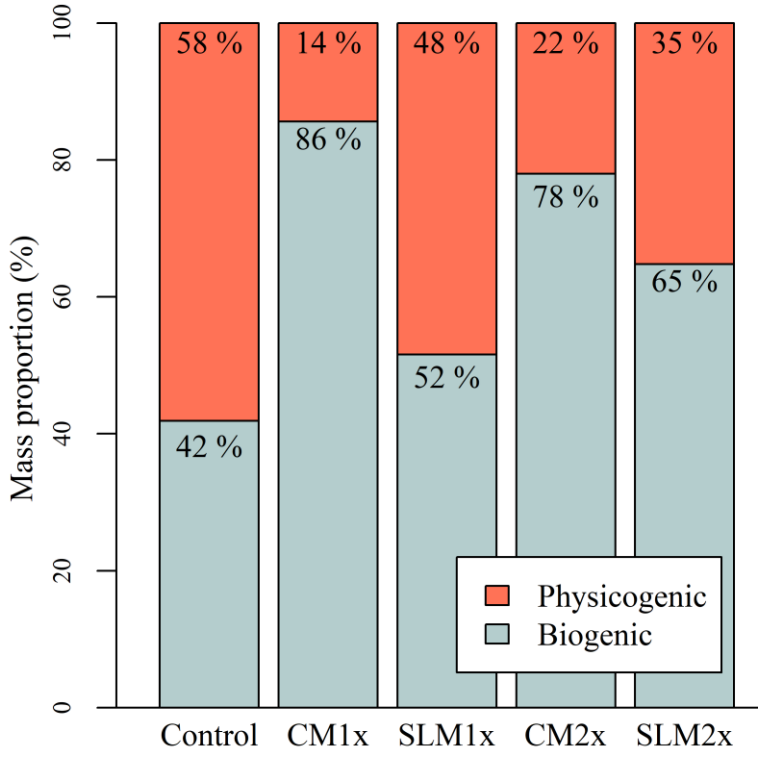
The data (n = 40) were evaluated by analysis of variance. The assumptions of residual normality and homoscedasticity were checked, and data transformation was unnecessary. The treatments were compared by Tukey's test at 5 % probability. All analyses were performed using the R environment v. 3.4.3 (R Core Team, 2017).

3.5 RESULTS

3.5.1 Aggregate Formation Pathways

The size class of the aggregates evaluated in the present study (19–8 mm) was the predominant class in all the samples, containing at least 62 % of the total mass. Chicken manure (CM) application highly increased biogenic aggregation. Swine liquid manure (SLM) also increased biogenic aggregation, but not to the extent that CM did (Figure 3.2).

Figure 3.2. Proportion of biogenic and physicogenic aggregates (19–8 mm) as a function of chicken manure (CM) and swine liquid manure (SLM) applications in doses that equal the crop's demand (1×) or provide twice the nutrients required to meet the crop's demand (2×).



3.5.2 Chemical Attributes

All attributes presented in Table 3.3 responded to the aggregate formation pathway. Biogenic aggregates had a higher nutrient content and CEC, and neutralized pH and Al^{3+} better than the physicogenic aggregates. The increase in Ca^{2+} and Al^{3+} neutralization, however, was restricted to biogenic aggregates influenced by CM, probably because of its higher Ca content than that of SLM (Table 3.2).

Comparison of the manures revealed that CM was superior to SLM for almost all attributes (Table 3.3). The exceptions were Mg^{2+}, which was not altered by the application of either manure, and P, for which SLM at the 1× dose was superior to CM. The increase of Ca^{2+} and neutralization of Al^{3+} by CM occurred only in biogenic aggregates. Compared to the control, SLM improved only the P and K^{+} content.

Table 3.3. Chemical attributes of biogenic and physicogenic aggregates after nine years of application of manures.

Attribute	pH		P	
Unit	-log[H^+]		mg kg^{-1}	
Treat.	Aggregates			
	Bio.	Phys.	Bio.	Phys.
Contr	4.98^{Ac}	4.80^{Bc}	19^{Ac}	13^{Bc}
CM 1x	5.55^{Aab}	5.03^{Bab}	59^{Ab}	17^{Bb}
SLM 1x	4.88^{Ac}	4.80^{Bc}	93^{Aa}	58^{Ba}
CM 2x	5.63^{Aa}	5.23^{Ba}	161^{Aa}	54^{Ba}
SLM 2x	4.98^{Abc}	4.93^{Bbc}	176^{Aa}	69^{Ba}
Attribute	CTC		Al^{3+}	
Unit	$cmol_c\ kg^{-1}$			
Treat.	Aggregates			
	Bio.	Phys.	Bio.	Phys.
Contr	12.20^{Acd}	10.36^{Bcd}	0.24^{Aa}	0.36^{Aa}
CM 1x	16.01^{Ab}	11.32^{Bb}	0.05^{Bb}	0.26^{Aa}
SLM 1x	11.75^{Ad}	9.61^{Bd}	0.36^{Aa}	0.53^{Aa}
CM 2x	18.05^{Aa}	13.48^{Ba}	0.06^{Bb}	0.21^{Aa}
SLM 2x	13.76^{Abc}	11.27^{Bbc}	0.41^{Aa}	0.43^{Aa}
Attribute	Ca^{2+}		Mg^{2+}	
Unit	$cmol_c\ kg^{-1}$			
Treat.	Aggregates			
	Bio.	Phys.	Bio.	Phys.
Contr	6.44^{Ab}	4.79^{Ab}	2.49^{Aab}	2.42^{Bab}
CM 1x	9.75^{Aa}	5.83^{Bab}	2.85^{Aa}	2.28^{Ba}
SLM 1x	5.42^{Ab}	4.41^{Ab}	2.50^{Ab}	1.70^{Bb}
CM 2x	11.71^{Aa}	7.89^{Ba}	2.92^{Aa}	2.26^{Ba}
SLM 2x	7.25^{Ab}	5.70^{Aab}	2.49^{Aab}	2.30^{Bab}
Attribute	K^+		V	
Unit	$cmol_c\ kg^{-1}$		%	
Treat.	Aggregates			
	Bio.	Phys.	Bio.	Phys.
Contr	0.39^{Ac}	0.16^{Bc}	76.0^{Ab}	70.2^{Bb}
CM 1x	0.88^{Aa}	0.47^{Ba}	84.2^{Aa}	75.6^{Ba}
SLM 1x	0.50^{Ab}	0.33^{Bb}	71.5^{Ab}	66.5^{Bb}
CM 2x	1.03^{Aa}	0.71^{Ba}	86.7^{Aa}	80.5^{Ba}
SLM 2x	0.50^{Ab}	0.24^{Bb}	73.9^{Ab}	72.9^{Bb}

Lowercase letters compare the manures and Uppercase letters compare the aggregates formation pathway by Tukey`s test, at 5% of probability. Bio.: Biogenic. Phys.: Physicogenic. CM: chicken manure. SLM: swine liquid manure. 1x or 2x: dose to supply one or two times the crop's depend for nutrients.

The biogenic aggregates had a high C content in all organic matter fractions (Table 3.4). However, the intensity of accumulation of organic matter fractions in biogenic aggregates seems to be dependent on the manure, as observed by VENTURA *et al.* (2018). Comparison of the different treatments revealed that the control had the lowest C content. However, CM increased the C content compared to SLM, except for C-humin, which depended only on the dose of the applied manure, not the type of manure.

Table 3.4. Total organic carbon and carbon content of humic substances in biogenic and physicogenic aggregates after nine years of application of manures.

Attribute	C		C-Humin	
Unit	g kg^{-1}			
Treat.	Aggregates			
	Bio.	Phys.	Bio.	Phys.
Contr	26.73^{Ad}	22.63^{Bd}	10.47^{Ac}	8.42^{Bc}
CM 1x	45.10^{Ab}	41.95^{Bb}	13.35^{Ab}	11.74^{Bb}
SLM 1x	35.65^{Ac}	29.51^{Bc}	13.54^{Ab}	11.25^{Bb}
CM 2x	49.80^{Aa}	46.69^{Ba}	17.02^{Aa}	14.50^{Ba}
SLM 2x	42.46^{Ab}	39.15^{Bb}	15.96^{Aa}	13.78^{Ba}
Attribute	C-Humic Acids		C-Fulvic Acids	
Unit	g kg^{-1}			
Treat.	Aggregates			
	Bio.	Phys.	Bio.	Phys.
Contr	3.71^{Ac}	3.30^{Bc}	3.16^{Ac}	2.76^{Bc}
CM 1x	9.15^{Aa}	8.59^{Ba}	5.37^{Aa}	4.81^{Ba}
SLM 1x	6.56^{Ab}	6.00^{Bb}	4.76^{Ab}	4.28^{Bb}
CM 2x	9.72^{Aa}	8.80^{Ba}	5.95^{Aa}	5.03^{Ba}
SLM 2x	7.73^{Ab}	6.88^{Bb}	5.50^{Aa}	4.77^{Ba}

Lowercase letters compare the manures and Uppercase letters compare the aggregates formation pathway, both by Tukey`s test, at 5% of probability. Bio.: Biogenic. Phys.: Physicogenic. CM: chicken manure. SLM: swine liquid manure. 1x: dose to supply one time the crop's depend for nutrients. 2x: dose to supply two times the crop's depend for nutrients.

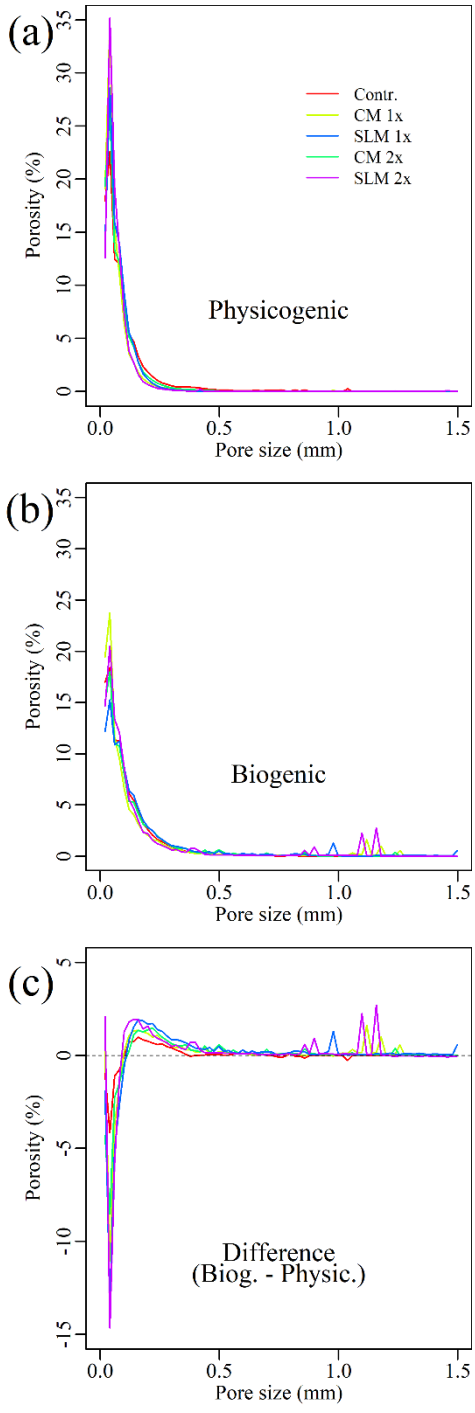
The amorphous form of iron sesquioxides are responsible for increasing the size of aggregates in soils (ZHAO *et al.*, 2017). In this study, the iron associated to amorphous sesquioxides presented an average of 2.91 ± 0.67 g kg^{-1}, which is consistent with these basalt-weathered soils (GHIDIN *et al.*, 2006). However, the absence of statistical difference suggests that these minerals were not affected

by the studied treatments. The results for each treatment are presented in Table S3.1.

3.5.3 Aggregate Porosity

The biogenic aggregates had a higher proportion of large pores than the physicogenic aggregates (Figure 3.3a, b). Regardless of the manure type or dose, pores with a diameter higher than 0.100 mm prevailed in biogenic aggregates (Figure 3.3c). The peaks between 0.800 mm and 1.300 mm also indicate the presence of biopores, formed by fauna activity. Images from some of the studied aggregates can be seen in Figure S3.1.

Figure 3.3. Distribution of pore size (a and b) and difference in pore sizes between physicogenic and biogenic aggregates (c). Negative and positive values in (c) show the predominance of pore sizes in physicogenic and biogenic aggregates, respectively.



3.5.4 Clay Dispersion

The studied layer (0.00–0.10 m) of this soil does not present significant slacking or spontaneous dispersion, as visually observed by Emerson dispersion test. However, these soils can present considerable amount of water-dispersible clay after the mechanical breakdown of aggregates (MELO; MACHADO; TAVARES FILHO, 2015). Despite the soil improvements caused by biogenic aggregation (Tables 3.3 and 3.4), the potential dispersion of the clay fraction was also increased (Table 3.5). The highest dispersion was found in biogenic aggregates formed under CM1× and CM2× treatments.

Table 3.5. Dispersion degree of clay in biogenic and physicogenic aggregates after nine years of application of manures.

Attribute	Dispersion degree	
Unit	%	
Treat.	Aggregates	
	Bio.	Phys.
Contr	31.3^{Ab}	25.8^{Bb}
CM 1x	35.5^{Aab}	27.0^{Bab}
SLM 1x	29.0^{Ab}	26.3^{Bb}
CM 2x	35.8^{Aa}	33.0^{Ba}
SLM 2x	28.3^{Ab}	26.5^{Bb}

Lowercase letters compare the manures and Uppercase letters compare the aggregates formation pathway, both by Tukey`s test, at 5% of probability. Bio.: Biogenic. Phys.: Physicogenic. CM: chicken manure. SLM: swine liquid manure. 1x or 2x: dose to supply one or two times the crop's depend for nutrients.

3.6 DISCUSSION

CM neutralized pH from values considered medium (4.5–4.9) to high (5.0–5.5) (PAULETTI; MOTTA, 2017), indicating improvements in soil conditions for vegetal growth. Previous studies have shown that soil can be acidified using SLM (ADELI et al., 2008, SCHLEGEL et al.., 2017). However, some authors observed an increase in soil pH after SLM application (LOURENZI *et al.*, 2016). Eghball (2002) suggests that the effect of manures and organic composts on soil pH depends on the

initial soil pH. The difference between the manures can be explained by the higher carbon input from CM that increases the biological demand for oxygen and induces electron transference to H^+, neutralizing soil pH (MORAN-SALAZAR et al., 2016).

The pH increase caused by CM induced Al^{3+} precipitation and may reduce the demand for limestone over time. This affirmation is reinforced by the increase in base saturation and Ca^{2+} and Mg^{2+} content (Table 3.3). Additionally, the increase in CEC, promoted by the increase in anionic organic radicals from soil organic matter, may reduce soil acidification by the reduction of base leaching (Table 3.3 and 3.4).

There are no critical values for Ca^{2+} and Mg^{2+} excess in these basalt-weathered soils and K^+ was considerably below the critical level of 10 % of the CEC (PAULETTI; MOTTA, 2017). To avoid a deficiency in the availability of these cations to plants, it is recommended that Ca^{2+} contributes 30 to 50 % of CEC and Mg^{2+} contributes 5 to 10 % of CEC. The proportion of Ca^{2+} and Mg^{2+} cations in the present study (2:1 to 4:1, respectively) suggests that no significant antagonism should be expected.

Ferralsols commonly have low P availability because of its strong adsorption to metallic sesquioxides (GUEDES *et al.*, 2016). When manure was applied, P availability was increased, especially in biogenic aggregates. Organic molecules from manure can compete for P-adsorption sites, increasing its availability (ZHU; LI; WHELAN, 2018). In addition, the constant application of manures directly increases P input, saturating adsorption sites and increasing its availability. This shows that biogenic aggregates can be an important P pool for plants. During soil exploration by roots, this nutrient can be absorbed, significantly reducing the need for other sources of P, such as mineral fertilizers.

CM was superior to SLM with respect to the improvement of soil physical and chemical attributes. The manure doses were calculated according to N or P content and, consequently, the higher C: N and C: P ratios of CM indicate that more C was added to the soil by CM than by SLM (Table 3.2). The higher carbon input probably caused the higher proportion of biogenic aggregation. Despite the higher C input by CM, the accumulation of C in the humin fraction occurred regardless of manure type but was affected by the applied dose. However, the higher amount of non-humified carbon under CM treatments suggests a higher decomposition of these fractions by soil biota.

