Development, optimization and use of a reduced-sample, water dispersible clay extraction technique for taxonomic horizon discrimination

By:

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DECLARATION

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ABSTRACT

Water dispersible clay (WDC) is defined as the colloid fraction which disperses in water without removal of cementing compounds or the use of dispersing agents. It is a commonly determined parameter and is used in many erosion models and is a proxy for aggregate stability and clay dispersivity. There is no standard method for determining WDC, and although modified particle size analysis (PSA) is the most common technique, numerous other methods are also employed to save time, bench space and reduce sample size. These methods have not been tested against the benchmark PSA method and vary in terms of agitation (time and type), extraction, measurement and expression of WDC. This makes comparison between these methods very difficult.

This study aims to develop, test and optimise a simple, reduced sample centrifuge method for determining WDC in order to allow analysis of archive samples and assess the use of WDC as a soil classification discriminator on a limited number of soils. A reliable and calibrated, reduced sample size method will be of value for measuring WDC in sample collections, such as the national profile soil collection housed at the Institute for Soil Climate and Water. This would allow for these valuable collections to be included in erosion models.

Archived samples of neocutanic B, yellow-brown and red apedal B horizons and borderline neocutanics/red apedal B horizons were selected for this study. Two reduced sample centrifuge methods (using pipetting and decanting to remove the clay suspension) were examined and their efficiency and accuracy was measured with respect to the sedimentation particle size analysis (PSA) method. For both the centrifuging methods the WDC and chemically dispersed clay, a mixture of sodium hexametaphosphate and sodium carbonate, called CDC were determined. This is the chemically dispersed clay without the removal of organic matter or cementing agents. The effect of ultrasonication and shaking time on WDC was assessed for the centrifuge-pipette method by physically agitating the soil with or without prior sonication, and increasing the initial shaking time incrementally from 1 to 30 hours. X-ray diffraction (XRD) analysis was carried out on the WDC and CDC extracts from the benchmark sedimentation method to establish if the mineralogy of these two fractions differed. The WDC and CDC was measured gravimetrically and by turbidity readings.

Water dispersible clay correlated poorly with total clay across all samples. The relationship between CDC and total clay was better, but the extraction efficiency of CDC to total clay was only 54%. The extraction efficiency of WDC is highly dependent on the physical agitation energy exerted on the samples. Increasing the headspace in the centrifuge tube increased the WDC extraction efficiency by 32% (absolute). Shaking time has a major influence on WDC extraction efficiency, with a minimum shaking time of 22 hours required to get maximum extraction. This demonstrates the need to standardise the method as numerous extraction techniques use less than 16 hours shaking time for WDC extraction. Sonication prior to shaking for 22 hours results in a WDC extraction efficiency of 94% for the new centrifuge method compared to the traditional PSA method. The centrifuge-pipette method was shown to be effective in selectively separating the < 2 µm phase, thus reducing the need for sedimentation. Turbidity is not a reliable technique to measure clay in a suspension, due to the clay mineralogy affecting turbidity. Model kaolinite and smectite did not give uniform turbidity readings. This means the gravimetric method cannot be replaced, but centrifugation has both a time saving and sample reducing benefit.

Neocutanic horizons tended to have WDC_h (the WDC fraction expressed as a function of CDC) content higher than the yellow-brown and red apedal horizons, and were distinguishable from red apedal horizons at a 95% confidence level. However, WDC cannot be used to distinguish neocutanic B from yellow-brown apedals horizons. This supported the tacit knowledge that neocutanic horizons have a less stable clay phase than red apedal horizons, but the distinction is not clear in the case of yellow brown apedals. Borderline neocutanic/red apedal horizons and typical neocutanic proved to have similar WDC_h content. Given the importance of clay stability in red apedal horizons, it was recommended they are classified as neocutanics rather than red apedals and a tentative threshold of 47% WDC_h be used to differentiate between horizons.

The new centrifuge technique for the extraction of WDC is a viable alternative to the PSA method and has the benefits of reducing sample size and extraction time and increasing the number of samples that can be analysed at one time. Standardisation of WDC is important due to the effects of agitation type and duration on the extraction efficiency. Furthermore, WDC_h shows promise as a classification aid and should be investigated further.

UITTREKSEL

Waterverspreibare klei (WVK) word gedefinieer as die kolloïede-fraksie wat versprei in water sonder die verwydering van sementerings-verbindings of met die gebruik van verspreidings-middels. Dit is ‘n parameter wat gereeld bepaal word en word in baie erosie studies gebruik. Dit word ook gebruik as ‘n proksie vir aggregaat-stabiliteit en klei-verspreibaarheid. Daar bestaan geen standaard-metode om WVK te bepaal nie, en al is gewysigde deeltjiegrootte analise (DGA) die mees algemene tegniek, word vele ander metodes ook aangewend om tyd en bankspasie te bespaar, sowel as monstergrootte te verminder. Hierdie metodes is nog nie teen die maatstaf DGA metode getoets nie en varieer vanaf hierdie metode in terme van agitasie (tydsverloop en tipe), ekstraksie, meting, en uitdrukking van WVK. Dit veroorsaak dat vergelyking tussen hierdie metodes baie moeilik is.

Hierdie studie beoog om ‘n eenvoudige, verminderde monster sentrifuge metode om WVK te bepaal te ontwikkel, toets en te optimiseer, ten einde die ontleding van argief-monsters toe te laat en die gebruik van WVK as ‘n grondklassifikasie onderskeider, op ‘n beperkte aantal gronde, te assesseer. ‘n Betroubare en gekalibreerde verminderde-monstergrootte metode sal van waarde wees vir die bepaling van WVK in monster versamelings, soos die nasionale grondprofiel versameling gehuisves by die Instituut vir Grond, Klimaat en Water. Dit sal toelaat dat hierdie waardevolle versamelings ook in erosiemodelle ingesluit kan word.

Argief-monsters van neokutaniese B, geel-bruin en rooi apedale B horisonne sowel as grensgeval neokutaniese/rooi apedale B horisonne is vir hierdie studie geselekteer. Twee verminderde monster sentrifuge metodes (deur pipettering en afskinking om die kleisuspensie te verwyder) is geëksamineer, en hul doeltreffendheid en akkuraatheid is gemeet met betrekking tot die sedimentasie deeltjiegrootte analise (DGA) metode. Vir albei van die sentrifugerings-metodes is WVK en chemiese verspreibare klei (CVK), deur ‘n mengsel van natrium hexametafosfaat en natrium karbonaat, bepaal. Hierdie is die chemiese verspreibare klei sonder die verwydering van organiese materiaal of sementeringsmiddels. Die effek van ultrasonikasie en skudtyd op WVK is geassesseer vir die sentrifuge-pipet metode deur die grond, met of sonder vorige sonikasie, fisies te agiteer en die aanvanklike skudtyd van 1 tot 30 uur inkrementeel te verhoog. X-straal diffraksie (XSD) analise is uitgevoer op die WVK en CVK ekstrakte van die maatstaf sedimentasie metode om vas te stel of die mineralogie van die twee fraksies verskil. Die WVK en CVK is gravimetries en deur troebelheid lesings gemeet.

Waterverspreibare klei korreleer swak met totale klei vir alle monsters. Die verhouding tussen CVK en totale klei is beter, maar die ekstraksie doeltreffendheid van CVK tot totale klei is slegs 54%. Die ekstraksie doeltreffendheid van WVK is hoogs-afhanklik van die fisiese agitasie energie uitgeoefen op die monsters. Verhoging van die hoofruimte in die sentrifugebuis het die WVK ekstraksie doeltreffendheid met 32%

(absoluut) verhoog. Skudtyd het ‘n groot invloed op WVK ekstraksie doeltreffendheid, met ‘n minimum skudtyd van 22 uur wat benodig word om maksimum ekstraksie te behaal. Hierdie bevinding demonstreer dat dit nodig is om die metode te standaardiseer want vele ekstraksie tegnieke gebruik minder as 16 uur skudtyd vir WVK ekstraksie. Sonikasie voordat daar geskud word vir 22 uur lei tot WVK ekstraksie doeltreffendheid van 94% vir die nuwe sentrifuge metode in vergelyking met die tradisionele DGA metode. Die sentrifuge-pipet metode is bewys as meer doeltreffend om die < 2µm fase selektief te skei, en verminder dus die behoefte vir sedimentasie. Troebelheid is nie ‘n betroubare tegniek om klei in ‘n suspensie te meet nie, as gevolg van die feit dat klei mineralogie die troebelheid affekteer. Model kaoliniet en montmorilloniet het nie uniforme troebelheid lesings gegee nie. Dit beteken dat die gravimetriese metode nie vervang kan word nie, maar dat sentrifugering albei tydbesparings en monster-verminderings voordele inhou.

Neokutaniese horisonne is geneig om ‘n WVK_h (Die WVK fraksie uitgedruk as ‘n funksie van CVK) inhoud te hê wat hoër is as dié van die geel-bruin en rooi apedale horisonne, en is onderskeibaar van rooi apedale horisonne by ‘n 95% vertroue vlak, maar WVK kan egter nie gebruik word om neokutaniese horisonne van geel-bruin apedale horisonne te skei nie. Hierdie bevinding ondersteun die implisiete kennis dat neokutaniese horisonne ‘n minder stabiele kleifase besit as rooi apedale horisonne, maar die onderskeiding is nie duidelik in die geval van geel-bruin apedale horisonne nie. Grensgeval neokutaniese/rooi apedale horisonne en tipiese neokutaniese horisonne bevat soortgelyke WVK_h inhoud. Gegewe die belangrikheid van klei-stabiliteit in rooi apedale horisonne, is dit aanbeveel dat hulle eerder geklassifiseer word as neokutaniese horisonne in plaas van rooi apedale horisonne, en ‘n proefnemende drempel van 47% WVK_h gebruik word om te onderskei tussen horisonne.

Die nuwe sentrifuge tegniek vir die ekstraksie van WVK is ‘n lewensvatbare alternatief vir die DGA metode en besit die voordele van monstergrootte en ekstraksietyd vermindering sowel as die aantal monsters te verhoog wat op een slag ontleed kan word. Standaardisering van WVK is belangrik as gevolg van die effekte van agitasie tipe en tydsduur op die ekstraksie doeltreffendheid. Verder toon WVK_h groot belofte as ‘n klassifikasie hulpmiddel en moet verder ondersoek word.