Despite Ferralsols presenting a good structure for vegetal growth, they commonly display considerable signs of compaction when used for agricultural purposes (TAVARES FILHO *et al.*, 2014). When studying the same type of soil as in the present study, these authors found that, under native vegetation, the aggregates had a polyhedral, sub-angular shape, no evidence of compaction, porosity easily visible to the naked eye, rough surfaces in the rupture planes, and low dry cohesion. However, under the no-tillage system, aggregates presented more evident signs of compaction, low or no porosity visible to the naked eye, deformed roots and smooth surfaces in the rupture planes, and high dry cohesion up to a depth of approximately 50 cm.

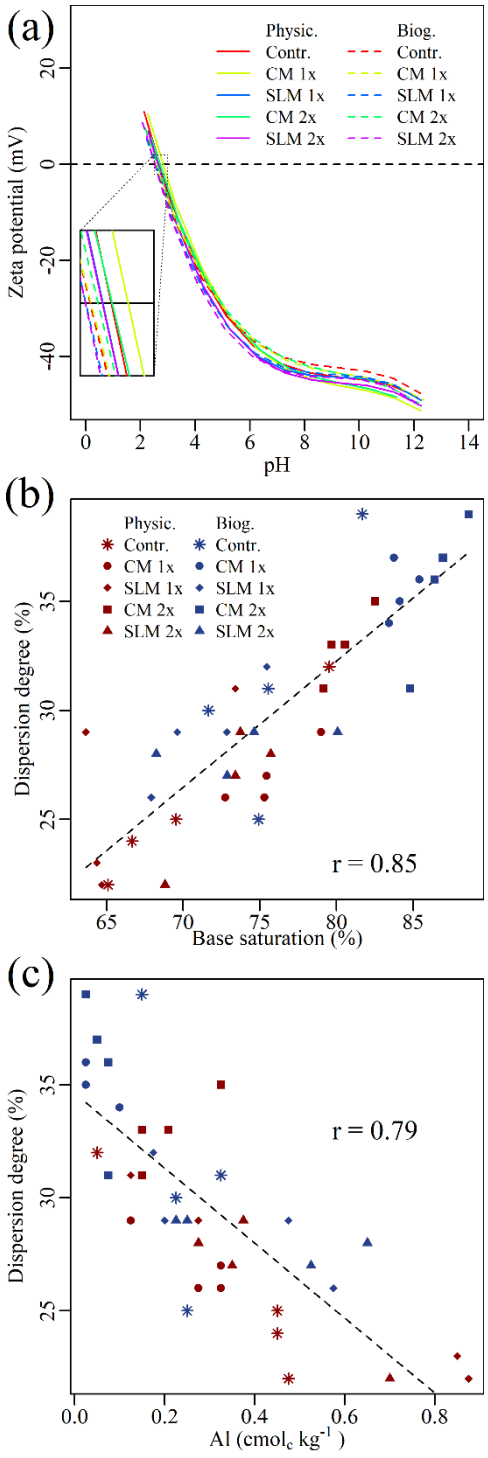
The use of manures, especially chicken manure, is an advantageous strategy for soil structural improvement. Manure application increased biogenic aggregation, which transformed pores < 0.100 mm into pores > 0.100 mm. Pores with a higher diameter are desirable, especially in soils with high clay content, because they increase oxygen diffusion and water infiltration and drainage (TAVARES FILHO *et al.*, 2014), thus reducing susceptibility to hydric erosion.

The findings of LIANG *et al.* (2018) suggest that, in undisturbed soils, pores > 0.100 mm help to protect organic matter against microbial decomposition. This can explain part of the carbon increment in biogenic aggregates, especially because the soil of the present study has not been plowed since 2007 and can also be considered an undisturbed soil. However, these authors studied aggregates between 2–1 mm and the distribution of microorganisms can be different in aggregates between 19–8 mm, especially in areas under manure application, as in the present study.

The soil of the present study has a high content of kaolinite and iron sesquioxides (Table 3.1) that tend to strongly interact with organic matter (PENG *et al.*, 2015; ZHAO *et al.*, 2017) and increase the stability of aggregates (REICHERT *et al.*, 2009; MARKGRAF *et al.*, 2012). This affirmation corroborates BARBOSA *et al.* (2015) who observed the increase in water-stable macroaggregates (> 0.250 mm) due to manure applications in the same experiment of our study. However, our results suggest that, after mechanical disruption, more clay is released from aggregates. This can occur because of unbalanced charges on the particle surfaces, caused by organic molecules or phosphorous adsorption (NGUYEN *et al.*, 2013), as

evidenced by the low pH value when the zeta potential becomes zero ($pH_{\zeta = 0\ mV}$) (Figure 3.4a).

Figure 3.4. Zeta potential as a function of pH (a) and the relationship between the degree of clay dispersion and base saturation (b) and exchangeable aluminum–Al^{3+} (c).



However, the small variation in $pH_{\zeta = 0\ mV}$ suggested that the changes unbalance caused by anion adsorption were secondary. The increase in the degree of clay dispersion was caused by the substitution of Al^{3+} for Ca^{2+}, Mg^{2+}, and K^{+} (Figure 3.4b, c). Al^{3+} has a high capacity to neutralize the charges originating from clay particles and its exchange by cations with a smaller flocculation capacity increases the net dispersive charge (RENGASAMY, 2018). When the repulsive forces between particles are strong enough, aggregates tend to breakdown (HU *et al.*, 2015).

The amount of dispersed clay depends on the capacity of aggregates to resist the mechanical forces applied and on the tendency of the clay to flocculate after being released from aggregates. The observed increase in organic matter content could increase the capacity of aggregates to resist disruption. However, the positive Pearson's correlation coefficient between the degree of clay dispersion and C (r = +0.42), C-humin (r = +0.33), C-fulvic acids (r = +0.35), and C-humic acids (r = +0.40) corroborates the affirmation that organic molecules were not capable of inhibiting the breakdown of aggregates.

The clay dispersion results highlight the need to prevent mechanical impacts on soil, such as the impact of raindrops and plowing. When dispersed, clay can induce soil surface sealing (HU *et al.*, 2012) and the clogging of pores in the soil subsurface (SPERA *et al.*, 2008), in addition to facilitating the transport of pollutants to water bodies (WANG; KELLER, 2009; MARTIN *et al.*, 2015).

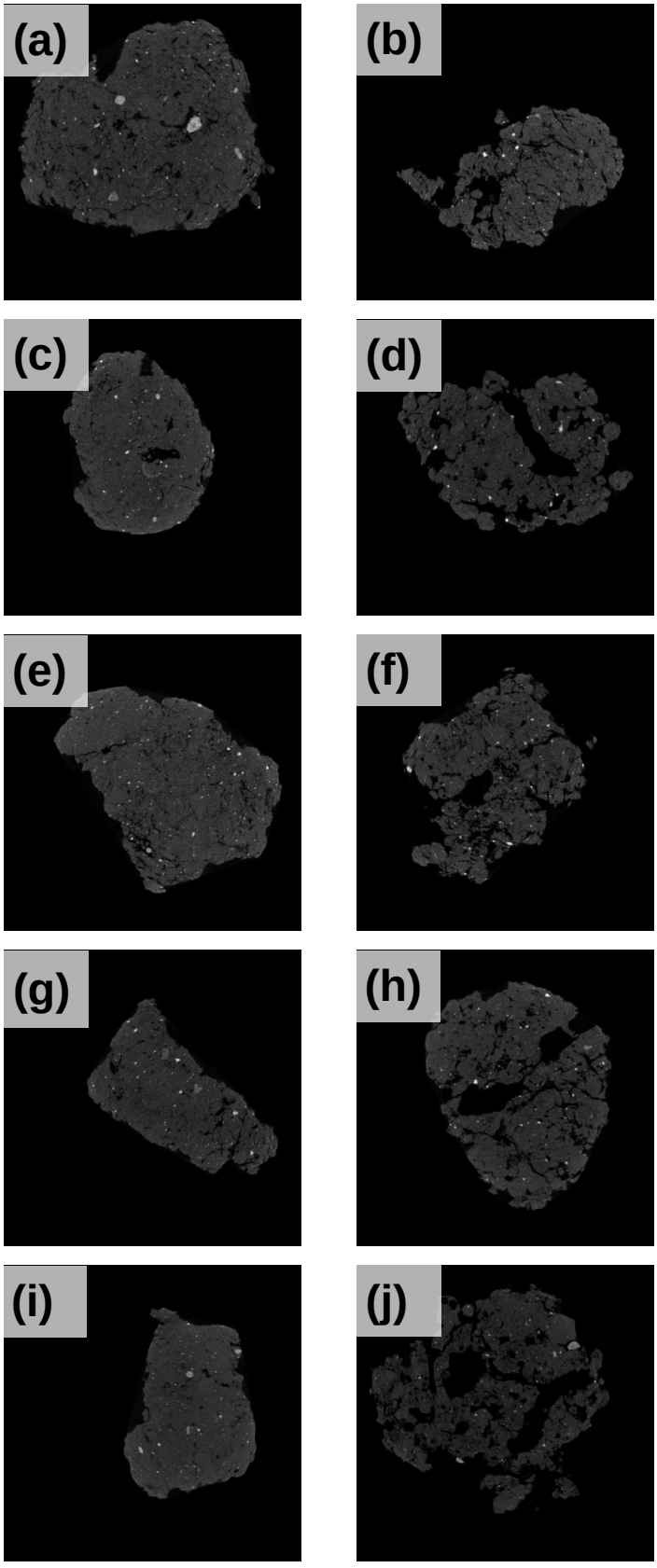
3.7 Conclusion

Biogenic aggregation intensifies soil structural and chemical improvement caused by manure application. The intensity of this improvement depends on the nutrient content of the manure and the rate of biogenic aggregation depends on the C input provided by the manure. Because of this, chicken manure was better than swine liquid manure in improving soil attributes. However, aggregates with high base saturation are more susceptible to dispersion and need to be protected from mechanical disrupting agents to avoid structural degradation.

3.8 Supplementary Material

3.8.1 Supplementary Figures

Figure S3.1. X-ray computed microtomography images of soil aggregates. Control physic. (a), Control biog. (b), CM1× physic (c), CM1× biog. (d), SLM1× physic (e), SLM1× biog. (f), CM2× physic (g), CM2× biog. (h), SLM2× physic (i), SLM2× biog. (j).



3.8.2 Supplementary Tables

Table S3.1. Iron associated to amorphous sesquioxides in biogenic and physicogenic aggregates after nine years of application of manures.

Attribute	$Fe_{Oxalate}$	
Unit	g kg^{-1}	
Treat.	Aggregates	
	Bio.	Phys.
Contr	3.25^{Aa}	2.62^{Aa}
CM 1x	3.43^{Aa}	3.13^{Aa}
SLM 1x	2.40^{Aa}	2.34^{Aa}
CM 2x	3.22^{Aa}	2.91^{Aa}
SLM 2x	2.73^{Aa}	3.09^{Aa}

Lowercase letters compare the manures and Uppercase letters compare the aggregates formation pathway, both by Tukey`s test, at 5% of probability. Bio.: Biogenic. Phys.: Physicogenic. CM: chicken manure. SLM: swine liquid manure. 1x or 2x: dose to supply one or two times the crop's depend for nutrients.

4 ARTIGO B: CAN CLAY RE-FLOCCULATE AFTER MACROAGGREGATES BREAKDOWN IN SOILS?

4.1 ABSTRACT

Increase in organic matter content is one of the most important factors favoring stabilization of macroaggregates in soils. However, organic matter is also known to inhibit the re-flocculation of suspended clay, which implies that re-flocculation is unlikely to happen after clay is released by the breakdown of macroaggregates. In this study, we investigated whether clay re-flocculation is possible after the mechanical breakdown of water-stable macroaggregates. Profiles of three Ferralsols weathered from basaltic rocks were studied to create a natural gradient of organic matter, macroaggregates stability, and clay re-flocculation capacity. Macroaggregates stabilized mainly by inorganic bonds showed high clay re-flocculation capacity after breakdown. Organic bonds increased the proportion of water-stable macroaggregates, but, after breakdown, the released clay showed high charges imbalance, thereby inhibiting its re-flocculation. However, re-flocculation still prevailed over dispersion in clay saturated with organic matter when the pH and base saturation were low, and Al^{3+} was high.

Key words: Zeta potential. Clay dispersion. Organic matter.

ARGILA PODE REFLOCULAR APÓS A QUEBRA DOS MACROAGREGADOS EM SOLOS?

4.2 RESUMO

O aumento no conteúdo de matéria orgânica é um dos fatores mais relevantes favorecendo a estabilização de macroagregados em solos. Entretanto, a matéria orgânica também inibe a refloculação de argila suspensa, o que implica na improbabilidade de refloculação de argila liberada pela quebra de macroagregados. Nesse estudo, nós investigamos se a refloculação de argila é possível após a quebra mecânica de macroagregados estáveis em água. Perfis de três Latossolos intemperizados de basalto foram estudados para criar um gradiente natural de matéria orgânica, estabilidade de macroagregados, e capacidade de refloculação de

argila. Os macroagregados estabilizados principalmente por ligações inorgânicas apresentaram elevada capacidade de refloculação de argila após a quebra. Pontes orgânicas elevaram a proporção de macroagregados estáveis em água, mas, após a quebra, a argila liberada apresentou elevado desbalanço de cargas, inibindo a refloculação de argila. Entretanto, a refloculação ainda prevaleceu sobre a dispersão em argila saturada com matéria orgânica quando o pH e a saturação por bases são baixos e o conteúdo de Al^{3+} é elevado.

Palavras-chave: Potencial zeta. Dispersão de argila. Matéria orgânica.

4.3 INTRODUCTION

Water-stable macroaggregates are related to a higher resistance of soils against hydric erosion (LU *et al.*, 2016). It is well accepted in literature that organic matter is, if not the most, one of the most important factors favoring the stability of macroaggregates in water (BRONICK; LAL, 2005; MELO *et al.*, 2018). Besides the bonding between mineral particles promoted by organic molecules, root system and fungi hyphae are important agents of physical support against disrupting agents (CARDOSO *et al.*, 2013).

Another well documented phenomenon in the literature is the inhibition of flocculation of suspended clay by organic molecules (AMÉZKETA, 1999; NGUYEN *et al.*, 2013). Highly weathered clay minerals tend to naturally flocculate because the positive and negative charges are balanced. However, the excess of negative charges caused by the adsorption of organic molecules intensifies the repulsive forces between particles, keeping the suspension dispersed (NGUYEN *et al.*, 2009; NGUYEN *et al.*, 2013). This is harmful for soils and water bodies, because particles that cannot flocculate are less likely to reaggregate and are more easily transported, carrying with them nutrients and pollutants (MARTIN *et al.*, 2015).

These observations imply that clay re-flocculation is not expected after macroaggregates breakdown in soils. This happens because macroaggregates tend to present a higher concentration of organic matter, which can intensify charge imbalance and inhibit the re-flocculation of the released clay. As clay flocculation is considered a mandatory step prior to microaggregation (CARDOSO *et al.*, 2013), this

could have implications on aggregate turnover of soils exposed to disrupting forces, such as plowing or raindrop impact.

Studies usually focus on either clay dispersion/re-flocculation or macroaggregates stabilization (BOTTINELLI *et al.*, 2017; BASGA *et al.*, 2018; LIPIEC *et al.*, 2018; MELO *et al.*, 2018). Thus, there is a lack of information regarding how these processes are related and the associated influence of organic matter, which limits the understanding of soil structural dynamics. In this study, we investigated whether clay re-flocculation is possible after the mechanical breakdown of water-stable macroaggregates.

4.4 MATERIAL AND METHODS

4.4.1 Description of sampling sites

Soil samples were collected in three municipalities from the state of Paraná, Brazil: Guarapuava, Londrina, and Marechal Cândido Rondon (Rondon). All soils were classified as Ferralsols (IUSS WORKING GROUP WRB, 2015) and were formed from basaltic rocks from the Serra Geral Formation. According to Köppen's climatic classification, the climate of Guarapuava is Cfb – humid subtropical with a temperate summer – and that of Londrina and Rondon is Cfa – humid subtropical with a hot summer.

Guarapuava and Londrina soils have been cultivated under no-tillage system and the cultivation system in Rondon is soil plowing until 0.25 m with annual crops. In each area, samples were collected from three different soil profiles; with ten samples collected from each profile, totaling 30 samples per site and 90 samples in the present study. The selected sites and soils attributes, including the range of sampling depth, are presented in Table 4.1.

Table 4.1. Selected sites and soil attributes.

Attribute	Unit	Site		
		Guarapuava	Londrina	Rondon
Elevation	m	1043	566	250
Temperature[1]	°C	17.2	21.1	20.1
Precipitation[2]	mm $year^{-1}$	1938	1641	1656
Sampling depth[3]	cm	0 – 60	0 – 100	0 – 60
Clay[4]	g kg^{-1}	715	750	719
Silt[4]	g kg^{-1}	211	117	148
Sand[4]	g kg^{-1}	74	133	133
pH[4]	-log[H^+]	4.55	4.97	4.95
CEC[4]	$cmol_c$ kg^{-1}	12.62	11.35	11.55
Fe_{Dit}[5]	g kg^{-1}	174	319	239

[1]Average annual temperature. [2]Average total annual precipitation. [3]Sampling depths: Guarapuava and Rondon (0-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-25 cm, 25-30 cm, 30-35 cm, 35-40 cm, 40-50 cm, 50-60 cm); Londrina (0-10 cm, 10-20 cm, 20-30 cm, 30-40 cm, 40-50 cm, 50-60 cm, 60-70 cm, 70-80 cm, 80-90 cm, 90-100 cm). [4]Average values considering all depths. [5]Dithionite-extractable iron; performed at the 40-60 cm layer.

4.4.2 Stability of aggregates in water

Soil aggregates (< 19 mm), previously air-dried, were wet by capillarity for 10 min and sieved underwater for 15 min with 45 vertical cycles per minute. For each sample, 50 g of aggregates were analyzed in triplicate (CASTRO FILHO; MUZILLI; PODANOSCHI, 1998). Sieves with openings of 8, 4, 2, 1, 0.5, and 0.25 mm were used and the aggregate stability index (ASI) was calculated according to the formula:

$$ASI\ (g\ kg^{-1}) = \frac{1000 \times Mass_{>0.25\ mm}}{Mass_{Sample}}, \quad (1)$$

Where ASI is the aggregate stability index, $Mass_{>0.25\ mm}$ is the mass of water-stable aggregates retained in the sieves with openings of 0.25 mm or larger, in dry-basis (105 °C), and $Mass_{Sample}$ is the total mass of the sample in dry basis (105 °C).

The mass of the sand fraction was not discounted from the > 0.25 mm aggregates because, in these soils, the sand is part of the water-stable aggregates (CASTRO FILHO; MUZILLI; PODANOSCHI, 1998). Larger vegetal and faunal residues were manually removed prior to analysis.

4.4.3 Mechanically water-dispersible clay and re-flocculation capacity

The mechanically water-dispersible clay was obtained after shaking 20 g of sieved soil (< 2 mm) with 100 cm^3 of distilled water at 200 rotations per minute (RPM) for 16 h. After shaking, the suspension was transferred to 1000 cm^3 sedimentation cylinders and then the volume was filled with distilled water for settling (soil:water ratio of 1:50 m:v). The quantification of particles in suspension was performed by gravimetry in an aliquot containing particles ≤ 0.002 mm. The particles' settling velocity in the sedimentation cylinder was calculated according to Stoke's law.

As a highly disruptive method was used, most of the clay was released from the aggregates. Thus, the capacity of the clay to re-flocculate and settle could be assessed by the re-flocculation capacity (RC) calculated as:

$$RC\ (g\ kg^{-1}) = \frac{1000\times(\text{Total clay}-\text{Dispersed clay})}{Total\ clay}. \quad (2)$$

4.4.4 Particle-size distribution, zeta potential and point of zero charge

Particle-size distribution was determined in the same way as for the mechanically water-dispersible clay. However, instead of shaking with 100 cm^3 of distilled water, 100 cm^3 of NaOH (0.1 mol l^{-1}) solution was used. Total clay and total silt were extracted based on the respective settling velocities and quantified by gravimetry. Total sand was calculated by difference.

Zeta potential was analyzed in the suspensions containing the water-dispersible clay (extracted with distilled water) and in the suspensions containing the total clay (extracted with NaOH). The quantification was performed by electroacoustic spectroscopy in a Zeta-APS from Matec™. In the total clay suspensions, zeta

potential was obtained at different pH values, after successive addition of HCl (3 mol l^{-1}) by an automatic burette coupled to the equipment. The addition of HCl was performed at least until the zeta potential value changed from negative to positive. The value of the pH at zeta potential = 0 mV (point of zero charge - PZC) was estimated by polynomial regression models and all the adjustments presented at least a R^2 = 0.97.

4.4.5 Total organic carbon content (TOC)

Total organic carbon was obtained after organic matter oxidation in 0.5 g of soil with $K_2Cr_2O_7$ in a sulfuric medium. After oxidation, the remaining Cr^{6+} was quantified by titration with Fe_2SO_4. Diphenylamine was used as the indicator.

4.4.6 pH and exchangeable cations

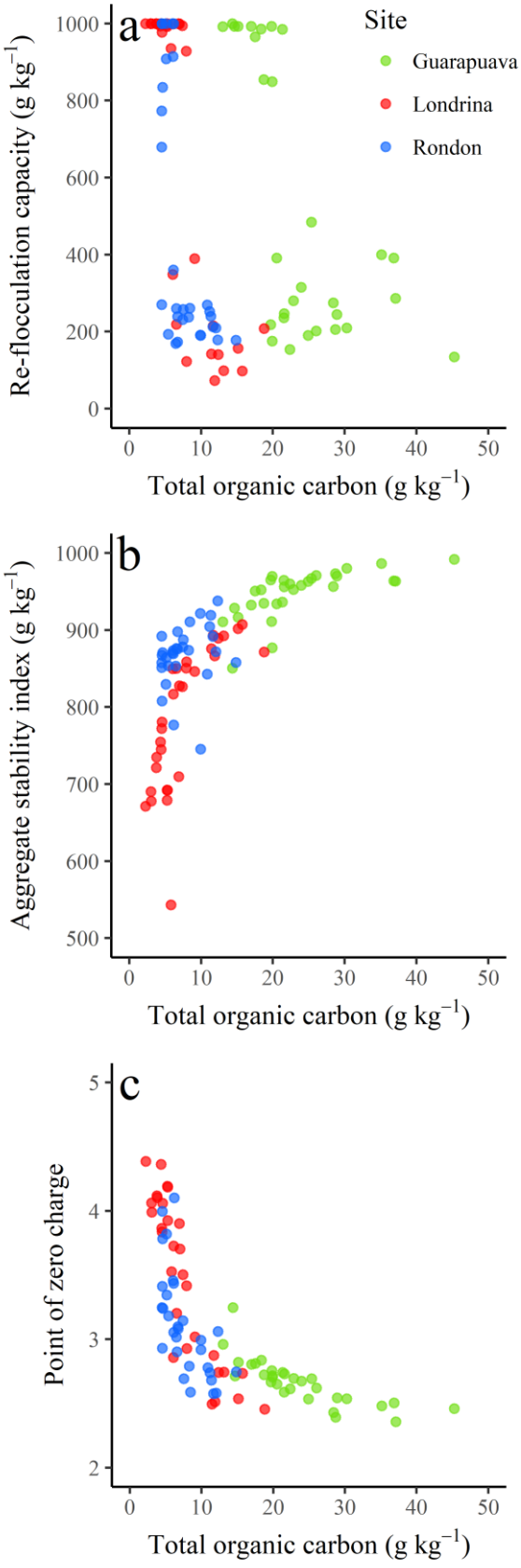
The pH was measured in $CaCl_2$ (0.01 mol l^{-1}) solution in a soil:solution ratio of 1:2.5 (*m:v*). Exchangeable Al^{3+}, Ca^{2+}, and Mg^{2+} were quantified by titration with NaOH (Al^{3+}) and by atomic absorption spectroscopy (Ca^{2+} and Mg^{2+}) after extraction with KCl (1 mol l^{-1}). Exchangeable K^+ and Na^+ were quantified by flame photometry after extraction with Mehlich-1 solution (HCl, 0.05 mol l^{-1} and H_2SO_4, 0.0125 mol l^{-1}). The potential acidity (H + Al^{3+}) was estimated by potentiometry after soil equilibrium with Shoemaker–McLean–Pratt (SMP) buffering solution. The cations exchange capacity was calculated by the sum of H + Al^{3+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+. The base saturation was calculated by the ratio between the basic cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) and the cation exchange capacity (values were expressed as percentages).

4.5 RESULTS

The sampling scheme allowed a high amplitude of all studied variables (Figure 4.1). The re-flocculation capacity of all soils was reduced by organic matter increment (Figure 4.1a). However, some Guarapuava samples re-flocculated

with high values of TOC, when compared to Londrina and Rondon soils. This resulted in high values of ASI co-existing with high values of re-flocculation capacity (Figure 4.1a and Figure 4.1b).

Figure 4.1. Re-flocculation capacity (a), aggregate stability index (b), and point of zero charge (c) as a function of total organic carbon.

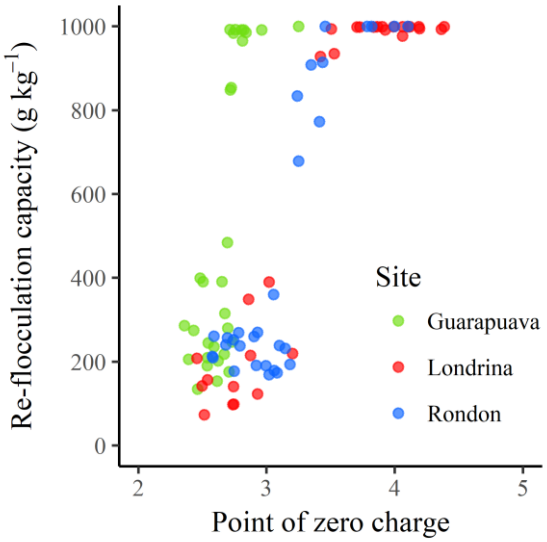


In all samples, water-stable macroaggregates prevailed over microaggregates (ASI > 500 g kg^{-1}, Figure 4.1b). In the samples with low organic matter content, this was probably caused by the high clay content associated with the high weathering stage of these soils (MELO *et al.*, 2018), allowing the formation of inorganic bonds. The highest values of ASI in each soil were found in the top layers, where the re-flocculation capacity approached 0 g kg^{-1} (Table S4.1).

The point of zero charge was reduced by increment in organic matter (Figure 4.1c). These soils present a considerable amount of iron oxides (Table 4.1) and kaolinite (Figure S4.1), which contain high PZC and results in the presence of positive charges at acidic pH. When these clay minerals are bonded to organic matter, the proportion of positive charges is reduced, thereby lowering the PZC values.

RC values tended to be either very high (close to 1000 g kg^{-1}) or very low (close to 0 g kg^{-1}), unlike ASI, and PZC which were well distributed within the range of the observed values (Figure 4.1). This behavior shows that the dispersion/flocculation of the suspended clay fraction is highly responsive to changes in the charge balance around the PZC. The association between PZC and RC also reveals the same pattern (Figure 4.2), and additionally, indicates that re-flocculation occurred mainly by electrostatic forces. These results corroborate those of NGUYEN *et al.* (2009), who also found a steep change in clay dispersion when associating surface charge to the transmission of clay suspensions.

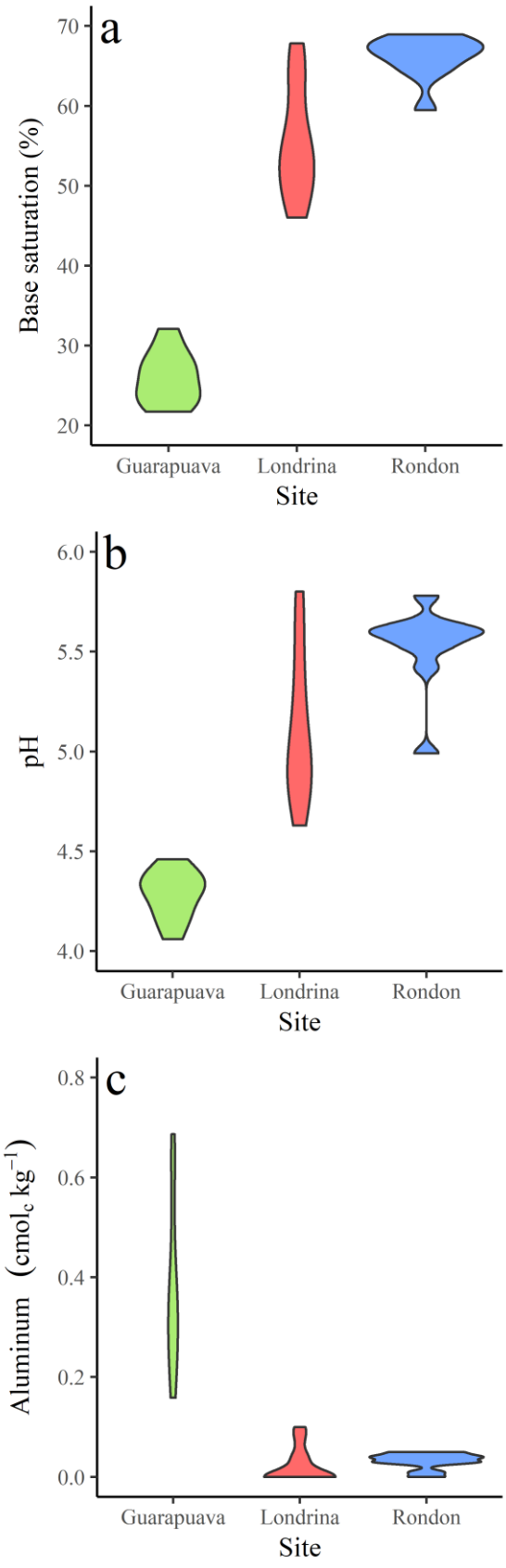
Figure 4.2. Re-flocculation capacity as a function of the point of zero charge.



ASI could be explained by TOC regardless the studied soil (Figure 4.1b), while the association between TOC and FC was dependent on the soil (Figure 4.1a). Guarapuava soil presented the capacity to re-flocculate under higher values of TOC and lower values of PZC (Figure 4.1a, Figure 4.1c and Figure 4.2). This suggests that Guarapuava soil presents some distinction that influences RC more than ASI and allows the re-flocculation of the clay under conditions of higher charge imbalance on the surface of the particles.

To explain this, it is important to highlight that PZC measurements were performed in the total clay fraction after dispersion with NaOH solution. Because of this, the differences observed in PZC occurred mainly because of particle properties such as mineralogy and formation of organo-mineral associations. The effect of exchangeable cations has a minimal influence on these PZC results, because they are replaced by Na^{+} during clay extraction. In Figure 4.3 we show the base saturation, pH, and Al^{3+} of samples with re-flocculation capacity ≥ 500 g kg^{-1}, which suggests that these attributes were responsible for favoring re-flocculation of organic matter-saturated clay in the Guarapuava soil.

Figure 4.3. Base saturation (a), pH (b), and Al^{3+} (c) of samples with re-flocculation capacity ≥ 500 g kg^{-1}. The shape of the box plots shows distribution of the data.



The lower base saturation and pH values of Guarapuava soil implies a higher Al^{3+} saturation. In acidic conditions, Al^{3+} prevails over other Al-hydroxide species. Al^{3+} has a higher capacity to neutralize the electric field of particles than basic cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) and, because of this, a higher re-flocculation capacity is expected in this soil. This suggests that the chemical conditions of Guarapuava soil induces the re-flocculation of the clay fraction, despite the higher organic matter content and higher charges imbalance (Figure 4.1c and Figure 4.2).

For Londrina and Rondon soils, clay re-flocculation is caused mainly by the high PZC, which in turn is caused by the low organic matter content (Figure 4.1a and Figure 4.2). For Londrina and Rondon samples with a re-flocculation capacity ≥ 500 g kg^{-1}, the charge imbalance is so low that Al^{3+} is not required to re-flocculate the clay. The dispersion and flocculation behavior of clay can be explained by the net dispersive charge (RENGASAMY, 2018); particles with negative surface potential attract cations to the surface, which neutralize the electric field generated and reduces the surface area for hydration (RENGASAMY; TAVAKKOLI; MCDONALD, 2016). When the neutralization of the electric field is strong enough, which is commonly achieved by the adsorption of polyvalent cations, particles tend to flocculate.

4.6 DISCUSSION

We studied profiles of soils weathered from comparable parent materials, but different climatic and agricultural management conditions to obtain a natural gradient of TOC, RC, ASI, and PZC. These basalt-weathered Ferralsols were chosen because they re-flocculate naturally (without the addition of flocculants) after aggregates breakdown, and because they do not present significant textural change along the soil profile (Table S4.1). This would allow the understanding of the concomitant effect of organic matter over clay re-flocculation and the stability of macroaggregates. We studied only Ferralsols because other soil classes are unlikely to present clay re-flocculation, once this phenomenon is commonly found in soils with a relatively high presence of positively-charged minerals.