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DEDICATION

This thesis is dedicated to my mother, Nomandawa Eutricia Dinwa, who always emphasizes the importance of education as a tool to unlock one’s full potential. I do not know anyone more resilient, hardworking and passionate to serve others than you, Magaba. I’d also like to dedicate this thesis to my uncle and late aunt, Jimmy Phakamile and Nozaziso Jeanette Qhashu respectively, for being a source of support throughout my life and for instilling in me an insatiable thirst to seek knowledge and a desire to explore and discover.

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GENERAL INTRODUCTION

The tendency of clay to disperse is a common phenomenon which occur in soils, the rate at which this occurs when soils are exposed to water has significance on the stability of the soil aggregates. The presence of stable soil aggregates is a desirable characteristic for maintaining a balance between the physical, biological activity and crop growth so that the agricultural productivity is sustained (Amézketa, 1999). The clay fraction with a natural tendency to disperse when exposed to water without the removal of cementing agents or the use of dispersing agents is known as water dispersible clay (WDC) (Burt, Reinsch and Miller, 1993; Seta and Karathanasis, 1996; Mujinya et al. 2013). It has been used as to assess many soil features and soil management practices such as surface crusting and sealing (Mills and Fey, 2004). Other workers have used WDC to assessing tillage practices (Pagliai, Vignozzi and Pellegrini, 2004; Igwe, Zarei and Stahr, 2006). This phase has also been shown to be a possible transporting mechanism of strongly sorbing contaminants (Seta and Karathanasis, 1996; De Jonge, Kjaergaard and Moldrup, 2004a). Soils subjected to frequent tillage and intensive cultivation often have crust formation which can significantly reduce the infiltration rate and increase runoff, which induces soil erosion (Unger, 1992; Zejun et al. 2002). Mobile soil colloids facilitate the transport of strongly sorbing contaminants which increases the risk of them being released to drainage water in high concentrations (Villholth et al. 2000; Petersen et al. 2003).

Water dispersible clay is an important parameter as it is recognised as an important soil property with respect to predicting soil erosion and its use in soil classification systems. It is used as an input parameter in soil erosion models such as the Watershed Erosion Prediction Programme (WEPP) (Brubaker, Holzhey and Brasher, 1992). The World Reference Base (WRB) soil classification system also uses it to distinguish between ferralic and argic subsoil horizons (Soil Survey Staff, 2014; IUSS Working Group WRB, 2015). However, one problem with WDC is that there is currently no standardisation in its determining which often becomes problematic when interpreting WDC data and relating threshold values to distinguish between horizons. The most accepted method to determine WDC is similar to particle size analysis (PSA) without the removal of cementing agents or addition of a dispersing agent. This method is referred to as the sedimentation-pipette (adjusted PSA) method from hereon. There are, for example, numerous methods used for WDC for which there has been no calibration to sedimentation methods. Given that physical agitation is the only dispersion mechanism in WDC extraction it is important to establish how this influences its extraction efficiency.

Another potentially problematic aspect of the WDC method is the lack of clarity on how it should be expressed. It is frequently expressed as a fraction of total clay, or as a percentage of total soil. Only if the WDC is extracted under the same physical conditions (but without removal of cementing agents or addition of dispersing agent) as the PSA used to determine total clay, can it be expressed over total clay. Determining WDC over total soil is more accurate if the WDC and total clay are determined using different methods. However, it has limited comparison use in relating different soils with different clay contents. In addition, most WDC methods require a large amount of soil, which means WDC cannot be determined on soil collection samples. A reliable and calibrated, reduced sample size method would thus be of value for measuring WDC in sample collections, such as the national profile soil collection housed at the Institute for Soil Climate and Water. This would allow for this valuable collection to be included in erosion models or used in classification queries.

Clay stability is an important characteristic of soils and is often associated with pedogenic processes such as lessivage. Morphological features, such as clay cutans and bleached topsoils are often an expression of an unstable clay phase (Fey, 2010; Le Roux, 2015). In fact Le Roux (2015) established that the only statistical difference between bleached and non-bleached topsoils from red Oakleaf soil forms in the Western Cape was WDC. Given the WRB's use of WDC as classification criteria, it is possible that this criterion may also be a potential discriminator between horizons that have stable micro-aggregate structure (e.g. red and yellow-brown apedal B horizons) and soil such as neocutanics, which show evidence of clay mobilisation in the forms of cutans. In order to test this, numerous samples need to be analysed for WDC. The logical option for this is to use archived samples, such as the national profile soil collection. However, before this can be achieved a reliable reduced sample procedure for WDC needs to be developed.

Aims and objectives

This study aims to develop, test and optimise a simple, reduced sample centrifuge method for determining WDC in order to allow analysis of archive samples and, then using this method, to assess the use of WDC as a soil classification discriminator on a limited number of soils. To achieve these goals, the following series of research objectives were set:

i. Comparing a simple, reduced sample, centrifuge-pipette method with the benchmark sedimentation-pipette method,
ii. Improving the WDC extraction efficiency of the centrifuge-pipette method by assessing the effect of agitation and measurement procedures on the WDC extracted and,
iii. Applying the improved method to archived samples to assess the potential of WDC as a discriminator between neocutanic and red and yellow-brown apedal B horizons on a limited number of profiles.

Thesis layout

This study is divided into five chapters. Chapter one includes the general literature overview. The second chapter deals mainly with testing water and chemical dispersible clay extraction techniques in comparison to the standard particle size analysis method; the first objective will be satisfied in this chapter. In the third chapter, a rapid and reduced sample size centrifuging method for measuring WDC is optimised which is structured around the second objective. Chapter four applies this optimised centrifuge method to archived samples from selected regions to assess whether neocutanic horizons have a higher WDC content compared to red and yellow brown apedal horizons. The last objective is dealt with in this chapter. The fifth and concluding chapter in this thesis summarises the research findings and significance, recommendations are made and future study prospects are provided.

Chapter 1 : Clay stability and movement in soils

1.1 Introduction

Unstable aggregates and the loss of soil structure are a product of clay dispersion. In order to understand clay dispersion, particularly WDC, it is important to understand the concept of aggregate instability and how this is a precursor for clay movement in soil. A wide range of interdependent properties influence the speed at which the soil will disperse. Fortunately, according to Igwe and Udegbunam (2008), measuring these soil properties is easy and ideal to understanding WDC better. This literature review focuses on internal and external factors of WDC. The inclusion of WDC in erosion models, how WDC facilitates the transport of contaminants and its use in WRB soil classification system will be discussed.

1.2 Properties of water dispersible clay

1.2.1 The role of soil pH, exchangeable cations and sodicity on aggregate stability and WDC

The relevance of pH is that it controls a wide range of reactions occurring in soils. Clay dispersion is influenced by soil pH, as the pH increases the negative charge on the clay particles increases (Amézketa, 1999). The presence of polyvalent cations cause clay to flocculate at pH lower than 5 and when monovalent cations are present dispersion tends to be favoured, at pH values greater than 6.5 (Gal et al. 1984). At these high pH values there is accumulation of Ca^{2+} concentrations, generally classified a clay stabilising cation. However, if there is a strong dominance of Na^{+} clay dispersion becomes favoured (Soil Survey Staff, 2014). The consensus among soil scientists is that clay tends to be more stable at lower pH values and dispersion is promoted when the soil pH is high. The difference between soil pH and its zero point of charge (pH_{ZPC}) is also an indicator of clay dispersion potential. Seta and Karathanasis (1996) stated that WDC is enhanced if repulsion forces are produced as result of this difference between pH. However, when the soil pH is near the point of zero charge colloid dispersion is negligible (Gillman, 1974). In contrast, Jozefaciuk et al. (1995) studying changes in WDC content on a range of pH values, in soils taken from humus horizons treated with acid, found that at low soil pH the WDC fraction became higher for the soils they studied. These workers attributed this to disruption in soil aggregates due to the influence of protonation and acidic destruction of the solid phase. Furthermore, Nguetnkam and Dultz (2011), studying soils collected along a toposequence of oxisols indicated that soil pH is inversely proportional to surface charge. From the above studies, it is evident that the pH of soils controls many properties of clay dispersion and WDC.

Exchangeable cations have an important role in the structural stability of soils because they balance the negative charges of clay minerals. Norton et al. (1999) explained that cations follow the hierarchy sequence of polyvalent> divalent> monovalent, in order of flocculating power. It is generally stated that poly- and divalent cations increase flocculation rather than dispersion of clay. Igwe, Zarei and Stahr, (2006) found contradictory results that exchangeable cations such as Ca^{2+} and Mg^{2+} increase WDC and water dispersible silt (WDSi) content (Igwe, Zarei and Stahr, 2006). These divalent cations acted as dispersing agents (Igwe, Akamigbo and Mbagwu, 1999) to clay thereby promoting the dispersibility of clay. This is in contrast to the work by Harris, Chesters and Allen (1996) who noted that Ca^{2+} and Mg^{2+} act as aggregating agents to clay sized fraction. Bronick and Lal (2005) also indicated that the presence of these bivalent cations improves soil structure by forming complexes between clay particles with organic matter. In general, it appears that the presence of Ca^{2+} and Mg^{2+} on clay dispersion is not consistent.

An equally important exchangeable cation affecting aggregate stability and clay dispersion in soils is exchangeable Na^+. Sodium is considered a highly dispersive agent that actively enhances breakdown of aggregates, this makes soils enriched in Na^+ vulnerable to easily disperse in water (Sumner, 1993; Van Zijl, Ellis and Rozanov, 2014). This is because the exchangeable Na^+ affects the viscosity and the swelling of clays when they are submerged in water (Igwe, 2001). Igwe (2001) working on some semiarid soils in Northern Nigeria found a significant correlation between exchangeable Na^+ and WDC. The relationship between WDC, exchangeable sodium percentage (ESP) and exchangeable sodium ratio (ESR) has been examined by Shainberg, Warrington and J. M. Laflen (1992). Both ESP and ESR are indices used for assessing soil sodicity. These workers found that even a small amount of exchangeable Na^+ is enough to cause a considerable effect on clay dispersion and that dispersion increases with rising ESP in soils. The ESR has the same effect on clay dispersion as ESP (Igwe, 2001). Together with ionic strength, exchangeable Na^+ can cause aggregate slaking under condition that were previously unfavourable for clay dispersion (Igwe, Zarei and Stahr, 2006). Despite acting as a dispersion agent for clay, under oversaturated situations the excess Na^+ can act as a flocculating agent and this can also have some negative influences in soil structure (Emerson, 1977). Igwe (2001) emphasized that there was no significant relationship between Na^+ adsorbed and WDC; and that the results obtained explained only the general trend for WDC and therefore not suggested for prediction purposes.