The analysis of mechanically water-dispersible clay reveals the potential of dispersion when the soil is subjected to disrupting forces (RENGASAMY, 2002). The forces experienced in field conditions are not expected to be as strong as

the these used in our study (16 h at 200 RPM). However, to evaluate the re-flocculation capacity of the clay fraction, the clay needs to be previously suspended. Because of this, the procedure used here can be considered adequate for the purposes of the present study, as most of the clay is released by the intense mechanical shaking.

Despite organic matter being the major source of charges imbalance in these soils, its dispersive effect is not expressed until aggregates are broken. These aggregates do not present spontaneous clay dispersion, as observed by the Emerson's test (Figure S4.2). However, the amount of dispersed clay in the surface layer (rich in organic matter) was very high after mechanical shaking (Table 4.2). This implies that the organic bonds between particles need to be broken so that the imbalance of charges is intensified, and clay dispersion is increased.

To reconfirm this premise, we also measured the water-dispersible clay released after aggregates stability analysis (WDC_{agr}) (low disruption forces) in the samples from the surface layer and compared this with the content of mechanically water-dispersible clay (Table 4.2). The increment in clay dispersion when aggregates are mechanically disrupted supports the idea that the dispersive effect of organic matter is not expressed until the clay-clay organic bonds are broken. This agrees with the observation of LIPIEC *et al.* (2018) that machinery traffic induced clay dispersion on the surface layer of a Luvisol, after the breakdown of aggregates.

Table 4.2. Dispersed clay in the top layer obtained after aggregates stability in water analysis (WDC_{agr}) and after mechanical dispersion (MWDC).

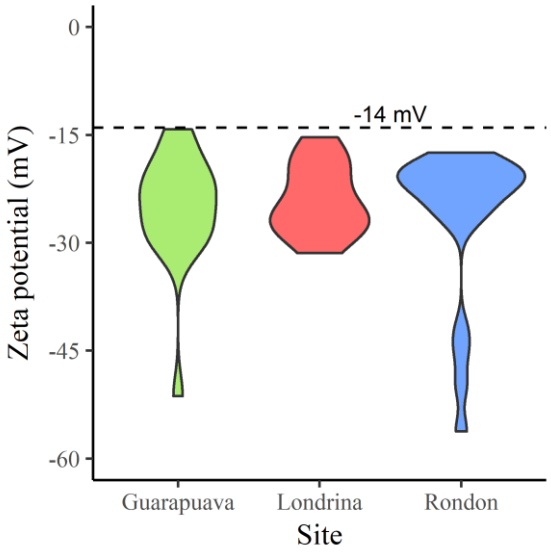
Site	WDC_{agr}	MWDC
	g kg^{-1}(clay basis)	
Guarapuava	0 b	730 a
Londrina	13 b	846 a
Rondon	5 b	780 a

Lowercase letters compare the attributes within each soil by *t*-test at 5 % probability. MWDC: mechanically water-dispersible clay. Sample depth: Guarapuava (0 – 5 cm); Londrina (0 – 10 cm); Rondon (0 – 5 cm).

The increment in clay dispersion caused by the addition of low-weight organic molecules is reported in the literature (AMÉZKETA, 1999; NGUYEN *et al.*, 2013); however, humified organic matter can increase the resistance of aggregates against disrupting agents. This is implied by the need for organic matter oxidation before particle size analysis in soils with more than 5 % of organic matter in many protocols of soil analysis. Our results, however, show that even naturally stabilized soil organic matter can inhibit clay re-flocculation if the clay-clay organic bonds are broken.

We also measured the zeta potential of the mechanically water-dispersible clay to check the threshold zeta potential value above which re-flocculation prevails over dispersion. The measurement in samples with high re-flocculation capacity was not possible, because clay could not be separated from the silt particles without chemical pre-treatment, which would have affected the zeta potential of the clay. The results for all soils were very consistent (Figure 4.4) and show that when zeta potential is higher than -14 mV, clay tends to re-flocculate. Differences between the soils were not expected, because zeta potential was measured in the clay that remained dispersed in suspension after 4 h of settling.

Figure 4.4. Zeta potential in the mechanically water-dispersible clay. The shape of the box plots shows the distribution of the data.



It might be relevant to highlight that despite the coexistence of high clay re-flocculation capacity and macroaggregates stabilization in Guarapuava soil,

the former prevailed over dispersion only on sub-surface samples, from a depth of 30 cm (Table S4.1). In this sense, the protection of the soil surface against disrupting agents should not be neglected even in soils with high re-flocculation capacity. Once aggregates were broken, no re-flocculation in the topsoil could be observed even in an acidic Ferralsol (Guarapuava), and the potential for particle transport and surface crusting can be high.

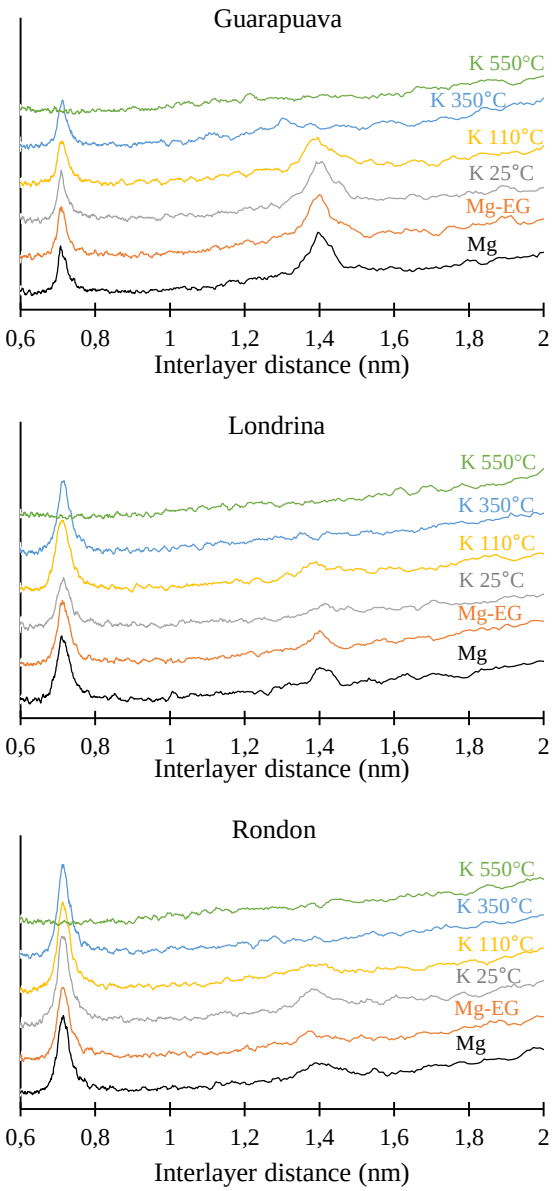
4.7 Conclusion

Macroaggregates can be stabilized by both inorganic and organic bonds. Macroaggregates stabilized mainly by inorganic bonds can show high clay re-flocculation capacity after breakdown, if the charges in clay minerals are balanced - a trait commonly associated with a high level of weathering. Organic bonds increase the proportion of water-stable macroaggregates, but, after breakdown, the released clay show high charges imbalance, thereby inhibiting its re-flocculation. However, re-flocculation can still prevail over dispersion in clay saturated with organic matter when the pH and base saturation are low, and Al^{3+} is high.

4.8 SUPPLEMENTARY MATERIAL

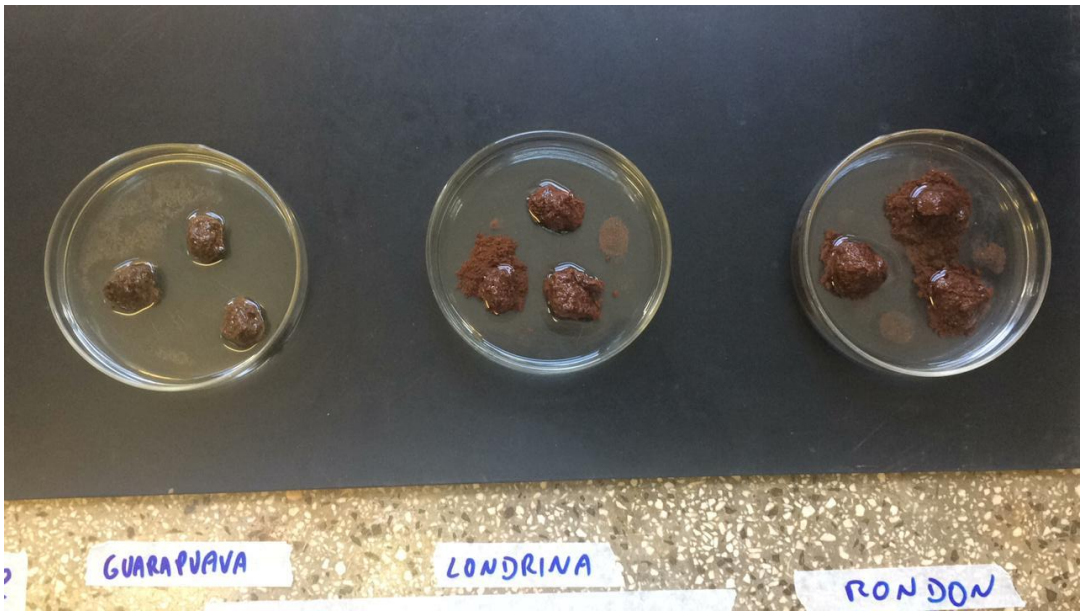
4.8.1 Supplementary Figures

Figure S4.1. X-ray diffractometry of phyllosilicates in the clay fraction in the studied soils (40 – 60 cm depth).



The clay fraction was extracted with NaOH, flocculated with $MgCl_2$, the organic matter was oxidized with H_2O_2' and metallic sesquioxides were removed by Dithionite-Citrate-Bicarbonate-Na. After these procedures, a portion of the clay was saturated with KCl and was subjected to different temperatures. The Mg-saturated clay was saturated with ethylene glycol.

Figure S4.2. Emerson's test on aggregates from the top layer.



Picture taken 24 hours after the addition of water. Samples depth: Guarapuava (0 – 5 cm); Londrina (0 – 10 cm); Rondon (0 – 5 cm).

4.8.2 Supplementary Tables

Table S4.1. Selected soil attributes in different depths.

Depth (cm)	Total clay (g kg^{-1})			Total organic carbon (g kg^{-1})			Re-flocculation capacity (g kg^{-1})		
	Guarapuava	Londrina	Rondon	Guarapuava	Londrina	Rondon	Guarapuava	Londrina	Rondon
0-5	643	697	685	39.7	16.6	12.5	270	150	220
5-10	670		694	28.7		10.6	250		240
10-15	704	734	687	26.5	12.1	10.1	340	150	230
15-20	706		706	26.4		7.3	220		240
20-25	702	746	706	23.9	10.6	7.9	230	400	210
25-30	729		720	20.8		6.8	480		250
30-35	748	742	727	19.6	7	5.2	740	490	540
35-40	749		748	18.6		5.8	790		720
40-50	749	750	763	19.1	7.3	5.1	950	540	940
50-60	745	760	754	15.8	6.2	5.4	950	950	970
60-70	----------	779	----------	----------	4.7	----------	----------	1000	----------
70-80	----------	750	----------	----------	4.5	----------	----------	1000	----------
80-90	----------	774	----------	----------	5.1	----------	----------	990	----------
90-100	----------	768	----------	----------	3.5	----------	----------	1000	----------

5 ARTIGO C: A NEW APPROACH ON THE STRUCTURAL STABILITY OF SOILS: METHOD PROPOSAL

5.1 ABSTRACT

Water-dispersible clay analysis is used to evaluate soil structural stability, and two clay classes are quantified from it: the water-dispersible clay and the aggregated clay. We suggest here that three clay classes exist in soils with respect to structural behavior, and we propose a method for their quantification. Here, the aggregated clay is divided in two new classes, non-dispersible clay and water-re-flocculable clay. The method is based on a ten-fold dilution of the suspension obtained from water-dispersible clay analysis and successfully allowed the quantification of the proposed clay classes. The proposed method is inexpensive and does not require extra soil or chemical dispersants. Based on the distribution of these classes in different soils, seven groups of clay structural stability were defined. The method provides insights regarding soil structure-related processes, such as soil surface crusting, soil pore clogging, hydric erosion, and particles transport.

Key words: Soil structural stability. Aggregation. Clay dispersion.

UMA NOVA ABORDAGEM ACERCA DA ESTABILIDADE ESTRUTURAL DE SOLOS: PROPÓSTA DE MÉTODO

5.2 RESUMO

A análise de argila dispersável em água é utilizada para avaliar a estabilidade estrutural do solo e duas classes são por ela quantificadas: a argila dispersável em água e a argila agregada. Nós sugerimos nesse estudo que três classes de argila existem em solos com relação ao comportamento estrutural e propusemos um método para sua quantificação. Aqui, a argila agregada é dividida em duas novas classes, a argila não dispersável e a argila refloculável em água. O método é baseado em uma diluição de dez vezes da suspensão obtida da análise de argila dispersável em água e permitiu com sucesso a quantificação das classes de argila propostas. O método apresenta baixo custo, não requer solo extra e não requer dispersantes químicos. Baseado na distribuição dessas classes em diferentes solos, setes grupos de estabilidade estrutural de argila foram definidas. O método pode

fornecer novas ideias sobre processos relacionados à estabilidade estrutural dos solos, como o selamento superficial, entupimento de poros, erosão hídrica e transporte de partículas.

Palavras-chave: Estabilidade estrutural do solo. Agregação. Dispersão de argila.

5.3 INTRODUCTION

Soil structure is essential for its adequate functioning and can be defined as the result of the union of primary particles in aggregates and the porous space formed between them (MARSHALL; HOLMES; ROSE, 1996). Aggregate stability is an indicator of soil structural persistence against disrupting agents, such as raindrops or mechanical plowing, under field conditions. The water-dispersible clay (WDC) analysis evaluates how soil clay responds to mechanical forces and hydration; therefore, it is an evaluation of microaggregate stability (IGWE; OBALUM, 2013).

When released from aggregates, the clay fraction induces the formation of crusts on the soil surface (ROSA *et al.*, 2013), reducing its macroporosity, pore connectivity (SPERA *et al.*, 2008; MARCHUK *et al.*, 2012), and hydraulic conductivity (ARIENZO *et al.*, 2012), and increasing the susceptibility of soils to water erosion (IGWE; OBALUM, 2013). These changes reduce soil quality, favor the transport of particles to water bodies (WANG; KELLER, 2009), and harm the development of crops and the adequate functioning of soils.

From WDC analysis, two classes of clay are obtained: WDC, that is released from aggregates and remains dispersed after a period and the aggregated clay (AC), the difference between total clay and WDC. AC has been used as an indicator of structural stability (IGWE; OBALUM, 2013; NGUETNKAM; DULTZ, 2014; TAVARES FILHO *et al.*, 2014; BASGA *et al.*, 2018). We suggest here, however, that AC cannot accurately quantify the stability of soil microstructure, as it is composed of two distinct clay classes, that are defined in the present study. The term aggregated clay can vary among studies and the term used in this study was taken from Igwe and Obalum (2013).

The proposed classes are the non-dispersible clay (NDC), that is not released from soil aggregates and the water-re-flocculable clay (WRC), that is released from soil aggregates but because of the particles (e.g. high point of zero

charge) or medium (e.g. high electrolyte concentration) conditions, tends to flocculate. To quantify these classes can be advantageous, as the WRC is supposed to have higher transport susceptibility than the NDC, due to the temporary suspension of the clay in the former. Therefore, the WRC is not indicative of resistance against mechanical forces but is indicative of charge balances on the particle surfaces, commonly present in Ferralsols. However, the lack of available methods to quantify these classes limits the understanding of the related processes.

Quantification of NDC and WRC separately can be possible based on the differences between the forces that cause aggregation of these classes. The aggregates formed by clay flocculation are unstable during the period of analysis, as they are kept mainly by electrostatic forces and are destabilized with changes in the physical and chemical conditions of the medium (VALMACCO *et al.*, 2016). In this sense, it can be possible to destabilize the aggregates formed by flocculation and quantify the WRC without inducing the dispersion of the clay from the stable aggregates (NDC). The reduction of clay concentration (i.e. dilution of the suspension) reduces the number of collisions by Brownian motion and help to maintain the suspensions dispersed (BURD, 2013) and, additionally, the use of dispersants in low concentration can help to keep the suspension containing WRC dispersed during the period of analysis.

Our hypothesis is that, regarding structural behavior, three classes of clay can exist in soils (WDC, WRC and NDC) instead of the two currently quantified classes (WDC and AC). Therefore, we aimed to test if the quantification of the proposed clay classes in soils is possible by performing dilutions and adding dispersants to the suspensions obtained from water-dispersible clay analysis.

5.4 MATERIAL AND METHODS

5.4.1 Studied Soils

Eight soils were sampled under different edaphoclimatic conditions in the State of Paraná, Brazil (Figure 5.1). These soils were classified as: Londrina (Ferralsol), M. C. Rondon (Ferralsol), Guarapuava (Ferralsol), Umuarama (Acrisol), Cerro Azul (Cambisol), Ponta Grossa 1 (Cambisol), Ponta Grossa 2 (Histosol), and

Morretes (Ferralsol) (IUSS WORKING GROUP WRB, 2015). In each area, three points were used to form a composite sample in each of the studied layers (0–20, 20–40, and 40–60 cm). The description of soil attributes within the 24 samples is presented in Table 5.1. The diffractograms of samples from the 40–60 cm layer are presented in Figure S5.1. Additionally, supplementary information about the sampling sites are presented in Table S5.1.

Figure 5.1. Soil sampling sites in Paraná State, Brazil.

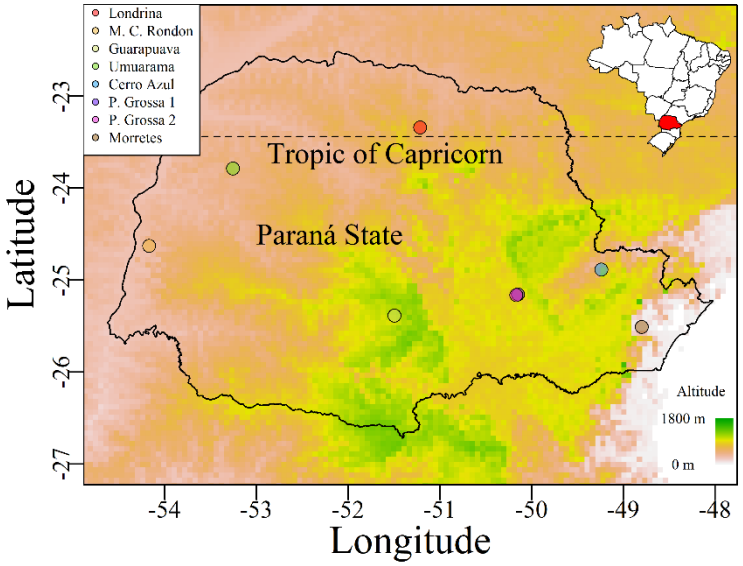


Table 5.1. Descriptive statistics of the studied samples.

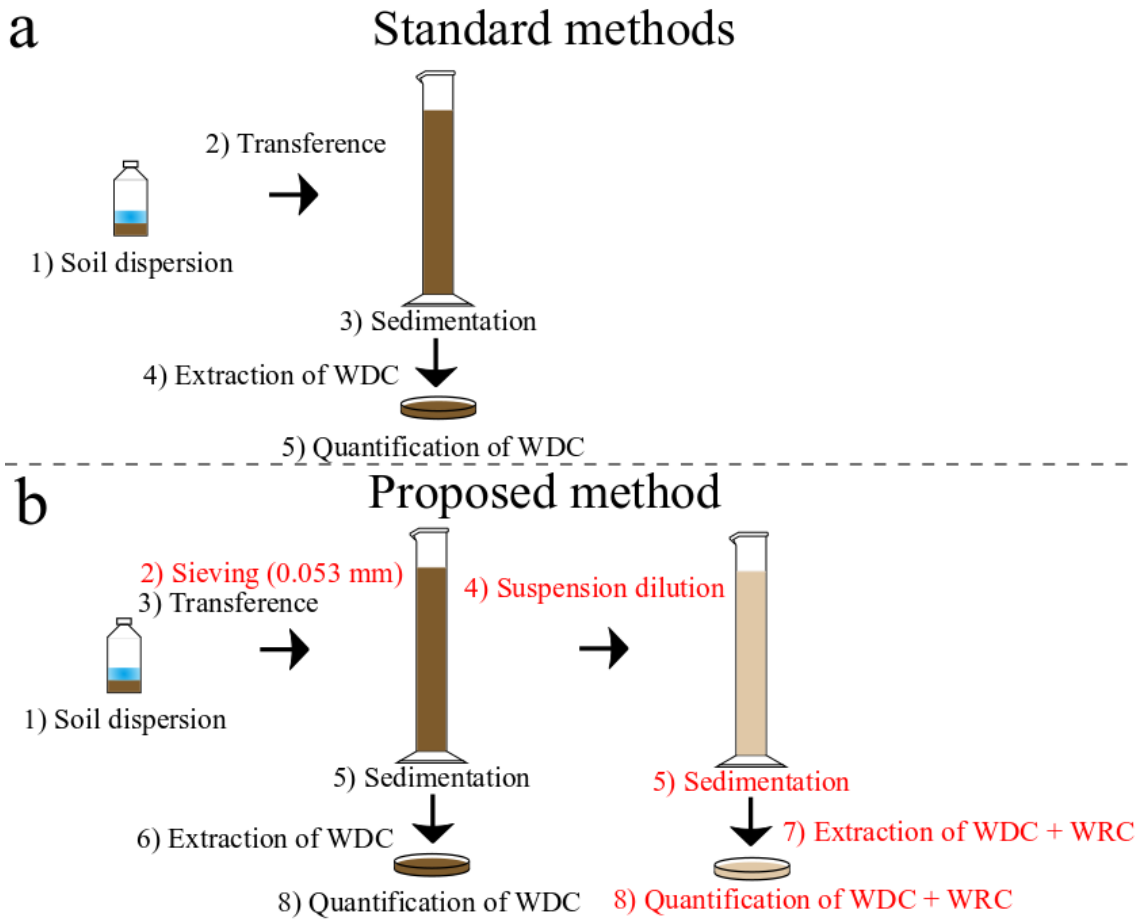
Attribute	Unit	Minimum	Mean	Maximum	St. Dev.
WDC	% (*m:m*)	0.96	56.68	87.58	25.73
Sand	% (*m:m*)	4.46	22.65	83.52	24.83
Silt	% (*m:m*)	4.17	21.67	39.12	8.76
Clay	% (*m:m*)	11.03	55.68	75.08	19.14
Fe_2O_3	% (m:m)	0.92	14.11	31.93	10.22
OM	% (*m:m*)	0.88	3.88	9.38	2.71
pH_{CaCl2}	-log(mol L^{-1})	3.91	4.57	5.67	0.60
ΔpH	---------	-2.00	-1.10	-0.70	0.29
P	mg kg^{-1}	0.46	9.61	53.8	13.87
CEC	$cmol_c$ kg^{-1}	4.51	12.58	21.82	5.03
Al^{3+}	$cmol_c$ kg^{-1}	0.00	1.49	6.26	1.78
Ca^{2+}	$cmol_c$ kg^{-1}	0.16	2.70	12.79	2.71
Mg^{2+}	$cmol_c$ kg^{-1}	0.03	1.01	3.21	0.77
K^+	$cmol_c$ kg^{-1}	0.04	0.23	1.02	0.25
Na^+	$cmol_c$ kg^{-1}	0.00	0.003	0.07	0.01
H^+	$cmol_c$ kg^{-1}	2.73	7.16	12.85	3.33

WDC: water-dispersible clay after 16 h shaking at 200 RPM. Sand: total sand. Silt: total silt. Clay: total clay. Fe_2O_3: Extracted with DCB (only 40 – 60 cm layer evaluated). OM: organic matter. pH_{CaCl2}: 1:2,5 (*m:v*) soil:solution ($CaCl_2$ 0.01 mol l^{-1}). ΔpH = pH_{KCl} – pH_{H2O}. P: phosphorous (Mehlich-1). CEC: cation exchange capacity. Al^{3+}: exchangeable Al. Ca^{2+}: exchangeable Ca. Mg^{2+}: exchangeable Mg. K^+: exchangeable K. H^+: exchangeable H.

5.4.2 Proposed method

The standard water-dispersible clay analysis in soils involves, in general, the following steps (Figure 5.2): 1) soil dispersion (which can either be spontaneous, caused just by hydration, or mechanical (RENGASAMY, 2002)); 2) transference to the sedimentation container (commonly not present when spontaneous dispersion is evaluated); 3) particles sedimentation (prior homogenization of the suspension is required); 4) extraction of an aliquot containing the dispersible clay and 5) quantification of WDC in the extracted aliquot.

Figure 5.2. Procedures involved in standard water-dispersible clay analysis (**a**) and in the proposed method (**b**). The additional procedures are shown in red.



The proposed method involves some additional steps, shown in red in Figure 5.2b: 2) sieving of the sample (through a 0.053 mm sieve); 4) diluting the original suspension (prior homogenization of the suspension is required); 5) sedimentation of the particles (prior homogenization of the suspension is required); 7) extraction of the aliquot containing the WDC and the WRC and 8) quantification of the particles in the extracted aliquot. The final protocol for quantification of the clay classes is presented in detail in section 5.1.

5.4.3 Studied Treatments

Different treatments were tested according to their capacity to separate the classes of clay (Table 5.2). The negative control (Untreated – Untr.) is the suspension directly obtained from mechanical WDC analysis (after step 3 in

Figure 5.2b). All other treatments are derived from this suspension. These treatments involve dilution of this suspension and in some cases, addition of chemical dispersants.

Table 5.2. Treatments tested in the study.

Treatment	Dilution[a]	Dispersant (%)[b]
Untr.	No	No
D00	Based on clay content (Table 5.3)	No
D01	Based on clay content (Table 5.3)	1
D02	Based on clay content (Table 5.3)	2
D04	Based on clay content (Table 5.3)	4
D10	Based on clay content (Table 5.3)	10
D100	Based on clay content (Table 5.3)	100
10×D00	Ten-fold	No

[a]Dilution performed in the suspension obtained from mechanical WDC analysis using 20 g of soil and 1 l of distilled water for sedimentation (1:50 *m:v* soil:water ratio) (after step 4 in Figure 5.2b). [b]Dispersant concentration in relation to the concentration used for particle-size analysis, according to Teixeira et. al (2017). The dispersant was added after the dilution of the suspensions.

Table 5.3. Dilution of the suspension obtained from mechanical water-dispersible clay analysis as a function of the total clay content of the sample.

Total clay	Initial concentration of clay in suspension[a]	Dilution	Final concentration of clay in suspension
% (*m:m*)	% (*m:v*)	$V_{final}/V_{initial}$	% (*m:v*)
0 – 10	0.0 – 0.2	1 (no dilution)	0.0 – 0.2
10 – 20	0.0 – 0.4	2	0.0 – 0.2
20 – 30	0.0 – 0.6	3	0.0 – 0.2
30 – 40	0.0 – 0.8	4	0.0 – 0.2
40 – 50	0.0 – 1.0	5	0.0 – 0.2
50 – 60	0.0 – 1.2	6	0.0 – 0.2
60 – 70	0.0 – 1.4	7	0.0 – 0.2
70 – 80	0.0 – 1.6	8	0.0 – 0.2
80 – 90	0.0 – 1.8	9	0.0 – 0.2
90 – 100	0.0 – 2.0	10	0.0 – 0.2

[a]Clay concentration in suspension, considering the use of 20 g of soil and 1 l of distilled water for sedimentation. The lower limit is based on a hypothetical soil with no dispersion and the upper limit is based on a hypothetical soil with total dispersion. V_{final}: volume of the suspension after dilution. $V_{initial}$: volume of the suspension before dilution.

For most treatments, the dilution of the suspensions was based on the total clay content of the sample (Table 5.3). For example, the suspension from a soil with 75% of total clay was diluted eight-fold, while a suspension from a soil with 15% of total clay was diluted two-fold. This was performed to reduce the variation in particle concentration after dilution (last column in Table 5.3). In addition, a treatment with a ten-fold dilution, regardless of the total clay content of the sample, was tested without the addition of dispersants (10×D00 treatment) (Table 5.2).

The positive control (D100) was diluted according to the total clay content of the sample and 100 % of dispersant concentration used for particle-size analysis was used (Table 5.2). Additionally, different concentrations of dispersants were tested. 1%, 2%, 4%, and 10% of dispersant concentration used for particle-size analysis (Table 5.2). The dispersant solution was added only after dilution of the suspensions (after step 4 in Figure 5.2b).

5.4.3.1 Chemical dispersant

We used a mixture of sodium hexametaphosphate – $(NaPO_3)_6$ and sodium hydroxide – NaOH to inhibit clay flocculation, as some soils cannot be efficiently dispersed using only NaOH (TEIXEIRA *et al.*, 2017). We chose the concentration proposed by TEIXEIRA *et al.* (2017) for particle-size analysis, as a positive control, once its finality is the complete dispersion of soil primary particles. The concentration of this solution is $(NaPO_3)_6$ – 0.038 mol l^{-1} and NaOH – 0.1 mol l^{-1} and 25 mL are used to disperse 20 g of soil. We opted to use 10 mL of the solution (instead of 25 mL) and, to keep the original proportions, we prepared it 2.5 times more concentrated ($(NaPO_3)_6$ – 0.095 mol l^{-1} and NaOH – 0.25 mol l^{-1}).

5.4.4 Laboratorial procedures

5.4.4.1 Mechanical water-dispersible clay

The samples were air-dried and sieved (2 mm) prior to all analyses. For mechanical water-dispersible clay analysis, 20 g of soil were dispersed in 100 mL of distilled water by shaking at 200 rpm in an orbital horizontal direction for 16 hours.

The shaking containers had 500 mL capacity and a circular bottom with 6.5 cm diameter. The dispersed samples were transferred to sedimentation containers with 1 l capacity, that were filled with distilled water. The soil:water ratio during sedimentation was 1:50 *m:v* (20 g l^{-1}).

5.4.4.2 Total clay

Total clay was quantified the same way as mechanical WDC but using 100 mL of NaOH 0.1 mol l^{-1} during the shaking. For soils with more than 5 % of organic matter, oxidation with H_2O_2 was performed. The oxidized soil samples were used only for total clay analysis.

5.4.4.3 Spontaneously water-dispersible clay

For spontaneously water-dispersible clay analysis, the protocol presented in RENGASAMY (2002) was applied. However, different amounts of soil (0.2 or 2 g) were dispersed in 100 mL of distilled water. We used different amounts of soil to achieve the same soil:water ratio as the Untr. (1:50 *m:v*) and 10×D00 (1:500 *m:v*) treatments.

5.4.4.4 Quantification of particles in suspension

The quantification of particles in suspension was performed either by gravimetry or spectrophotometry at 420 nm, previously calibrated with each of the 24 samples. The calibration was based on gravimetric measurements of suspended particles and yielded R^2 > 0.97. The models obtained during calibration are presented in Table S5.2. The sedimentation time to extract the clay fraction (Ø < 0.002 mm) was based on Stoke's law. Specifically, the clay fraction was obtained after 4 hours of sedimentation at 5 cm depth.

5.5 RESULTS

5.5.1 Protocol for the quantification of the clay classes

The proposed protocol for the quantification of the clay classes is presented in this section. This protocol, which is equivalent to 10×D00 treatment, was chosen as the best method among all the tested treatments. The results obtained by applying this protocol in different samples, its validation, and comparison with the other treatments are presented in the following sections.

As mentioned in section 2.2, the proposed protocol consists of some additional steps in the WDC protocol (Figure 5.2). The protocol presented below includes the WDC protocol described in section 5.4.1. The WDC protocol outlined can be altered as per requirements. However, the magnitude of the three clay classes will change, as discussed in section 5.6.2.

1) Using containers of 500 mL capacity with circular bottom having a diameter of 6.5 cm, weight 20 g of air-dry soil (sieved at 2 mm) and add 100 mL of distilled water. Shake at 200 rpm in an orbital horizontal direction for 16 hours. Another sample needs to be dried at 105 °C to determine the water content in the air-dry sample.

2) After mechanical dispersion of the soil, remove the particles > 0.053 mm by wet-sieving. Particles ≤ 0.053 mm must be completely washed from the sample. Particles > 0.053 mm are not used.

3) Transfer the sieved suspension (containing particles ≤ 0.053 mm) to a sedimentation container (1 L capacity) and fill the volume with distilled water. This suspension will be used to quantify the WDC content (WDC suspension).

4) Homogenize the WDC suspension and rapidly extract an aliquot (10 to 100 mL). This aliquot will be diluted to inhibit clay flocculation. Aliquot extraction needs to be quick so that the original particle size distribution of the WDC suspension can be preserved.

5) Transfer this aliquot to another sedimentation container and dilute it ten-fold (i.e. 100 mL of suspension to 900 mL of water). This suspension will be used to quantify the water-dispersible clay plus the water-re-flocculable clay content (WDC + WRC suspension).

6) Homogenize both suspensions (WDC and WDC + WRC) and leave for sedimentation.