1.2.2 Effect of soil organic material on water dispersible clay

Inconsistent results have been presented regarding the relationship between soils with high WDC and organic material. The general understanding on organic material is that they act as a binding agents for aggregates but can act as a disaggregating agent in soils depending on the form and concentration in the soil (Bronick and Lal, 2005; Igwe, Zarei and Stahr, 2006). Mbagwu, Piccolo and Mbila (1993) showed that organic matter either increased clay dispersion or had no effect on aggregate stability of some soils treated with humic substances. This notion was also observed by Goldberg, Suarez and Glaubig (1988) who indicated that organic matter may disaggregate, stabilise, or have no effect on soil structure. These workers found organic carbon to negatively correlate with soil dispersion. The consequence was explained by Heil and Garrison (1993a, 1993b) to be a result of i) the obstruction of positively charged clay minerals by the negatively charged organic carbon, ii) polyvalent cations binding to organic matter and iii) the repulsion caused when adsorbed polymers overlap. This consequently reduces the complexing ability of organic carbon to soil aggregates.

Igwe, Zarei and Stahr (2006) studying soils with low organic carbon, indicated that the organic carbon failed at correlating with WDC but loaded the highest in principal component analysis (PCA) for soil variables influencing hardsetting properties. This meant that organic carbon could be used to manipulate hardsetting for their soils. Paradelo, van Oort and Chenu (2013) also noted that amending soils with manure decreased the degree of deterioration of soil aggregates which caused the decline in WDC contents. From the above discussion it is evident that WDC content can somewhat be reduced through incorporation of organic material in soil and this could contribute to stabilise soil structure enabling the formation of stable bonds between clay and organic material (Chenu, Bissonnais and Arrouays, 2000).

1.2.3 Effect of mineralogy, Fe and Al content on WDC

Clay mineralogy and the oxide content influences the WDC in soils. For example, Seta and Karathanasis (1996) studied six soil samples with diverse soil properties found that the WDC fractionation was influenced by the presence of kaolinite and Fe and Al oxide content. Similarly, in a floodplain where soils were susceptible to hardsetting, Igwe, Zarei and Stahr (2006) indicated that Fe and Al oxide contributed significantly to the WDC content of the soils they studied. Six, Elliott and Paustian (2000) also observed this trend and emphasizes that these factors are important in stabilising soils. The low charge on kaolinite accounts for the low dispersive nature of these minerals, whereas clay dominated by more reactive minerals have a highly dispersive tendency (Seta and Karathanasis, 1996). Illite and smectite have been found to increase WDC (Igwe, Zarei and Stahr, 2006). This is in contrast to the findings by Seta and Karathanasis (1996) who stated that illite had no effect on WDC. Kjaergaard et al. (2004b) demonstrated that for WDC with similar mineralogical composition displayed large variations of flocculation behaviour. These workers concluded that model predictions of colloid mineralogy could lead to inaccurate conclusions. Under field conditions the interaction between many properties influences the clay particles and it is the combined effect that determines the outcome. The difference between the work done by the workers above is that Igwe, Zarei and Stahr (2006) studied soils obtained from the A horizon while Seta and Karathanasis (1996) studied the B horizon which tend to have different dispersive potential.

In addition, when soils are low in Fe and Al oxides there is nothing to stabilise the clay and therefore there is a tendency for clay migration. It is commonly accepted that when there is clay movement, the

Fe and Al in those soils must be insufficient to reduce the tendency of clay to be stable (dispersive) in suspension. In these instances, it is typical that the WDC content would be higher than when these minerals are present. Seta and Karathanasis (1996) explained the lack of correlation between WDC and total clay to the be consequent of the Fe and Al oxide including dominance of kaolinite rich mineralogy. Despite the ongoing debates about which sesquioxides is the most effective aggregation agent, there are ample evidence supporting the notion that Fe and Al oxides have positive effects on structural stability, thus limiting WDC.

1.3 Water dispersible clay and physical stability of soils

The effect of dispersion and swelling are the root causes of the degradation of the physical properties in soil, especially soils which are high in sodicity (Sumner, 1993). It is common that, under these conditions, surface crusting and sealing will occur especially when clay particles are severely dispersed. For example, when soils have a high WDC content the clay may clog up the soil pores reducing water infiltration and even reduce aeration when the soil is dry. Clogged up pores not only reduces aeration in the soil but promote undesirable soil conditions for tillage practices. The prospect of generating runoff is increased when water infiltration through the profile is impeded, and this could result in detached soil being transported along with the moving water (Singer and Warrington, 1992; Amézketa, 1999). The likely outcome of this is an eroded topsoils exposing the bottom, much denser subsoil profile which could present challenges for root penetration. Because surface crusting and sealing pose potential restrain for roots to penetrate the profile, determining WDC would serve to predict the soils inclination to crust and seal (Mills and Fey, 2004).

Dispersion of clay when immersed in water also affects the hardsetting characteristics of the soil (Seta and Karathanasis, 1996; Igwe, Zarei and Stahr, 2006) however dispersion of clay is not a prerequisite. Hardsetting soils are hard when dry restricting root penetration and hampering moisture movement leading to reduced aeration (Igwe, Zarei and Stahr, 2006). These soils tend to loosen up when wet and temporarily loose some of their undesirable attributes but usually revert to the hard state when the conditions are conducive. Chartres, Kirby and Raupach (1990) observed that hard-setting occurs throughout the soil profile and noted that they are widespread in Australia in areas with xeric and ustic moisture regimes. Limiting hardsetting involves reducing aggregate disruption through dispersion and slaking (Daniells, 2012). Implying that management practises which promote resistance to slaking can be effective in limiting the measure of hard-setting of soils.

The quantity of WDC content in soil also controls the water retention characteristics, hydraulic conductivity (Shanmuganathan and Oades, 1982; Seta and Karathanasis, 1996), infiltration rate and consequently negatively affect crop production (Shainberg and Letey, 1984). When there is limited water movement in the soil, the hydraulic conductivity may be too low which might result in insignificant transportation of dispersed clay (Chittleborough, 1992). Kazman, Shainberg and Gal (1983) and Oster and Schroer (1979) indicated that soil surface is very sensitive to low hydraulic conductivity during infiltration more than subsurface horizons with low ESP of the same soil. These soils generally tend to be prone to erosion and crusting.

1.4 Colloid-facilitated transport

Dispersive clay can facilitate the transport of contaminants in soil and groundwater (McCarthy and Zachara, 1989; De Jonge, Kjaergaard and Moldrup, 2004a; McCarthy and McKay, 2004). For colloidal suspensions to facilitate contaminant transport they must be stable (resist aggregation in the soil environment). Because of the dynamic nature of particles and the interdependent factors which affect it, determining whether particles are stable or aggregated can be challenging. Clay that is unstable mobilises contaminants by binding them and transporting them where they would not have otherwise been mobile (De Jonge, Kjaergaard and Moldrup, 2004a). McCarthy and Zachara (1989) mentioned in a review on subsurface transport of contaminants that clay particles can act as a third phase in addition to the phases of contaminants and porous media. Therefore sparingly soluble contaminants have a strong inclination to bind to the solid phase which results in them moving faster than they generally would have, but not fast enough in comparison to groundwater (McCarthy and Zachara, 1989). Field and laboratory studies have revealed the association of contaminants to colloids. Water analysed from tile drains have revealed a linear relationship between the number of colloids and particulate P (De Jonge et al. 2004b). In addition, work by Grolimund et al. (1996) demonstrated that rapid transport of Pb can be facilitated by suspended in situ mobilised colloids.

1.5 Erosion models utilizing water dispersible clay

There is evidence suggesting a direct relationship between WDC and soil erosion (Igwe and Udegbunam, 2008). The susceptibility of soils to erosion can be determined using this parameter as it corresponds well to factors affecting erosion (Brubaker, Holzhey and Brasher, 1992). The WDC fraction and its indices have been successfully used in high rainfall areas (in Nigeria) to estimate soil erodibility potential (Amezketa, Singer and Le Bissonnais, 1995; Igwe and Agbatah, 2008; Calero, Barron and Torrent, 2008).

Determining the likelihood of soil erosion has proven to be a challenging task in the past because of the dynamic factors which affect it. To date, empirical models have been developed and applied to predict the likelihood of soils to erosion. They have not always been accurate in providing successful results to which, Amézketa, (1999), attributes to the lack of adequate global database to calibrate the models. However, they still remain easier to use when quantifying erosion compared to traditional methods, such as stimulated rainfall conditions (field or laboratory) or natural rainfall erosion plots (Truman, Bradford and Ferris, 1990; Bradford and Huang, 1993), which are time consuming and require extensive economic support. The WDC and water-dispersible silt (WDSi) have been identified to positively correlate with erodibility (Igwe, Zarei and Stahr, 2006). Middleton (1930) explained that the ratio of WDC and WDSi to total clay plus silt, which were coined dispersion ratio (DR), was a useful single criterion to differentiating between soils that were susceptible to erosion from those that were not. Igwe (2005) also showed that CDR (clay dispersion ratio) correlated with dithionite extractable iron (Fed). The CDR is a micro-aggregate stability index. The higher the CDR, the higher the amount of clay dispersed in water because of low micro-aggregate stability.A predictive model which use WDC and its indices includes the revised universal soil loss equation (RUSLE) (Igwe, 2005). The soil erodibility index (K), an index describing the inherent erodibility of a soil, is used in this model to assess and compared the contribution of other factors to erosion. Factors correlating substantially with this index contribute immensely to erosion. In soils from southeastern Nigeria, CDR and DR correlated substantially with the K-factor (Mbagwu and Bazzoffi, 1998). Igwe, Zarei and Stahr (2006) also found a positive correlation between WDC and CDR in Nigerian soils. Igwe (2005) observed that the WDC did not correspond with the applied CDR index but instead the DR was a good indicator for assessing the potential erosion of dispersive soils. Similar results were obtained in Ohio soils studied by Bajracharya, Lal and Elliot (1992). The CDR is a derivative of WDC and total clay and DR is an index of water-dispersible clay and silt combined (Igwe, 2005; Igwe and Udegbunam, 2008; Mujinya et al. 2013). Both indicate clay stability, the higher the values for CDR and DR, the lower the aggregation in soil and this lack of microaggregate stability can favour erosion. These indices can be used to predict erodibility and potential soils loss in tropical regions (Igwe, 2005; Igwe and Obalum, 2013).