7) After 4 hours, extract an aliquot (10 mL) at 5 cm depth from each suspension. These aliquots contain particles of diameter ≤ 0.002 mm (clay fraction), according to Stokes' law.

8) Quantify the clay concentration in the extracted aliquots through available methods (gravimetry, spectrophotometry, turbidimetry etc.).

9) To calculate the non-dispersible clay, the total clay content needs to be known. The classes can be calculated according to the following formulas:

$$WDC\ (\%) = \frac{M_{WDC}\ x\ Vol_{Cont}\ x\ 100}{Vol_{Aliq}\ x\ M_{Samp\ (105°C)}} \quad \text{Eq. 1}$$

$$WRC\ (\%) = \left[\frac{(M_{WDC+WRC})\ x\ Dilution\ x\ Vol_{Cont}\ x\ 100}{Vol_{Aliq}\ x\ M_{Samp\ (105°C)}}\right] - WDC \quad \text{Eq. 2}$$

$$NDC\ (\%) = TC - WDC - WRC \quad \text{Eq. 3}$$

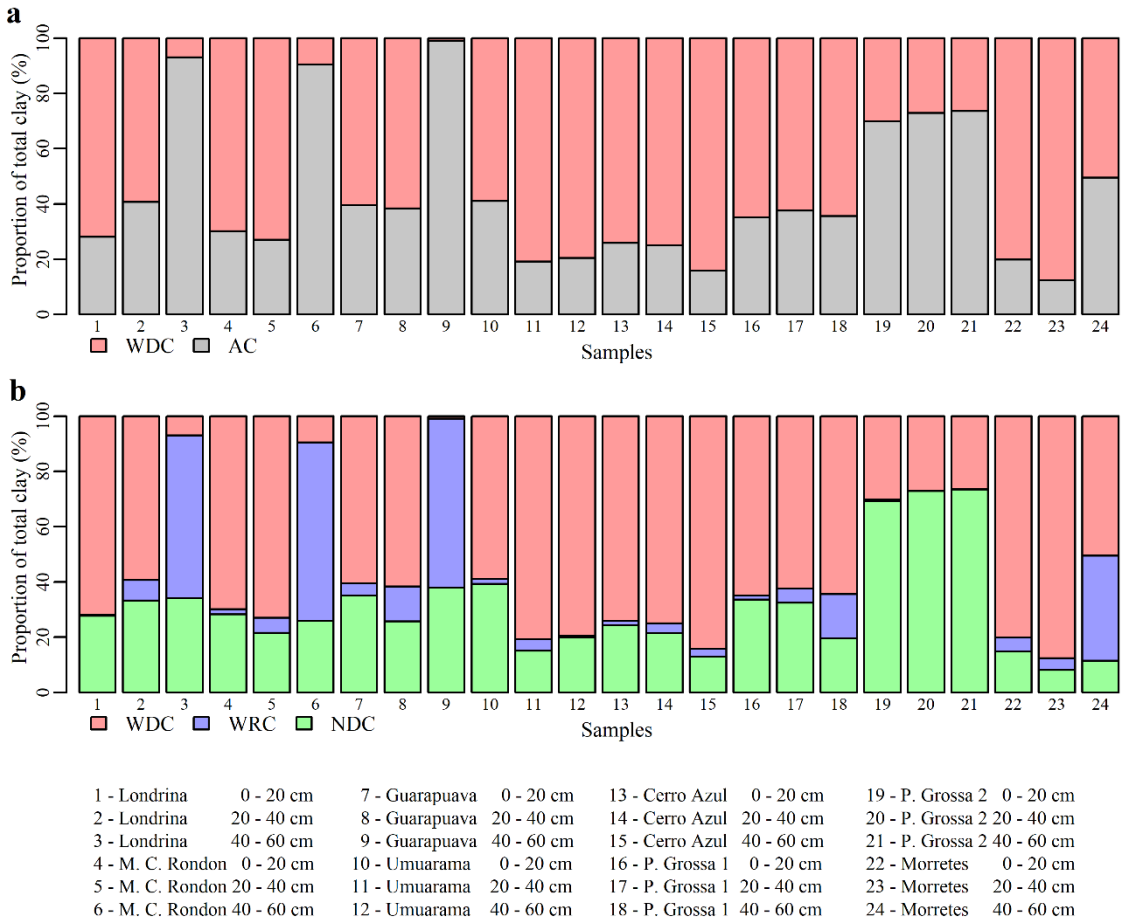
Where: WDC: water-dispersible clay (%); M_{WDC}: mass of water-dispersible clay in the extracted aliquot (g); Vol_{Cont}: final volume of the suspension in the sedimentation container (1000 mL); Vol_{Aliq}: volume of the extracted aliquot (10 mL); $M_{Samp\ (105°C)}$: mass of the sample corrected for the moisture content (g); WRC: water-re-flocculable clay (%); $M_{WDC+WRC}$: mass of WDC plus WRC in the extracted

aliquot (from the diluted suspension) (g); Dilution: dilution applied to the WDC suspension (10-fold). NDC: non-dispersible clay (%). TC: total clay (%).

5.5.2 Quantification of clay classes

The quantification of the three clay classes was possible for all soils analyzed (Figure 5.3). The gain of information with the proposed method become obvious through comparing Figure 5.3a and 5.3b. The proportion between WRC and NDC varied within the AC. This reveals that soils can have a high proportion of AC by having either a high amount of WRC or a high amount of NDC.

Figure 5.3. Clay classes according to the standard (**a**) and proposed (**b**) method in different soil samples. The classes were quantified after 16 hours in an orbital shaking at 200 rpm. WDC: water-dispersible clay. AC: aggregated clay. WRC: water-re-flocculable clay. NDC: non-dispersible clay.



Regarding the behavior of the released clay (WDC and WRC), most soil samples did not show a high proportion of WRC (Figure 5.3b). This is a result of the excess of negative charges, caused either by organic matter adsorption or by small contents of positively-charged minerals. Clay flocculation was associated with deeper layers (40–60 cm) of five soils: Londrina, M. C. Rondon, Guarapuava, P. Grossa 1, and Morretes (Figure 5.3a). As these soils presented the highest Fe_2O_3 content (Table 5.1), 9 to 32% of the clay fraction, heteroaggregation is probably the main mechanism causing flocculation in these samples.

5.5.3 Validating the obtained results

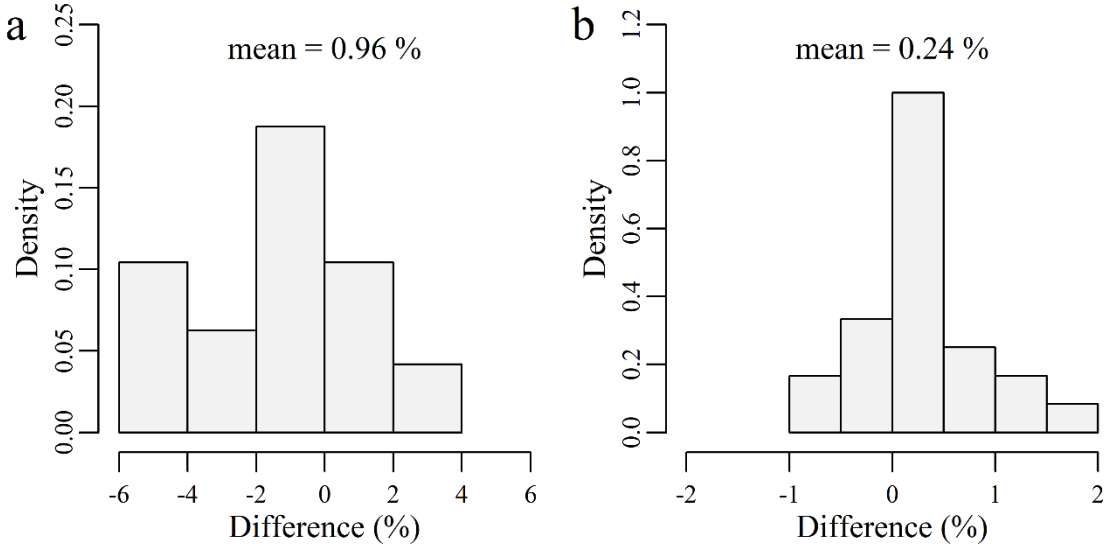
5.5.3.1 Is clay flocculation completely inhibited?

To test which treatments completely inhibit clay flocculation, we quantified the relative concentration of particles in suspension in relation to the initial concentration (t = 0), for 4 hours (Figure S5.2). Under D100, the reduction of particle concentration over time occurs because of the sedimentation of individual particles, and no flocculation is expected. A higher sedimentation rate is expected if flocculation is not inhibited, because floccules grow and settle faster. By comparing the treatments with D100, their capacity to inhibit flocculation can be assessed.

The results presented in Figure S5.2 show that all the treatments inhibited clay flocculation, except Untr. (negative control). As both treatments without dispersant addition (D00 and 10×D00) also inhibited clay flocculation (Figure S5.2), we selected the 10×D00 treatment as the most adequate. This treatment is easier to execute in the laboratory than D00, as the total clay content in the sample does not need to be previously known and no calculations are needed to dilute suspensions from samples with different clay content.

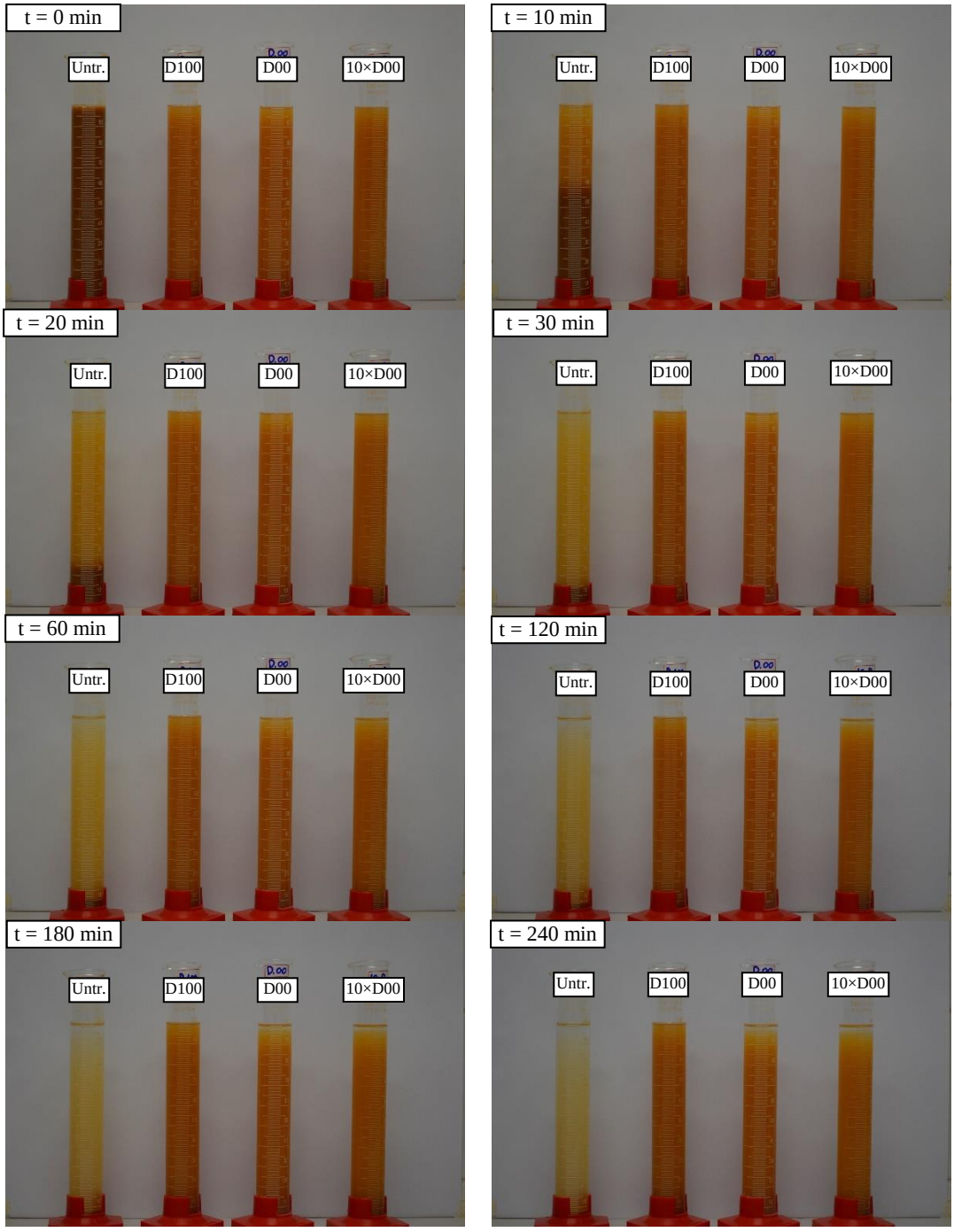
To summarize Figure S5.2, we used the data at t = 4 hours (Figure S5.2) and calculated the difference between the D100 (positive control) and 10×D00 treatments (D100 – 10×D00) (Figure 5.4a). Despite the values being presented in relative concentrations, these differences show that the errors are small and randomly distributed around zero, suggesting that flocculation was completely inhibited (Figure 5.4a).

Figure 5.4. Histograms showing the difference between the effects of D100 and 10×D00 treatments (D100 – 10×D00) on the relative clay concentration at 5 cm depth within the sedimentation cylinder after 4 hours of sedimentation (a), and the difference between the effects of Untr. and 10×D00 treatments (10×D00 − Untr.) on spontaneous clay dispersion (b) for all 24 samples. The results from the trials shown in Figure 5.4a and 4b are presented in Figure S5.2 and Table S5.3, respectively.



The inhibition of flocculation by dilution is partially caused by the reduction of electrolyte concentration, which increases the electric double-layer thickness and intensifies the repulsive forces between the particles (MAHANTA; MISHRA; KANSAL, 2014). In addition, the number of collisions by Brownian motion is reduced, maintaining the suspension dispersed for longer periods. The latter affirmation agrees with many models that predict the reduction of flocculation rate as a function of the dilution of colloidal suspensions (BERKA; RICE, 2004; BURD, 2013). This effect is shown in Figure 5.5, where a series of pictures was taken from suspensions of the Guarapuava (40–60 cm) sample.

Figure 5.5. Flocculation and sedimentation of suspensions from the Guarapuava sample (40–60 cm) under different treatments.



The inhibition of clay flocculation is evident when the treatments D00 and 10×D00 are compared to the negative (Untr.) and positive (D100) controls (Figure 5.5). However, at t ≥ 120 min, the top of the suspensions without dispersant (D00 and 10×D00) was relatively clean when compared to D100. This indicates that the attraction forces between the particles were not entirely overcome and that the inhibition of flocculation happened mainly due to the reduction of collision rate over

time. However, the results presented in Figure 5.4a show that the visually observed flocculation does not cause WRC underestimation during the sedimentation time of 4 hours at 5 cm depth.

5.5.3.2 Is NDC affected by the dilution?

Another possible interference caused by dilution of the suspension during 10×D00 treatment is the unwanted release of clay from stable aggregates (NDC), which could cause overestimation of WRC. The dispersion of NDC can happen because the reduction of electrolyte concentration by dilution can intensify the repulsive forces between particles (MAHANTA; MISHRA; KANSAL, 2014). To check this, we evaluated how the spontaneous dispersion of the clay fraction (aggregates-preserved samples) responds when a ten-fold dilution (equivalent to 10×D00 treatment) is applied (Table S5.3).

As expected, the D100 treatment caused high spontaneous dispersion because of the high concentration of dispersant. However, the differences in spontaneous dispersion between Untr. and 10×D00 treatments (10×D00 − Untr.) were small (Table S5.3). The distribution of these differences was centered on zero (Figure 5.4b) and the highest difference was +1.65 % for the Cerro Azul (0–20 cm) sample (Table S5.3).

The results presented in Figure 5.4 suggest that the method allows accurate quantification of the three clay classes. Figure 5.4a shows that clay flocculation is completely inhibited by 10×D00 treatment. Hence, WRC is not underestimated and NDC is not overestimated. Figure 5.4b shows that clay dispersion does not occur in stable aggregates (NDC) after dilution. Hence, WRC is not overestimated and NDC is not underestimated. WDC results are not affected by dilution because it is performed in the original suspension obtained from WDC analysis (Figure 5.2b).

5.6 DISCUSSION

5.6.1 Quantification of the clay classes

Regarding the structural behavior, our study shows that three classes of clay exist in soils, instead of two, as currently assumed. Our method is the first to allow their quantification and it can be applied regardless of soil type and protocol used for water-dispersible clay analysis. This method is inexpensive and easy to execute. It does not require extra soil, and does not require chemical dispersants. In addition, it requires equipment that is commonly found in laboratories that perform soil analysis.

Results shown in Figure 5.3 suggest that the proposed method improves the structural stability assessment of soils compared to the standard method. According to the standard method, the highest structural stability is found in the 40–60 cm layer of Ferralsols formed from basaltic rocks: Londrina, M. C. Rondon, and Guarapuava soils (samples 3, 6 and 9 in Figure 5.3a). The results from the proposed method reveal that most of the AC in these soils is composed of WRC, and that the NDC remains practically constant (Figure 5.3b). This corroborates the visual observation of flocculation in the laboratory and with zeta potential measurements, that show that the samples from 40–60 cm have more balanced charges than the upper layers (Figure S5.3).

In these soils, the correlations between the point of zero charge and WDC, WRC and NDC were -0.84^{**}, $+0.88^{**}$, and $+0.13^{ns}$, respectively. These correlations corroborate the current understanding of soil colloids behavior. Clay particles with positive net dispersive charge are released after the mechanical breakdown of aggregates (RENGASAMY, 2018), while a portion of the total clay remains non-dispersed (NDC) (Figure 5.3b). This stronger aggregation (NDC) can occur because of several organic and inorganic bonding mechanisms and the net dispersive charge is supposed to be zero (RENGASAMY; TAVAKKOLI; MCDONALD, 2016), explaining the absence of correlation with the point of zero charge. Within the released particles, the ones with a high net dispersive charge (low point of zero charge) remain dispersed (WDC), because the released cations are not concentrated enough to induce their flocculation, hence the repulsive forces prevail.

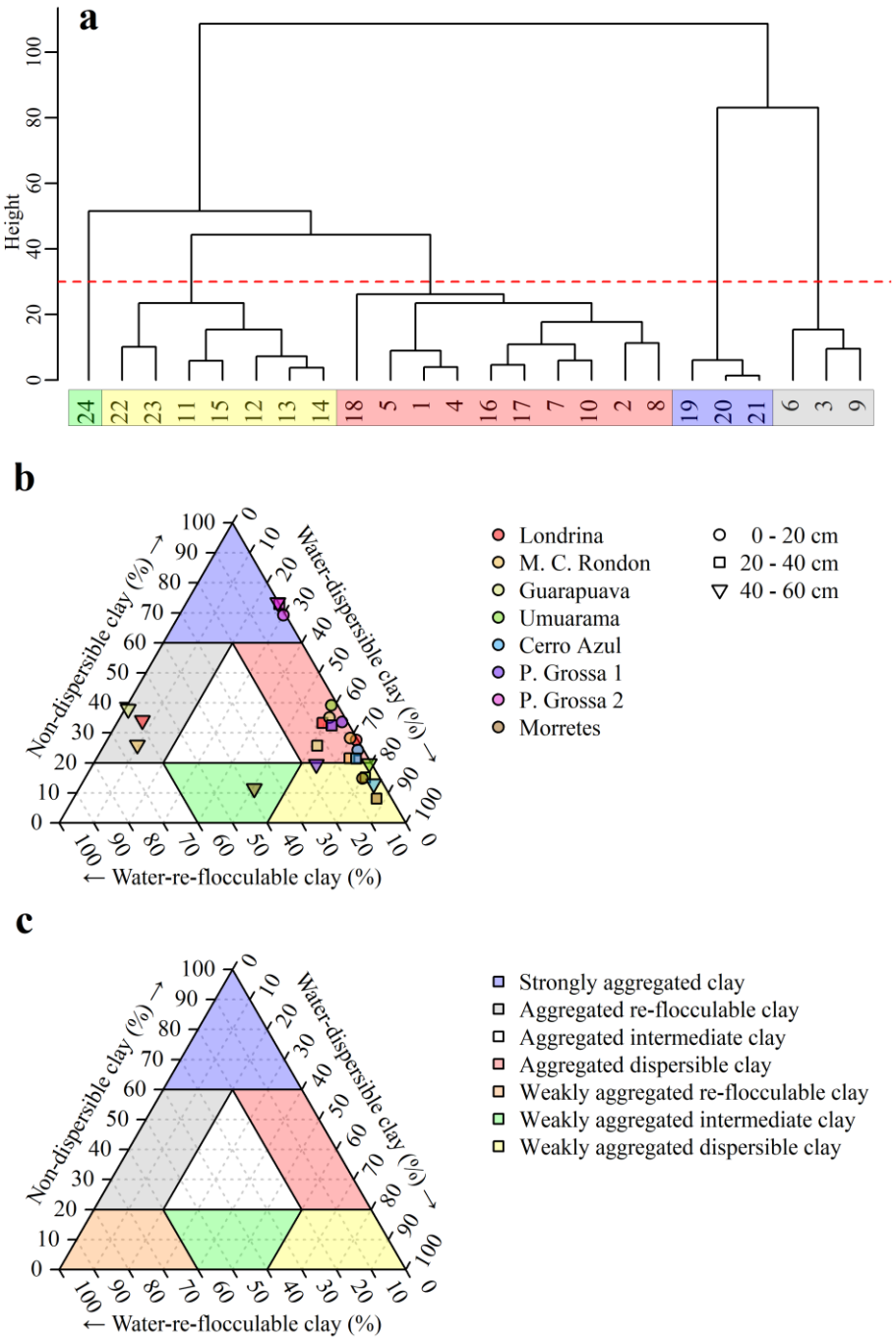
The particles with low net dispersive charge (high point of zero charge) flocculate again and settle (WRC) (Figure 5.3b).

Following our methodology, we found that Ponta Grossa 2 was the soil with the highest NDC content (samples 19, 20 and 21 in Figure 5.3b). This soil has the highest content of organic matter (> 9.2 %) and a high structural stability is expected. Because organic matter coats clay particles (NGUYEN *et al.*, 2013), it is also expected that all the released clay particles remain dispersed (WDC) instead of flocculated (WRC). This soil presented almost unquantifiable content of WRC (Figure 5.3b), which agrees with the expected result. In fact, all soils with flocculant behavior (Londrina, M. C. Rondon, Guarapuava, Ponta Grossa 1, and Morretes) presented a positive association between WRC and depth (Figure 5.3b), which is also associated to organic matter content.

The samples 10, 11 and 12 are from a sandy loam Acrisol in Umuarama and show a considerable clay increment with depth (11.03, 13.07, and 19.56 % of total clay, respectively). The layers with clay accumulation (samples 11 and 12) presented a lower structural stability (NDC) than the topsoil (sample 10) (Figure 5.3b). Because clay eluviation is present in this soil, the remaining clay in the top layer is the clay capable of aggregating itself until it forms aggregates large and resistant enough to avoid being transported. The higher NDC values of sample 10 agrees with this process.

Based on the clay classes, seven groups of clay structural stability could be delimited, and our samples were present in five of them (Figure 5.6). The cut height of 30 aimed to keep the number of groups at a minimum. This grouping separates the clay structural stability according to two criteria: 1) the capacity to remain aggregated (weakly aggregated: NDC ≤ 20 %, aggregated: 20 % < NDC < 60 %, and strongly aggregated: NDC ≥ 60 %) and 2) the behavior of the released clay (re-flocculable, intermediate, and dispersible – threshold values are variable).

Figure 5.6. Cluster analysis (a), grouping based on the clay classes (b), and stablished groups of clay structural stability (c).



These threshold values are only an initial suggestion based on the results from cluster analysis (Figure 5.6a, c). Here, we show that the classification of soils based on the proposed clay classes is possible. Future studies may suggest the addition of different groups or the establishment of different threshold values. Notably, these threshold values will also depend on the protocol used for WDC

analysis as it influences the magnitude of all clay classes. This influence is discussed in section 4.2.

This grouping allowed the approximation of samples with similar behavior (Figure 5.6). The subsoil of Ferralsols weathered from basalt (samples from 40–60 cm of Londrina, M. C. Rondon and Guarapuava soils) were classified as aggregated re-flocculable clay. Morretes Ferralsol had the subsoil classified as weakly aggregated intermediate clay. If the standard method was applied, these soils would show values of AC (WRC + NDC) varying from 49 to 99 % and would be grouped more closely to the P. Grossa 2 soil samples, that also have high AC, but with very different distribution of the clay classes (Figure 5.4 and Figure 5.6).

5.6.2 The influence of the WDC protocol on the proposed protocol

The principle of our method—dilution of the suspension obtained from WDC analysis—can be applied regardless the method used to assess the WDC content. As the particle concentration is a major variable inhibiting flocculation, it can be easily managed to allow the quantification of the proposed classes. This indicates that dilution can be applied to inhibit reflocculation in suspensions obtained from either highly or non-disruptive methods. However, WDC values are known to be method-dependent (BARRAL; ARIAS; GUÉRIF, 1998; PARADELO; VAN OORT; CHENU, 2013; CZYŻ; DEXTER, 2015). Because of this, the soil:water ratio and the energy input used in the WDC protocol will affect the dimension of all proposed clay classes.

For a given energy input, the soil:water ratio during sedimentation in the WDC analysis (step 5 in Figure 5.2b) will affect WDC and WRC. Higher soil:water ratios (more concentrated suspensions) will favor WRC over WDC, because the collision rate between particles as well as the ionic concentration will be higher. Lower soil:water ratios (more diluted suspensions) will favor WDC over WRC, because flocculation will be inhibited, as shown in Figure S5.2.

For a given soil:water ratio during sedimentation in the WDC analysis (step 5 in Figure 5.2b), the energy input during soil dispersion (step 1 in Figure 5.2b) will affect all three clay classes. The higher the energy input, the lower will be the NDC because more aggregates will be broken. Additionally, with the higher release

of clay from aggregates, WRC will be favored over WDC, because of the higher concentration of particles in suspension.

The ten-fold dilution is adequate for most existing protocols of WDC analysis. Some authors have been using higher soil:water ratios (1:5 to 1:31.5 *m:v*) than the ratio used in this study (1:50 *m:v*) (RENGASAMY, 2002; CZYŻ; DEXTER, 2015; GETAHUN; MUNKHOLM; SCHJØNNING, 2016), which could result in higher particle concentrations. However, the energy input in these studies is smaller than in our study (200 rpm for 16 hours), which reduces the amount of clay released to suspension. Therefore, the proposed ten-fold dilution is probably adequate to inhibit flocculation in most cases. When one is unsure about the accuracy of the quantification, the procedures performed in this study (section 5.3) can be replicated.

The energy applied in our study allowed for a good amplitude of the three clay classes (Figure 5.3). Because of this, the grouping of samples can become more evident (Figure 5.6), as well as the understanding of differences between soils. This was the main reason for choosing a highly dispersive method for mechanical WDC analysis. However, due to the high energy applied, the observed differences between the samples are probably more (but not exclusively) associated to pedogenetic factors than with soil management factors (PARADELO; VAN OORT; CHENU, 2013).

Despite the suitability of our method to quantify the proposed classes, it is important to highlight that the energy input and the soil:water ratio used in any protocol to quantify water-dispersible clay are not necessarily an accurate simulation of the field conditions (RENGASAMY, 2002). Clay dispersion is a dynamic soil attribute. With the drying and wetting cycles of the soil, the concentration of particles in the suspension also vary. Consequently, the WDC can flocculate with soil drying and WRC can stay dispersed with soil wetting. However, the results obtained from WDC analysis are supposed to correlate with soil behavior at some extent (IGWE; OBALUM, 2013).

A better understanding of the relationship between soil structural behavior and the proposed classes of clay is required in future studies. The WRC is supposed to be more transportable than the NDC, as the former stays in suspension while mechanical disturbances are experienced in soil solution (i. e. during rain). Additionally, when the mechanical disturbances are reduced, the WRC has higher potential to aggregate when compared to WDC. Because of this, the AC (obtained

from the current WDC methods) can lead to errors in the understanding of the processes related to the structural stability of soils, and our method can help to overcome the existing limitations.

5.7 Conclusions

Regarding the structural behavior, three classes of clay can exist in soils and our method allows their quantification. The proposed method is inexpensive and does not require extra soil or chemical dispersants. Based on the distribution of these classes in different soils, seven groups of clay structural stability were defined. This can help to understand soil structural behavior, such as the capacity of clay to resist against aggregate breakdown, to form new aggregates and the susceptibility to be transported.

5.8 Supplementary Material

5.8.1 Supplementary Methods

X-ray diffractometry analysis was performed for the total clay fraction. After extraction, the suspension containing the total clay fraction was flocculated using $MgCl_2$. Organic matter was oxidized by successive additions of concentrated H_2O_2. After oxidation, metallic sesquioxides were removed by the dithionite-citrate-bicarbonate method. The remaining clay was divided in two subsamples. These subsamples were saturated with $MgCl_2$ and KCl, respectively. The Mg-saturated clay was placed in two microscope slides. One of them was not treated and the other was saturated with ethylene glycol. Both were dried at room temperature (Mg and MG-EG diffractograms). The K-saturated clay was divided in four subsamples, placed in microscope slides and dried at 25 °C, 110 °C, 350 °C, and 550 °C (K 25, K 110, K250, and K550 diffractograms). After drying, the samples were analyzed by diffractometry in a X´Pert PRO MPD from PANalytical, using CuKα radiation, tension of 40 kV, current of 30 mA, and angular step of 0.02 °. Each angular step was read during 1 s.

Zeta potential analysis was performed in the total clay fraction. The quantification was performed in a Zeta-APS from Matec™ by electroacoustic spectroscopy. Zeta potential was obtained at different pH values, after successive addition of 3 mol l^{-1} HCl using an automatic burette coupled to the equipment. The value of the pH at the zeta potential of 0 mV (point of zero charge) was estimated by polynomial regression models.

5.8.2 Supplementary Figures

Figure S5.1. X-ray diffractograms in the clay fraction of the studied soils (samples from 40 – 60 cm soil depth).

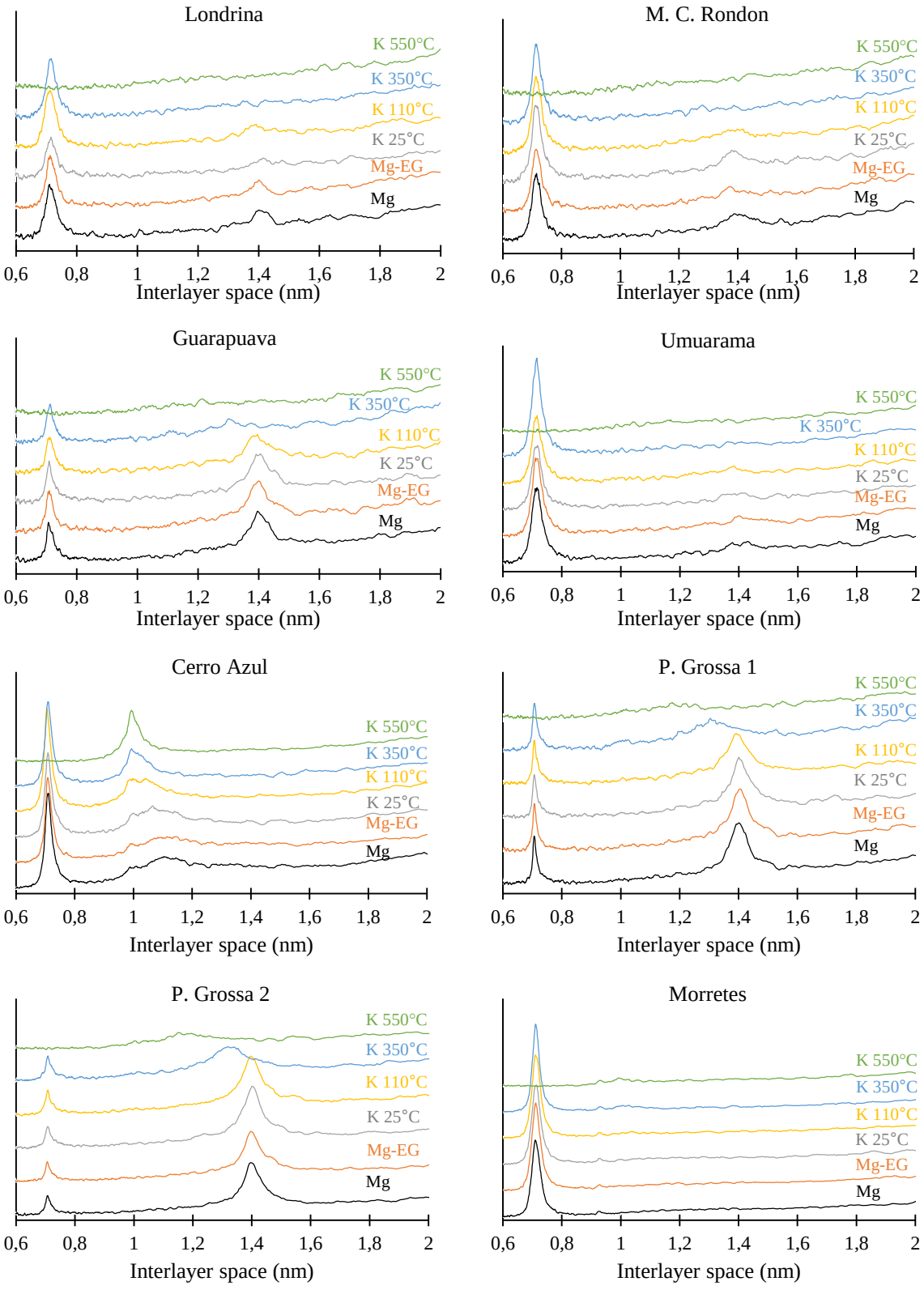


Figure S5.2. Relative concentration of particles in suspension at 5 cm depth within the sedimentation cylinder as a function of time.