Another erodibility index, aggregation index (AI), which derives from WDC and total clay ratio has also been used as an indicator of soil erodibility (Rhoton et al. 2007). This index can be used to ascertain the relative erodibility of watersheds, as most suspended sediments reflect all the different types of erosion. This supports the notion that the WDC content is a good parameter to use in estimating easily suspended sediments and typically corresponds well with the likelihood of erosion.

The WEPP of the USDA, mentioned in the general introduction, is a useful indicator of water erosion. One of the problems with using WDC as an input parameter is that WDC was not commonly measured during profile analyses and as a result it is not part of legacy databases. A paper by Brubaker, Holzhey and Brasher (1992) attempts to estimate the WDC content based on soil properties which have previously been determined on legacy data. This study highlights that existing soil information collected can potentially be used in estimating the water-dispersible clay content in soil. These workers also found that sorting the data by the ratio of CEC corrected for organic carbon (CCEC) to total clay significantly improved the overall fit of the model (Brubaker, Holzhey and Brasher, 1992). As a result of that the models did a better job estimating WDC because the activity of the clays were taken into consideration (Brubaker, Holzhey and Brasher, 1992). This meant that these soils could potentially be analysed using models to predict their erodibility.

1.6 WDC in classification systems

Water dispersible clay is used in the World Reference Base (WRB) soil classification system as a proxy for clay stability. Alongside other criteria's, WDC is used in differentiating between ferralic B and argic B horizons. It is specified in the WRB document that within 30 cm from the upper boundary, when the WDC is less than 10% the horizon is normally classified as ferrallic B and if it is greater than 10% it should be classified as an argic B horizon (IUSS Working Group WRB, 2015). Ferralic B horizons have a stable micro-structure which implies that by nature these soils should not have a mobile clay phase (Soil Survey Staff, 2014; IUSS Working Group WRB, 2015). Argic horizons however are characterised by clay movement, and as a result clay accumulates in the subsoil horizons forming textural contrast from A/E to B horizon (Soil Survey Staff, 2014; IUSS Working Group WRB, 2015).

This is a useful diagnostic tool because these two horizons can be similar. The logic of using WDC in this classification system is that because ferralic horizons have a stable clay phase compared to argic horizons they must have low WDC. If ferralic horizons contain a high WDC content it means that they are no longer stable and do not meet the criteria to be classified as ferralic subsoils. It is evident from the diagnostic criterion set for argic horizons that clay accumulation is a dominant process for these profiles. Ferralic horizons are quite similar to the South African red and yellow-brown apedal horizons while several horizons and soil properties meet the standard set for argic profiles (Fey, 2010). The WDC benchmark also helps if a ferralsol soil group has a ferralic and a argic horizon. The argic horizon in these instances must not have more than 10% WDC to fulfil the criteria for ferralsols.

1.7 Conclusions

Water dispersible clay affects various processes in soil and is often used as a proxy for aggregate stability and clay mobility in soil. It contributes towards soil degradation, surface crusting and sealing, it results in water erosion and facilitates the transport of contaminants. It is used in erosion models as an input parameter. Despite the recognised importance of WDC, determination of this clay fraction is not standardised. There is also no method suitable for determining WDC on reduced-sample sizes. A method for estimating the WDC content for reduced-sample sizes would therefore be beneficial for archived samples.

Chapter 2 : Testing water and chemically dispersible clay extraction techniques

2.1 Introduction

Water dispersible clay is a commonly determined soil parameter, however, there is no standardization of the extraction method and this is problematic when interpreting WDC data. The WRB method for WDC is described in one sentence as "the clay content found when the sample is dispersed with water without any pre-treatment to remove cementing compounds and without use of a dispersing agent" (IUSS Working Group WRB, 2015). This would imply an adjusted particle size analysis (PSA) method is used. In other words, sand phase was sieved, silt and clay determined by sedimentation followed by extraction using pipette method. All steps of the PSA were followed except the removal of cementing agents. For the case of brevity, this will be referred to as the adjusted PSA method. Although the PSA approach is the most common method used for determining WDC, numerous other methods are reported in the literature (summarised in Table 2-1) that show differences in shaking type, shaking time, soil-liquid ratio and clay separation and extraction method.

One problem with the PSA technique is the relatively large sample size (as much as 40g of soil is required for low clayey soils.) required for the particle size analysis (PSA) procedure as proposed by Gee and Or (2002). This holds challenges when only a small sample is available, for example archive samples. This procedure is also time consuming, labour intensive and requires numerous sedimentation flasks. In addition, PSA procedures vary in terms of the measurement of clay (pipette vs hydrometer) and in terms of agitation technique (electric mixer vs manual shaking).

Physical agitation is the only dispersion mechanism in WDC extraction. Agitation type and energy is important in WDC extraction procedures because insufficient mixing of samples could lead to aggregates not breaking down efficiently leading to misrepresentation of WDC measurements. There is supporting evidence suggesting that the higher the input energy soil aggregates are subjected to the greater their breakdown and release of WDC (Kjaergaard et al. 2004b, Czyż and Dexter 2015). Table 2-1 shows a range of agitation techniques have been used in WDC extraction including electric mixing, end over end and reciprocal shaking, sonication as well as a combination of manual and mechanical techniques. In PSA, both electric mixing and reciprocal shaking are used to agitate the soil suspension (Gee and Or, 2002). They are used interchangeably, but the electric mixer is the most commonly used as sample mixing is approximately 5 minutes compared to overnight with reciprocal shaker. For smaller samples electric mixing is not possible thus reciprocal shaker at high speed (El Swaify, 1980; Seta and Karathanasis, 1996) is recommended. The reciprocal shaking or electric mixing procedure is aggressive and is not a true representation of the conditions soils are subjected to under field conditions but can be used to estimate the upper-level of WDC dispersion. Although the agitation methods are interchangeable in PSA, in the absence of a dispersion agent, it is not known how agitation type affects the amount WDC extracted. Thus, establishing the effect of agitation type has on WDC extraction is an important step in standardising the extraction procedure.

Another aspect that contributes to agitation energy is agitation time. From Table 2-1 it can be seen that there is no consistency in shaking times used for WDC extraction. For example, Rengasamy et al. (1984) agitated samples for only 30 seconds, Barzegar et al. (1994) agitated samples for 2 hours, Nguetnkam and Dultz (2011) for 16 hours and Kjaergaard et al. (2004b) overnight. The effect of shaking time on WDC extraction efficiency has not been established and may be an important aspect of standardisation.

The sample size, sample volume and presence of dispersion agents also differs in WDC extraction methods (Table 2-1). Mujinya et al. (2013) used 10 g soil and 400 ml deionised water in a 1000 ml bottle, De Oliveira, De Costa and Schaefer (2005) used 30 g and 100 ml deionised water in a 200 ml bottle and Liu et al. (2016), used 1 g soil mixed with 100 ml pure water into a 250 ml beaker. Huang et al. (2016) used a 15 g soil sample in a 1000 ml of deionised water and adjusted the pH to 8-9 (by 0.01 mol/l NaOH). These different soil-solution ratios and vessel sizes may also have an effect on agitation energy and WDC extraction efficiency.

Although sedimentation is usually the method used for clay separation (Table 2.1). Seta and Karathanasis (1996) attempted to simplify and speed up the WDC extraction procedure by using a centrifuge method where soil suspensions were centrifuged (at 750 rpm for 3.5 minutes) instead of being gravimetrically settled. This method is based on the method of Mehra and Jackson (1958). The advantage of a centrifuge method is that it saves sedimentation time and reduces the need for glassware and laboratory space. The simplicity of this centrifuge method is very appealing but there have been no studies conducted comparing the extraction efficiency of such a method with the sedimentation technique.

The pipette and hydrometer methods are used interchangeable in traditional PSA analysis for clay measurement. Sensitivity of the hydrometer method can be an issue in soils with low clay contents (Elfaki et al. (2016)) and this may also be a factor in soils with low WDC. Seta and Karathanasis (1996) used a decant method for clay removal after centrifugation. None of these methods have been tested against each other for WDC measurement and could provide another source of variation in the techniques used.

A potentially problematic aspect of the WDC method is the lack of clarity in terms of how it should be expressed. Water dispersible clay is frequently expressed as a fraction of the total clay (Calero, Barron and Torrent, 2008; IUSS Working Group WRB, 2015; Le Roux, 2015). However, it is only correct to do this if the WDC is extracted under the same conditions as the PSA used to determine the total clay. Based on Table 2-1 it is clear that simpler methods are often used to determine WDC and this could lead to over or under estimation of WDC. Another option is to express the WDC extracted using a particular method as a percentage of the total soil (Rengasamy et al. 1984; Karathanasis, Johnson and Matocha, 2005; Igwe and Udegbunam, 2008; Paradelo, van Oort and Chenu, 2013; Liu et al. 2016). This is a more accurate expression of WDC if the WDC is determined via a method other the adjusted PSA technique. It also has the benefit of being easier to determine (a texture analysis is not required), but has limited comparative use in relating soils with different clay contents. Expressing WDC as a percentage of the total clay or as a percentage of the whole soil, can lead to confusion. Igwe (2005) tried to clarify the issue by introducing a different term called clay dispersion ratio (CDR) to express WDC as a fraction of the total clay phase (i.e. CDR=WDC/TC). However, this has not been overwhelmingly adopted with most workers still using the term WDC to express the amount of water dispersible colloids, as either a fraction of the total clay content or as a fraction of the fine earth. This adds to the uncertainty of the determination and creates the impression that the ratio in which WDC is expressed as has not been given much attention in the past. Another potential denominator for expressing WDC, is the fraction of clay dispersed in a mixture of sodium hexametaphosphate and sodium carbonate (without removal of aggregating agents), extracted in the same manner as WDC. This fraction would then serve as the upper limit of dispersive clay in any given soil in its naturally aggregated state. It would also solve the problem of comparing WDC with total clay when the two fractions are not determined under the same conditions. Such an approach has not been tested and will be explored in this study.