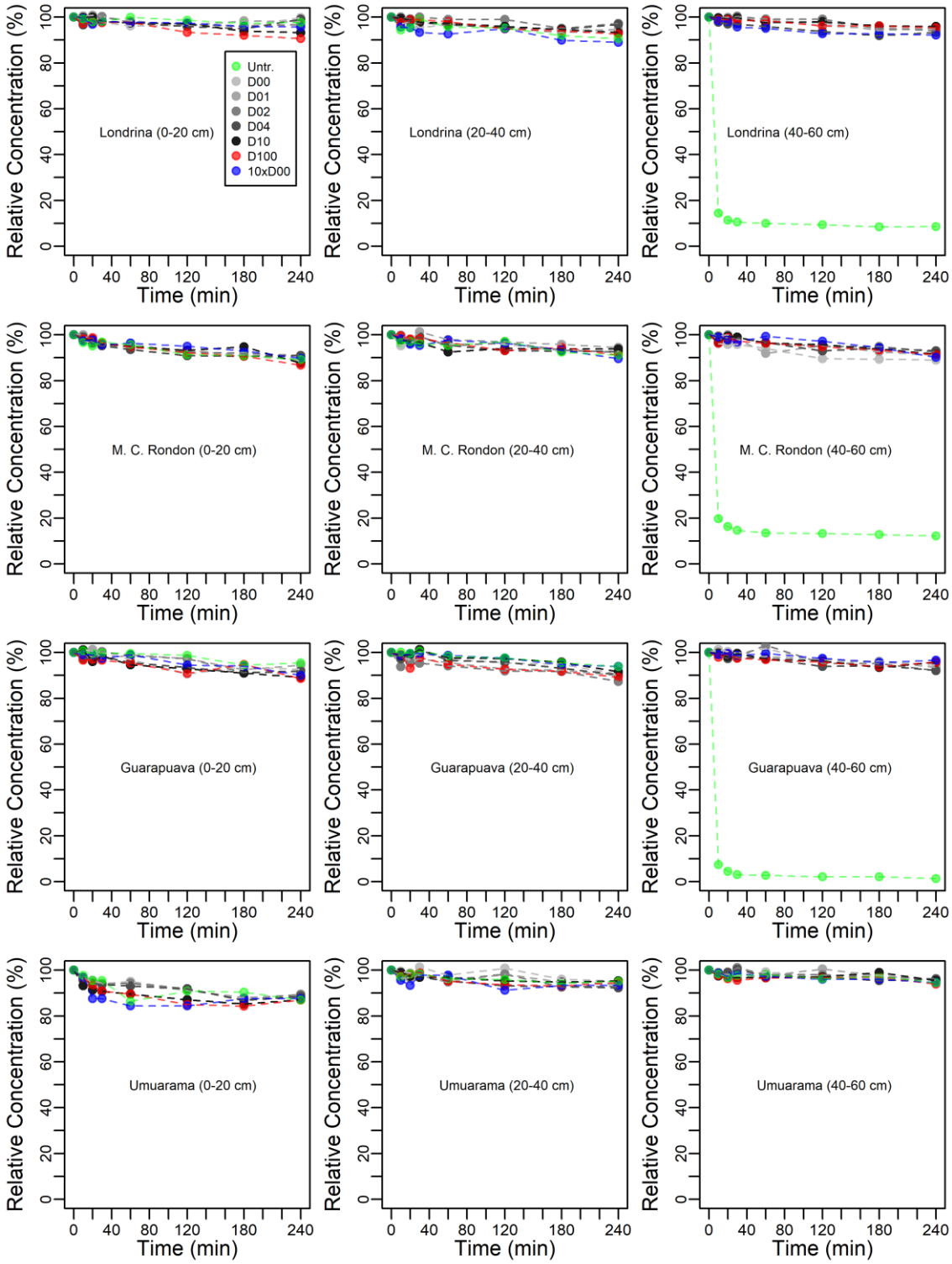


Figure S5.2. Continuation.

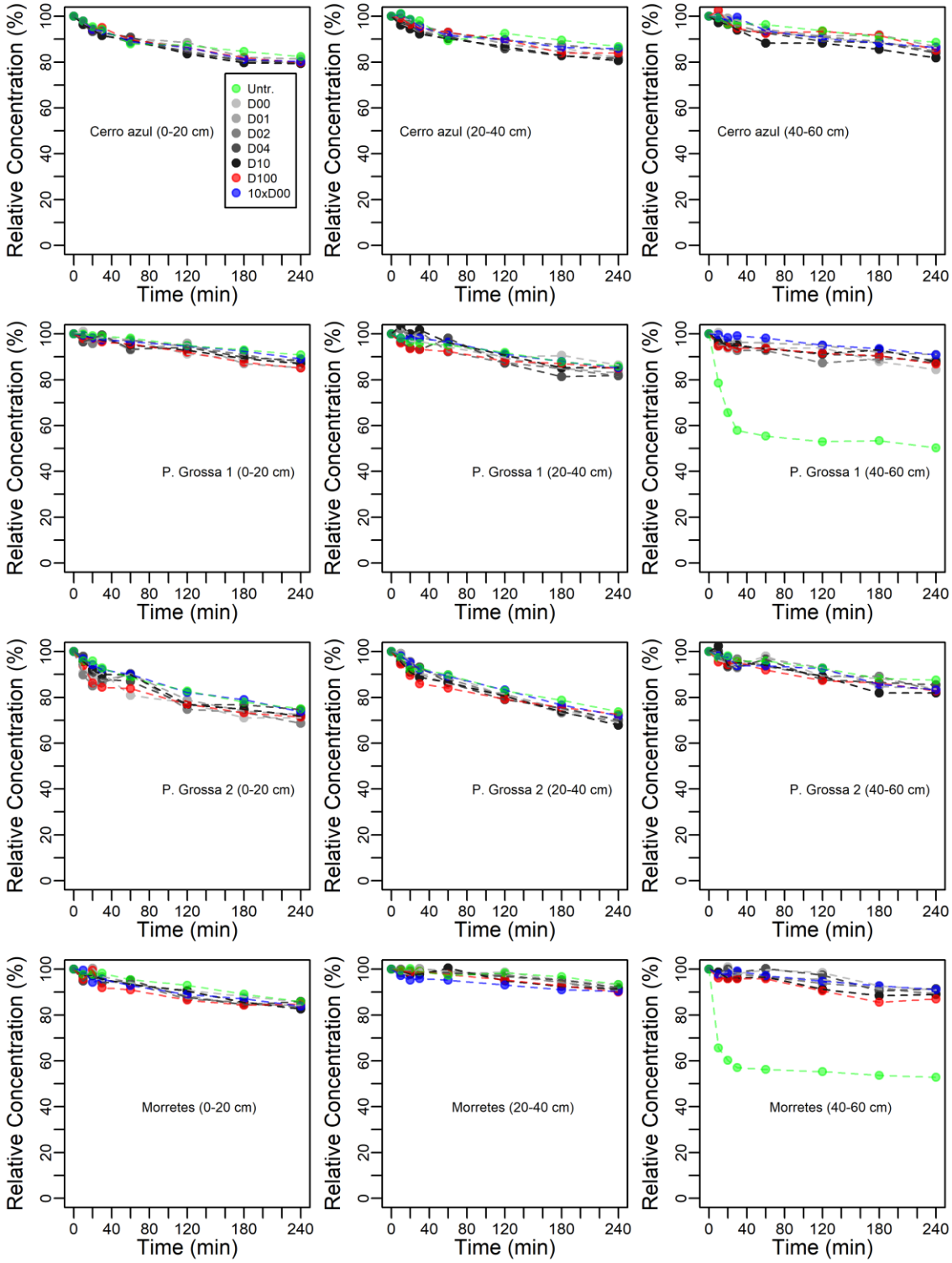
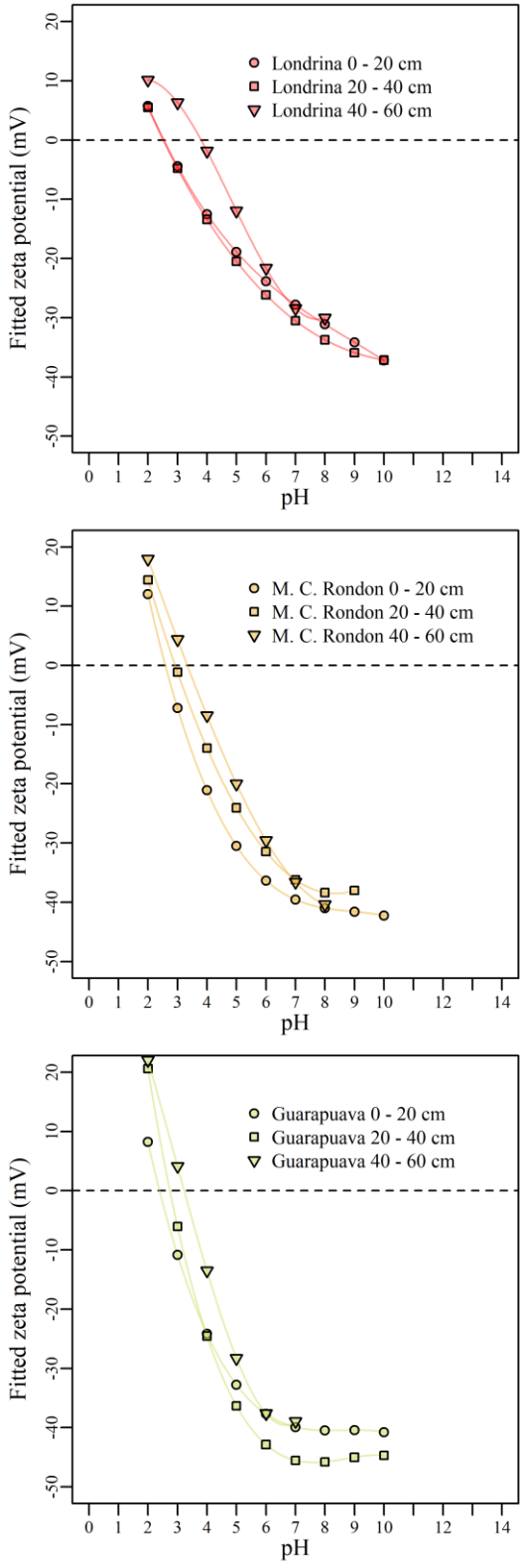


Figure S5.3. Fitted zeta potential of total clay as a function of pH in Londrina, M. C. Rondon, and Guarapuava soils.



5.8.3 Supplementary Tables

Table S5.1. Supplementary information about the sampling sites.

Site	Temp. ° C	Precip. mm year^{-1}	Lat. °	Long. °	Landscape position	Parent material
Londrina	21.1	1641	-23.3407	-51.2136	Upper	Basalt
M. C. Rondon	20.1	1656	-24.6279	-54.1690	Middle	Basalt
Guarapuava	17.2	1938	-25.3863	-51.4932	Upper	Basalt
Umuarama	22.2	1667	-23.7885	-53.2536	Upper	Sandstone
Cerro Azul	20.2	1360	-24.8859	-49.2400	Middle	Not ident.
P. Grossa 1	17.8	1554	-25.1547	-50.1485	Upper	Shales/siltites
P. Grossa 2	17.8	1554	-25.1624	-50.1654	Lower	Shales/siltites
Morretes	20.8	1977	-25.5103	-48.7985	Middle	Not ident.

Table S5.2. Calibration models for the quantification of particles in suspension by spectrophotometry at 420 nm.

Sample	Depth (cm)	Calibration curve	R^2
Londrina	0 - 20 cm	Abs = 7.80 + 6128 Concentration	0.99994
Londrina	20 - 40 cm	Abs = 4.64 + 5997 Concentration	0.99996
Londrina	40 - 60 cm	Abs = 7.95 + 5905 Concentration	0.99997
M. C. Rondon	0 - 20 cm	Abs = 0.79 + 5687 Concentration	0.99999
M. C. Rondon	20 - 40 cm	Abs = 5.87 + 5252 Concentration	0.99984
M. C. Rondon	40 - 60 cm	Abs = 5.90 + 5114 Concentration	0.99997
Guarapuava	0 - 20 cm	Abs = 4.94 + 3598 Concentration	0.99985
Guarapuava	20 - 40 cm	Abs = 3.24 + 3161 Concentration	0.99991
Guarapuava	40 - 60 cm	Abs = 4.03 + 3064 Concentration	0.99993
Umuarama	0 - 20 cm	Abs = -0.83 + 993 Concentration	0.99991
Umuarama	20 - 40 cm	Abs = -1.62 + 2334 Concentration	0.99957
Umuarama	40 - 60 cm	Abs = -1.01 + 5247 Concentration	0.99986
Cerro Azul	0 - 20 cm	Abs = -1.17 + 2702 Concentration	0.99969
Cerro Azul	20 - 40 cm	Abs = 1.01 + 2417 Concentration	0.99997
Cerro Azul	40 - 60 cm	Abs = 0.94 + 2066 Concentration	0.99997
P. Grossa 1	0 - 20 cm	Abs = 1.85 + 3537 Concentration	0.99962
P. Grossa 1	20 - 40 cm	Abs = -0.21 + 2989 Concentration	0.99999
P. Grossa 1	40 - 60 cm	Abs = 5.21 + 3178 Concentration	0.99978
P. Grossa 2	0 - 20 cm	Abs = -1.27 + 3105 Concentration	0.99985
P. Grossa 2	20 - 40 cm	Abs = -3.65 + 3022 Concentration	0.99989
P. Grossa 2	40 - 60 cm	Abs = -0.82 + 5226 Concentration	0.99982
Morretes	0 - 20 cm	Abs = -0.37 + 4522 Concentration	0.99993
Morretes	20 - 40 cm	Abs = 0.25 + 3336 Concentration	0.99998
Morretes	40 - 60 cm	Abs = 2.61 + 3123 Concentration	0.99983

Concentration values are in g L^{-1}

Table S5.3. Spontaneous clay dispersion under different treatments.

Sample	Depth	Untr.	10xD00	D100
	cm	% of total clay		
Londrina	0 - 20	0.08	0.21	2.57
Londrina	20 - 40	0.04	0.25	5.84
Londrina	40 - 60	0.01	0.09	8.51
M. C. Rondon	0 - 20	0.18	0.09	13.1
M. C. Rondon	20 - 40	0.11	0.16	8.08
M. C. Rondon	40 - 60	0.06	0.22	14.21
Guarapuava	0 - 20	0.13	0.21	0.50
Guarapuava	20 - 40	0.06	0.38	3.68
Guarapuava	40 - 60	0.01	0.03	4.90
Umuarama	0 - 20	0.67	1.56	5.01
Umuarama	20 - 40	1.25	0.90	24.79
Umuarama	40 - 60	1.45	0.64	74.24
Cerro Azul	0 - 20	1.18	2.83	12.33
Cerro Azul	20 - 40	2.20	3.14	17.52
Cerro Azul	40 - 60	2.05	3.02	27.86
P. Grossa 1	0 - 20	0.29	0.15	1.41
P. Grossa 1	20 - 40	0.10	0.36	2.47
P. Grossa 1	40 - 60	0.20	0.28	4.49
P. Grossa 2	0 - 20	0.38	0.51	2.98
P. Grossa 2	20 - 40	0.42	0.07	8.26
P. Grossa 2	40 - 60	0.17	0.35	2.08
Morretes	0 - 20	1.20	0.36	2.98
Morretes	20 - 40	1.18	2.44	22.24
Morretes	40 - 60	0.87	1.89	52.86

Untr.: suspension in the original concentration and without dispersant addition; 10xD00 (suspension diluted ten-fold, independently of the clay concentration, without dispersant addition); and D100 (diluted suspension, according to the total clay content, with addition of dispersant in 100 % of the concentration used for particle-size analysis).

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