From the above discussion it is clear that there is a lack of standardisation in the extraction and expression of WDC, which makes comparisons between soils and the use of threshold values problematic. Although a few simplified methods exist that use a smaller amount of soil than the PSA procedure, these methods have not been calibrated with the adjusted PSA procedure. This chapter aims at (i) comparing the WDC extraction techniques in terms of agitation type and clay determination methods commonly used in the adjusted PSA, (ii) establishing how WDC and chemically dispersible clay relate to total clay and if these two fractions differ in terms of mineralogy and finally, (iii) comparing a simple, reduced sample, centrifuge method with the adjusted PSA method.

Table 2-1: Methods commonly used to extract and measure water dispersible clay (WDC) together with the agitation type and time. Modified from Kjaergaard et al. (2004b) and updated

WDC settling methods	WDC extraction and/or measurement	Author(s)	Soil-liquid ratio	Agitation type[1]	Agitation time[2]
Sedimentation	**Pipette**				
	- Gravimetrically	Van Reeuwijk (2002)	1:20	End-over-end	Overnight
	- Not mentioned	Mujinya et al. (2013)	1:40	Not specified	Overnight (ns)
	- Spectrometrically	Rengasamy et al. (1984)	1:5	Mechanical stirrer	30 seconds
	- Gravimetrically	Yang et al. (2009)	1:4	Sonication	Not specified
	Hydrometer				
	-Gravimetric	Igwe (2001)	1:25	Mechanical agitation	8 hours
	Siphoning				
	- Gravimetrically	Kjaergaard et al. (2004b)	1:8	Reciprocal shaker and manual shaking	16 hours and 1 minute
	- Gravimetrically	Gregorich, Kachanoski and Voroney (1988)	1:5	Sonication	Varied (ns)
	- Gravimetrically	Gregorich, Kachanoski and Voroney (1988)	1:5	Laboratory shaker	20 minutes
	- Gravimetrically	Jozefaciuk et al. (1995)	1:10	Mechanical shaking	14 hours
	Decanting				
	- Gravimetrically	Nguetnkam and Dultz (2011)	1:2.5	Not specified	16 hours
	Extraction type not mentioned				
	- Gravimetrically	De Oliveira, De Costa and Schaefer (2005)	1:3.3	Horizontal and manual shaking Overhead stirrer	3 hours and 1 minute
	- Spectrometrically		1:5	End-over-end	30 seconds
	- Turbidity	Rengasamy et al. (1984) Barzegar et al. (1994)	1:5	Mechanical shaking	2 hours

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[1] Agitation type as described by worker(s)

[2] ns: hours were not specified in the paper

Table 2-1: (Continued) Methods commonly used to extract and measure water dispersible clay (WDC) together with the agitation type and time. Modified from Kjaergaard et al. (2004b) and updated

WDC settling methods	WDC extraction and/or measurement	Author(s)	Soil-liquid ratio	Agitation type[3]	Agitation time[4]
Centrifuging	Decant				
	- Gravimetrically	Seta and Karathanasis (1996)	1:20	Mechanical shaking	Overnight (ns)
	- Gravimetrically	Le Roux (2015)	1:20	End-over-end	Overnight (ns)
Settling method not mentioned	Extraction type not mentioned				
	- Dynamic light scattering	Poli et al. (2008)	1:36	(i) Stirrer and (ii) Sonication	10 hours + 90 min (i), 60 minute (ii)

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[3] Agitation type as described by worker(s)

[4] ns: hours were not specified in the paper

2.2 Materials and Methods

2.2.1 Soil samples

The soils used in this chapter were archived samples house in the Department of Soil Science. The majority of soils were collected and described by Le Roux (2015), but other soils were also included from other studies. Only subsoils from the B1 horizon were selected for this study. The locations of the soils used in this study are indicated in Figure 2-1. The samples were collected in close proximities and because the map is big they appear as one point in the Figure. For this chapter, only twelve samples (all from the study of Le Roux (2015) were used to develop and test the method. The physicochemical properties and soil classification for these soils is indicated in Table 2-2. In Chapter 2, which involved improvement of this method, only nine samples were used because of low sample volumes.

2.2.2 Textural analysis

Le Roux (2015) determined total clay using a laser particle size analyser. Total clay was also determined using the PSA method after removal of all aggregation agents (Gee and Bauder, 1986). The Fe and Al content were determined using atomic absorption spectrophotometer (AAS) and added to the colloidal fraction.

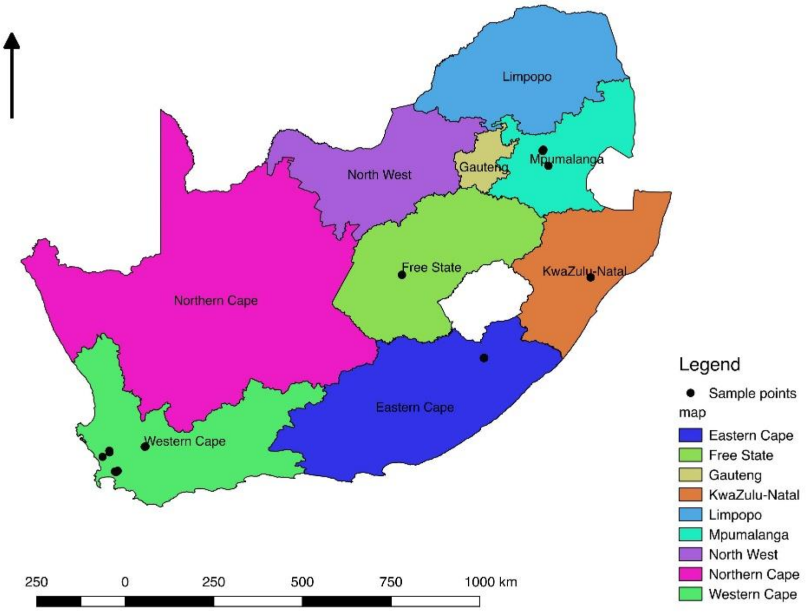

Figure 2-1: South African map indicating the (A) Western Cape and (B) Mpumalanga province from which the soil samples used in this study were obtained

Table 2-2: Physicochemical properties and the soil classification systems used to describe the selected B1 horizons in this chapter

Soil sample	**pH (water)**	**pH (KCl)**	**Sand**	**Silt**	**Clay**	**OC**	**Fe citrate-bicarbonate-dithionite (CDB)%**	**SA diagnostic horizons**[1]	**WRB FAO diagnostic horizons**[2]	**USDA Soil Taxonomy diagnostic horizons**[3]
			%					**Classification systems**		
Br 1.2	5.4	4.3	77.8	14.5	7.7	0.9	1.7	re	ferr	oxic
Pb 2.2	4.8	4.3	66.4	19.8	13.8	0.7	1.1	ye	ferr	oxic
Us 1.2	5.0	4.3	57.7	25.3	17.0	1.0	2.9	re	ferr	oxic
Bp 1.2	6.2	5.1	56.2	25.5	18.3	0.9	3.2	ne	arg	arg/kan
Hh 1.2	5.9	4.7	38.0	43.2	18.8	0.6	2.1	ne	arg	arg/kan
Hh 3.2	5.1	4.1	35.6	37.8	26.6	1.2	3.7	ne	arg	arg/kan
Hh 4.2	5.0	3.9	34.0	44.5	21.5	1.3	2.6	ne	arg	arg/kan
Mb 1.2	5.7	4.5	67.4	18.9	13.7	0.6	1.2	ne	arg	arg/kan
Pb 3.2	4.7	3.8	25.0	60.0	15.0	0.9	2.3	ne	arg	arg/kan
W3(1.2)	5.4	4.2	38.8	19.8	39.6	0.4	3.0	ne	arg	arg/kan
Bp 3.2	7.2	6.3	74.2	15.7	10.1	0.8	1.5	ye	argic/ferr	arg/kan
W2	5.4	4.0	10.2	22.1	65.7	0.8	Not available	pr	arg	arg

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[1] South Africa's (SA) taxonomy where: re – red apedal B, ye – yellow-brown apedal B, ne – neocutanic B and pr – prismacutanic B (Soil Classification Working Group, 1991)

[2] World Reference Base (WRB) taxonomy where: fe – ferralic, arg – argillic, orc – ochric (IUSS Working Group WRB, 2015)

[3] United States Department of Agriculture's Soil Taxonomy where: arg – argillic, kan – kandic (Soil Survey Staff, 2014)

2.2.3 Water dispersible clay and chemically dispersible clay extraction methods

2.2.3.1 Sedimentation methods: pipette and hydrometer measurements

The adjusted PSA method was used as a benchmark method for both WDC and chemically dispersible clay (CDC). The method is the same as particle size analysis (PSA), however there is no removal of binding agents. The WDC treatments added only deionised water while the CDC treatments had a 10 ml mixture of sodium hexametaphosphate and sodium carbonate (10%) added in each 1000 ml water volume prior to dispersing samples. Two separate sedimentation mixing methods were used to disperse the WDC and CDC, an overhead electrical mixer (Hamilton Beach HMD200 Single-Spindle Drink Mixer 120V) and a reciprocal shaker supplied by Scientific Manufacturing Paarden Eiland Cape Town. The soil was mixed for 5 minutes using electrical mixer and 24 hours when the reciprocal shaker was used (Soil Cassification Working Group, 1991). A mechanical impeller physically mixes the soil in a mixing machine in the electric mixer. While a horizontal motion mixes the soil in reciprocal shakers. The sand was separated from silt and clay using a 2 mm sieve. The WDC and CDC were extracted from each agitation method by pipette, and the hydrometer readings were taken for both treatments at the same time intervals. All extractions were done in triplicates.

2.2.3.2 Reduced sample centrifuge method

The reduced sample centrifuge method was based on the centrifugation method of Seta and Karathanasis, (1996) but modified in terms of sample size and extraction procedure. Two extraction treatments were used for the centrifuge method. In one treatment clay was extracted after centrifugation by decantation (centrifuge-decant) and in the other treatment the suspension was accurately pipetted (centrifuge-pipette). For both the centrifuge-decant and centrifuge-pipette methods 2.5 g soil was added into centrifuge tubes, with or without dispersing agent. Chemical dispersing agent was made up using the guideline specified by the Soil Classification Working Group (1991). A 0.5 ml mixture of sodium hexametaphosphate and sodium carbonate (10%) aliquot and 49.5 ml distilled water was added into 50 ml polypropylene tubes for the CDC samples, while 50 ml deionised water was added with no chemical dispersant for the WDC samples. The centrifuge tubes were placed horizontally on a high-speed reciprocal shaker (ca. 148 rpm) for 20 hours. The samples were monitored in random intervals to ensure that mixing was effective. All samples were centrifuged (Sigma 2-16P, Germany) at 800 rpm for 3.5 minutes as described by Le Roux (2015). For the decanted samples, the supernatants were carefully poured out up to the 7.5 ml mark whereas for the pipette method a fixed 42.5 ml was extracted using a Lowy pipette. Three replicates were extracted for both WDC and CDC, oven dried at 105 °C (overnight) and weighed using a 0.001 g decimal place scale.

2.2.4 Mineralogy for the WDC and CDC suspension

The method proposed by Harris and White (2008) was used to determine the mineralogy of the WDC and CDC separated for XRD. No cementing agents were removed during sample pre-treatment. The WDC and CDC mineralogy was determined on ten samples (included in Table 2-2 excluding samples W2 and W3). For each sample Mg-saturation were prepared. The K-saturation was not performed because the soils analysed did not contain any 14 Å peaks. The clay fraction was pipetted and flocculated by adding 1M HCl. The Mg-saturated slurry was agitated on reciprocal shaker supplied by Scientific Manufacturing Paarden Eiland Cape Town and centrifuged (Sigma 2-16P, Germany). The samples were washed twice with 0.5 M $MgCl_2$ and distilled water to remove excess Cl^- ($AgNO_3$) and then oven dried at 105 °C (overnight). Finely ground clay powders were sent to iThemba Laboratories in Cape Town for XRD analysis at angles ranging from 4 to 60 degrees.

2.3 Results and Discussion

2.3.1 Hydrometer vs pipette methods for determining WDC and CDC

Hydrometer and pipette methods were compared for the determination of WDC and CDC following sedimentation. The results are expressed both per kg soil (Figure 2-2 a and c) and per kg total clay (Figure 2-2 b and d). The WDC is also expressed as a function of CDC (Figure 2-3). There is a very strong correlation (R^2=0.98) between WDC determined by the pipette and hydrometer when expressed per kg clay and per kg soil. The correlation between methods for CDC (g/kg_{clay}) is weaker (R^2=0.61), and improves when expressed per kg soil (R^2=0.89), (Figure 2-2 c and d). The intercepts for CDC (g/kg_{soil}) and WDC (g/kg_{clay}) are statistically different from zero ($p<0.05$). This could indicate a systematic error that the hydrometer may not be sensitive enough to detect low clay contents. The standard error is reduced for both fractions when they are expressed as a proportion of total soil rather than the clay fraction. The reasons for this are likely to be two-fold: i) error generated from determining total clay and ii) magnification of the error by normalisation with a smaller component of the total soil. Due to the much higher proportion of CDC, the magnification of the error is greater, especially when expressed per total clay. When WDC is expressed as a percentage of CDC, an extremely good correlation is obtained between the two methods with gradient close to 1 and a low standard error (Figure 2-3). This supports the justification of point i) above relating to error in total clay determination as CDC is a much simpler parameter to determine than total clay.

Despite the good correlation between the two methods for WDC, hydrometers are buoyancy-based apparatus and have a detection limit of 1% (Sheldrick and Wang, 1993). The pipette method is more sensitive than the hydrometer method Elfaki et al. (2016) and would be more practical for reduced sample set-ups. Because of this, only the sedimentation-pipette method (hereafter called the adjusted PSA method) was used to set the WDC benchmark for this study and was used to determine the extraction efficiency of other methods. To reduce the effect of error in the total clay determination all further extraction methods will express WDC and CDC as a percentage of the soil.

2.3.2 Relationship between CDC, WDC and total clay (TC)

Figure 2-4 presents CDC and WDC determined using the adjusted PSA method and total clay determined in the same manner after the removal of all cementing and binding agents. A strong correlation ($R^2 = 0.89$) was found between CDC and total clay (Figure 2-4 a). The relationship between these factors is expressed by the equation, $y = 0.54x + 35.20$, which describes the chemically dispersed-sedimentation method CDC extraction efficiency. Even though there is a good relationship the slope for these two factors is relatively low ($m = 0.54$), indicating that on average only 54% of the total clay is extracted when cementing agents are not removed. The remainder of the clay is locked up into organically bound or sesquioxide bound aggregates. Given the low OC content (Table 2-2) and their advanced stage of weathering, sesquioxide stabilization of aggregates is likely to be the greatest contributor accounting for the low clay extraction using only chemical dispersant. The WDC has a poor correlation ($R^2 = 0.11$) with total clay (Figure 2-4 b). In a study conducted by Curtin et al. (1994) on samples with total clay ranging from 20-63%, a positive correlation between total clay and WDC was observed. A positive correlation between these factors was also observed by Vendelboe et al. (2012) and Brubaker, Holzhey and Brasher (1992). Kjaergaard et al. (2004b) observed a negative correlation between WDC and clay content. While Seta and Karathanasis (1996) found no correlation with clay contents ranging between 21-75%. These workers used samples obtained from topsoils with varying soil types. Thus, it would appear there is no universal pattern in the relationship between WDC and total clay. This would be expected given the wide range of physicochemical conditions that favour clay dispersion. For example, the E-horizons (albic) generally have a low total clay content and the tendency of this clay content to disperse is greater than most horizons (Fey, 2010), therefore soils with similar clay content do not necessarily reflect the same dispersion pattern because other features associated with the soil have a role in its dispersion.

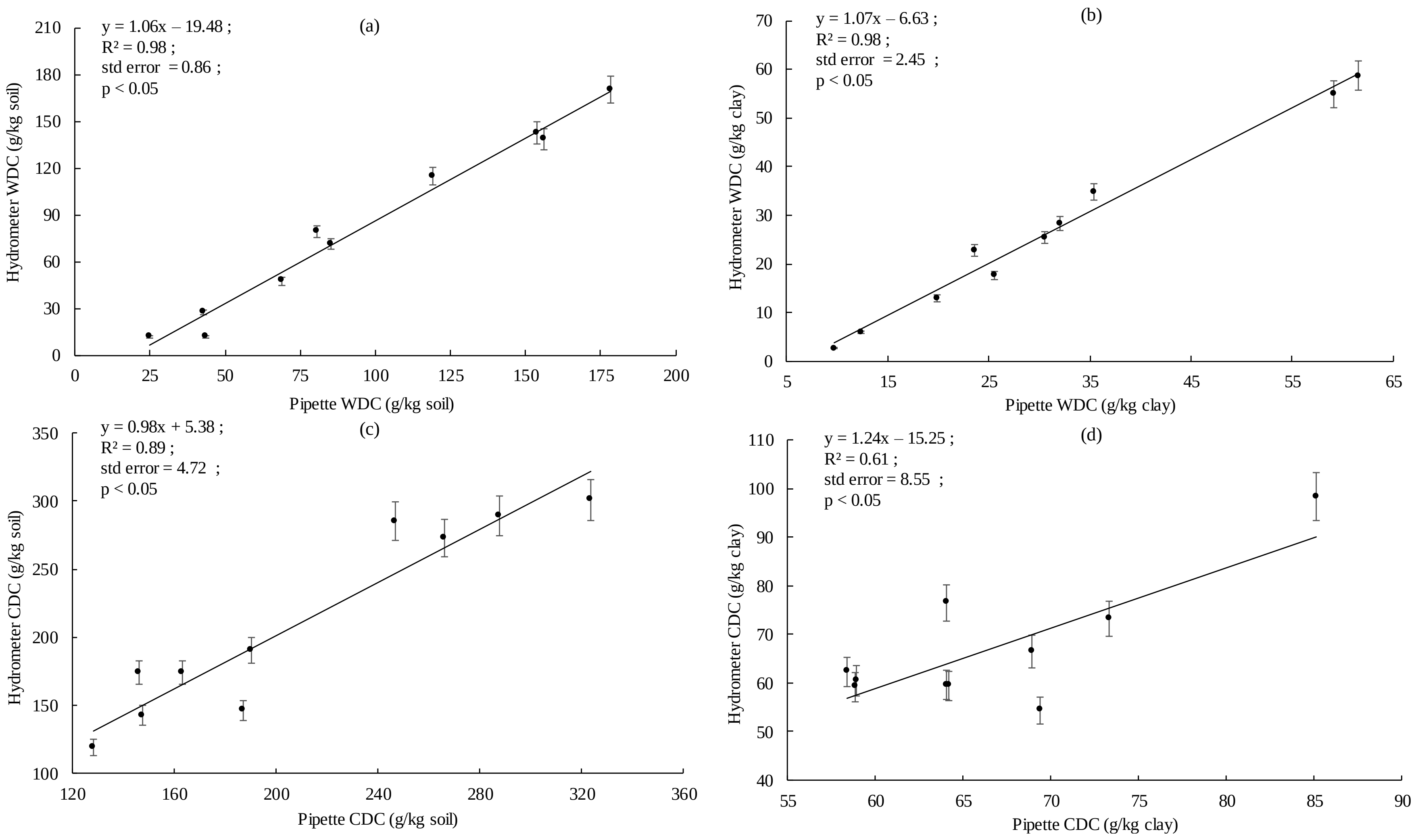

Figure 2-2: The sedimentation-pipette versus hydrometer method, expressed for WDC a) per kg soil and b) per kg clay and for CDC expressed c) per kg soil and d) per kg clay

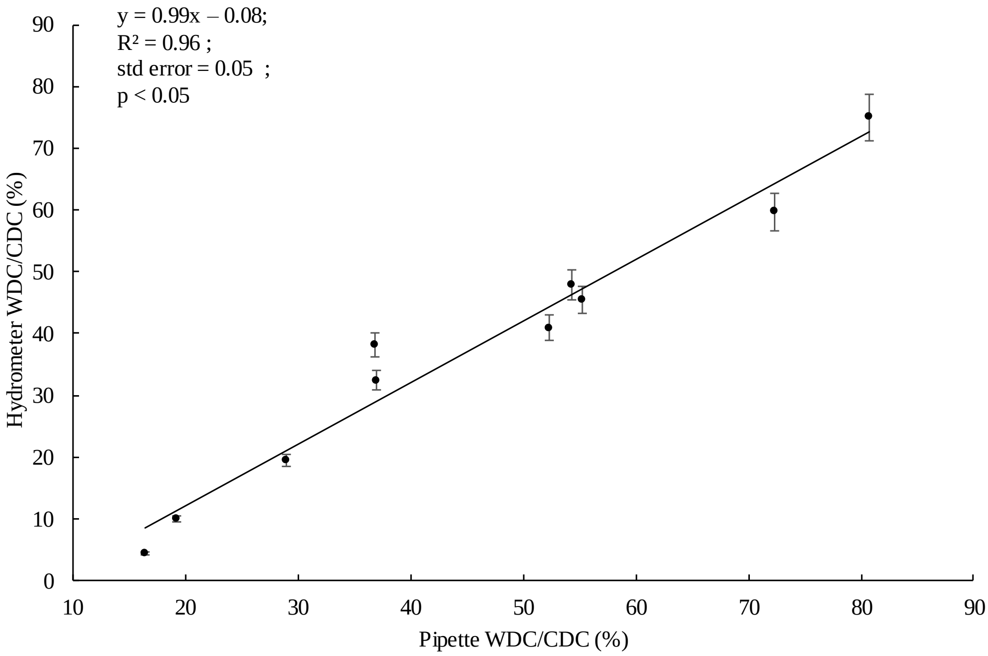

Figure 2-3: The sedimentation-pipette method versus hydrometer method where WDC is expressed as a fraction of the chemically dispersed clay (CDC) percentage

2.3.3 Mineralogy of water dispersible clay and chemically dispersible clay

In order to establish if WDC differed mineralogically to CDC in these soils x-ray diffraction analysis was carried out on the WDC and CDC sedimentation extracts. The soils show similar results. Representative patterns for the two fractions are shown for sample Pb 2.2 (Figure 2-5) with the remaining patterns presented in Appendix B (B1-B9). The patterns show that both WDC and CDC extracts show both kaolinite and illite (7.21, 3.59, 2.50 Å), followed by smaller peaks of mostly goethite (4.17, 2.69) and hematite (2.69 Å), (Figure 2-5). The intensity and sharpness of the kaolinite peaks for both WDC and CDC infers a crystalline mineralogy. Importantly there appears to be no mineralogical difference between WDC and CDC. This trend is consistent to the observation by Seta and Karathanasis (1996) who found no difference in the mineralogical composition of WDC and sodium dispersible clay fractions. Additionally, these workers also found that these two fractions were dominated by kaolinite which influenced the WDC content recovered negatively. They deduced this to the presence of variable charge properties present on kaolinite minerals which reduces clay dispersibility (Seta and Karathanasis, 1996).

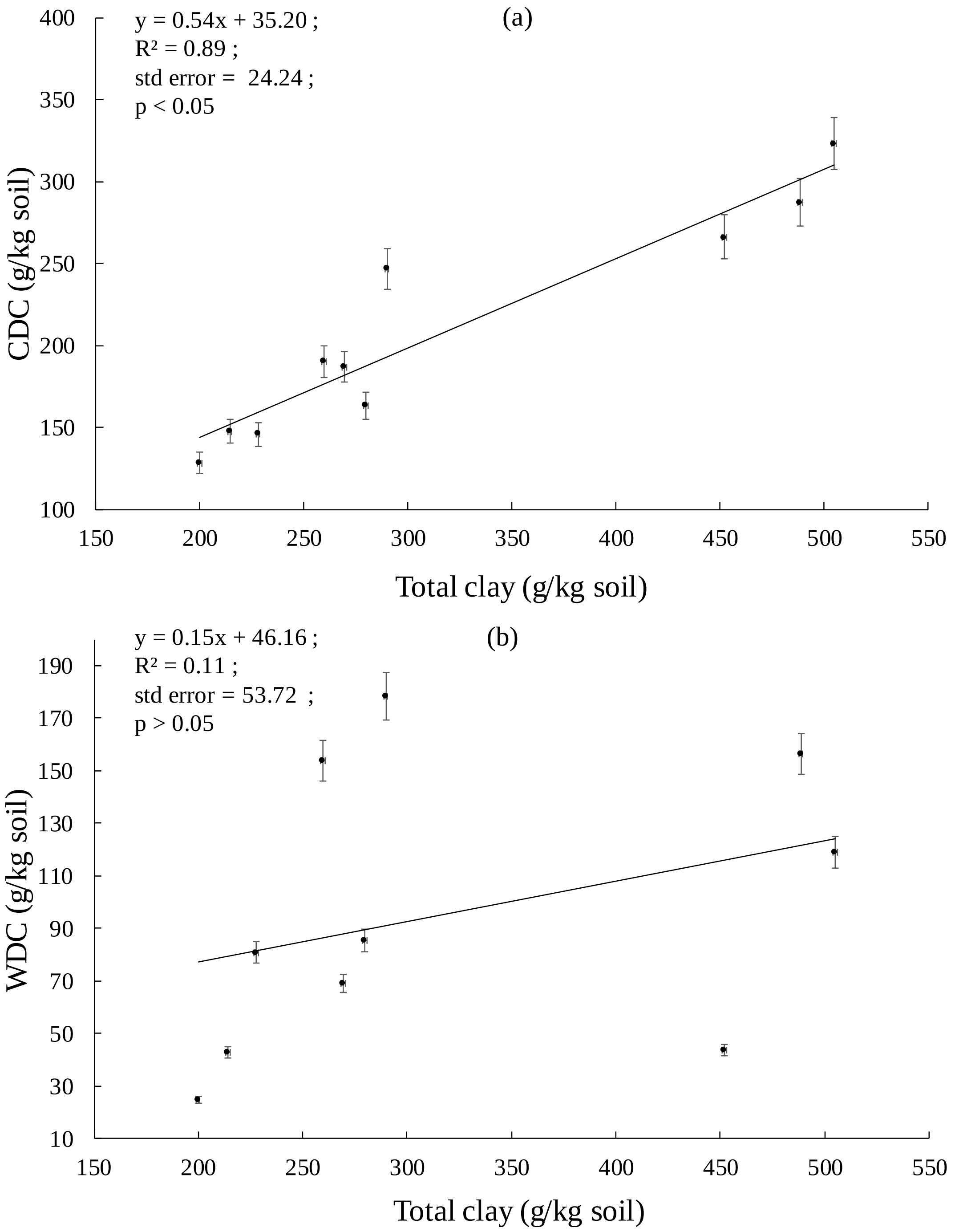

Figure 2-4: The relationship between a) chemically dispersible clay (CDC) and b) water dispersible clay (WDC) as determined by sedimentation-pipette and total clay for 10 apedal soils. The error bars indicate standard error of the mean

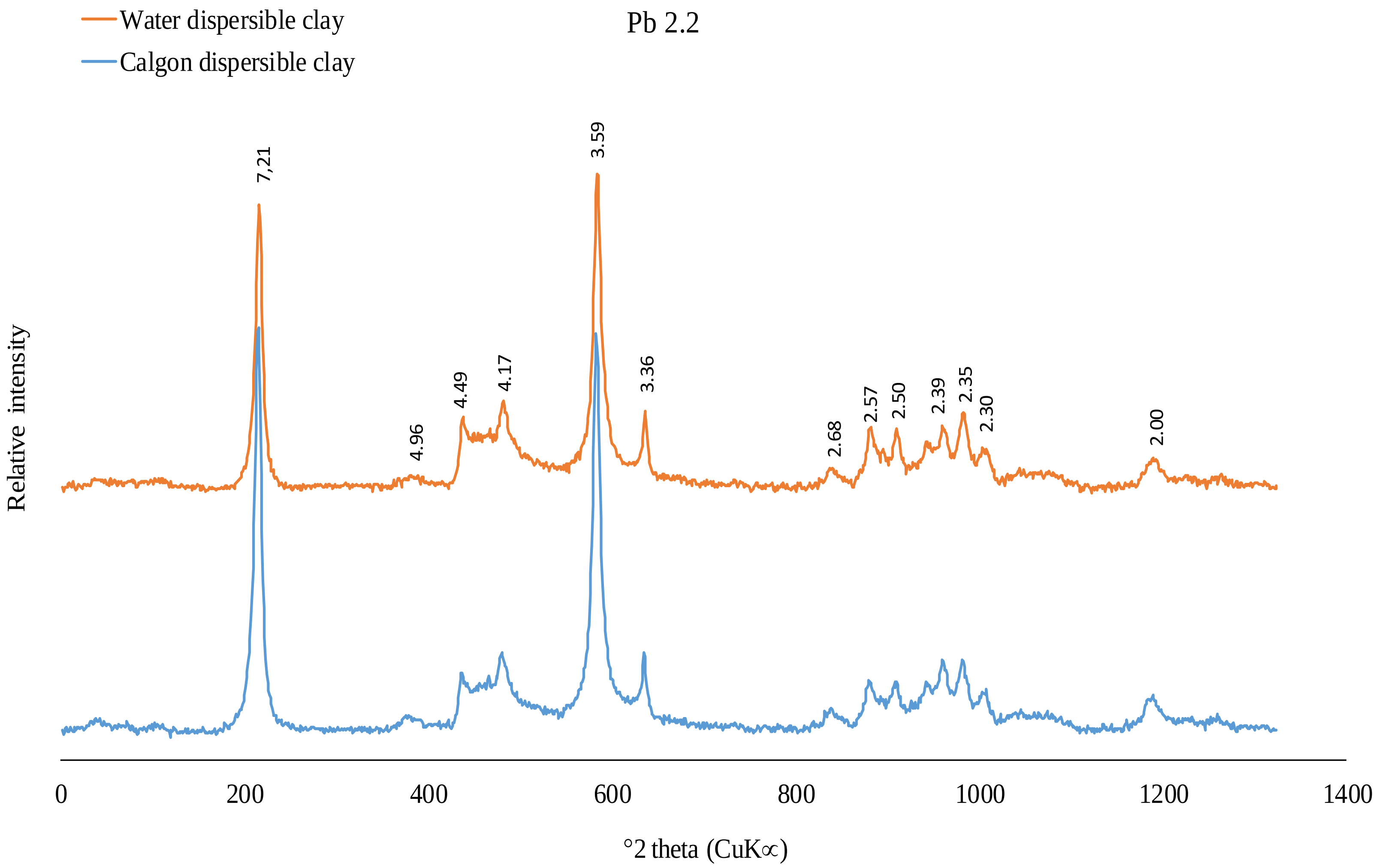

Figure 2-5: X-ray diffraction patterns of WDC and CDC separated from the subsoil of profile Pb 2.2 found in these two treatments.

2.3.4 Assessment of a reduced sample centrifugation method for determining WDC and CDC

A reduced-sample centrifuge-decant method was used to extract the WDC and CDC which was compared to the adjusted PSA method (Figure 2-6 a and b). This decanting method was suggested by Seta and Karathanasis (1996) who after centrifuging poured out the suspension and determined the clay fraction gravimetrically. The CDC extracted using this method has a relatively high correlation (R^2 =0.86) with a good extraction efficiency (105%, (Figure 2-6 b)) compared to the adjusted PSA method. The WDC correlation is lower (R^2 =0.72) with a very poor extraction efficiency (29%). Decanting is far less accurate and controllable than pipetting, therefore the method was repeated instead the clay was pipetting from the centrifuge tubes. The results for the centrifuge pipette method are shown in Figure 2-6 c and d. There is a reasonably strong correlation (R^2 >0.84) between the centrifuge-pipette method and the adjusted PSA method, for both WDC and CDC extractions. There is a very good extraction efficiency for CDC (91%) but, the centrifuge-pipette method only extracts half (49%) the WDC compared to adjusted PSA. The higher dispersion produced in CDC compared to WDC is an indication that the dispersion produced by the reciprocal shaker is assisted by the dispersion agent used during agitation. Expressing the WDC as a percentage of CDC slightly improved the WDC extraction efficiency for both methods, improving the decant method from 29% to 32% and from 49% to 55% for the pipette method (Figure 2-7 a and b). The pipette method reproducibility is more reliable compared to the decant method (coefficient of variation (CV) = 2.58% and 11.58%, respectively). The higher CV in the decant method probably has to do with the lack of control in decanting suspensions and problems associated with extracting unwanted fractions (i.e. silt) which would misrepresent the WDC. To establish if the centrifuge-pipette method was extracting colloids of the right fraction a particle size analysis was conducted on the CDC of sample W3 (Figure 2-8). This sample was selected due to the abundance and easy access of the sample (collected from the Stellenbosch research farm). These results show that 99.4% of colloids are <2 um, which suggests the centrifuge method is appropriate for clay separation.

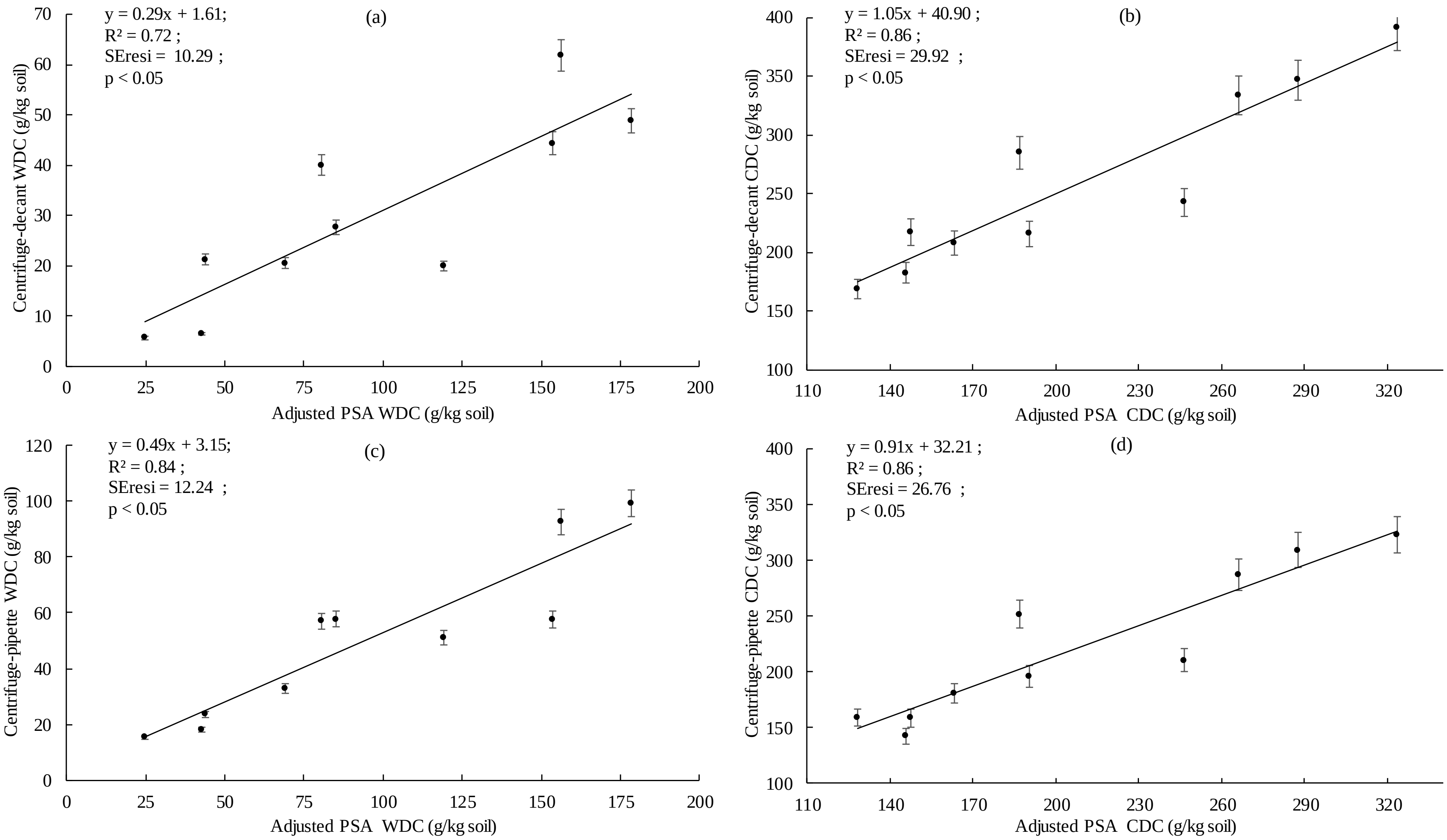

Figure 2-6: WDC and CDC extracted using the centrifuge-decant (a and b) and centrifuge-pipette (c and d) methods compared to the adjusted PSA method, expressed as a function of total soil

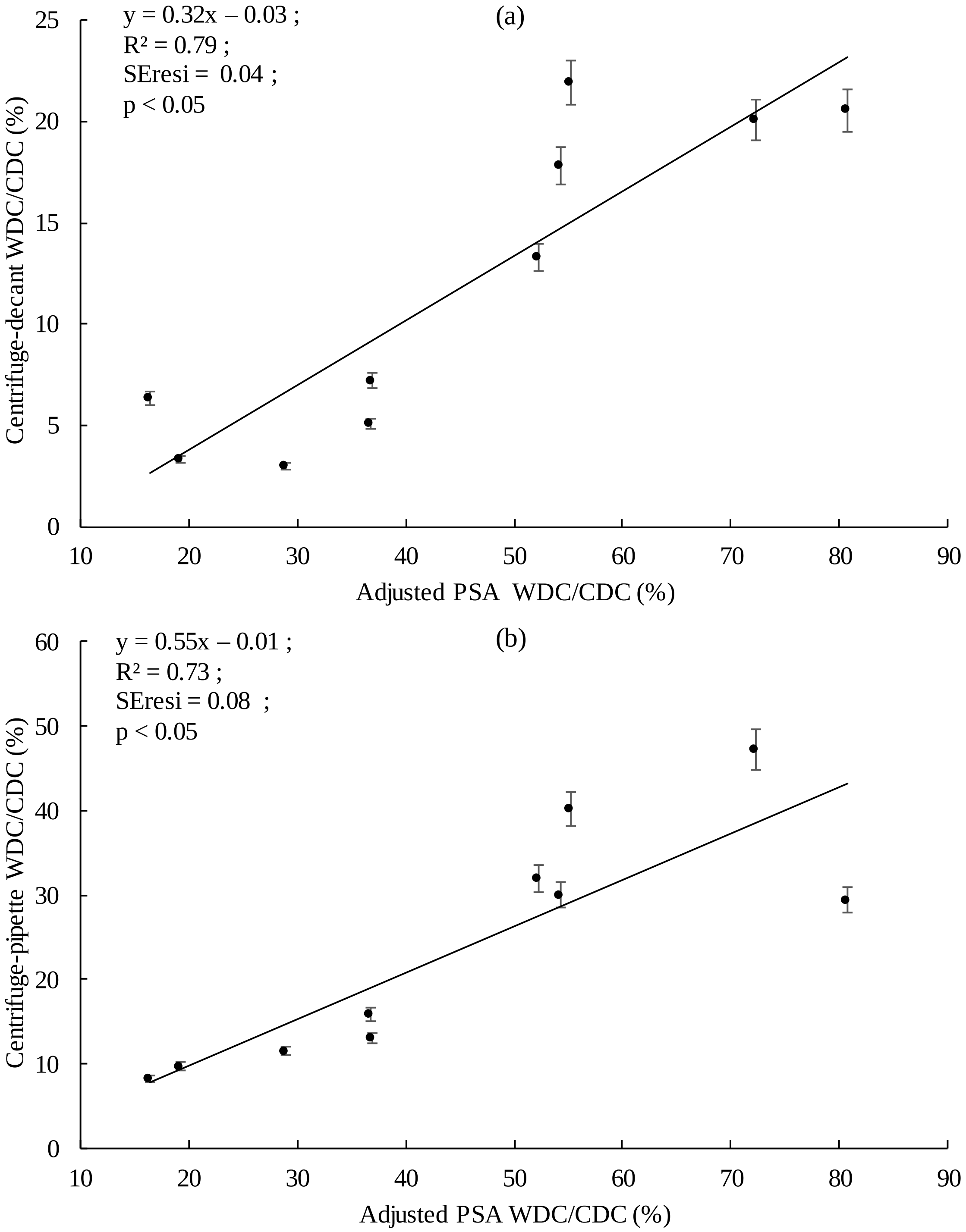

Figure 2-7: WDC percentage extraction efficiency of the (a) centrifuge-decant and (b) centrifuge-pipette method compared to the adjusted PSA method expressed as a function of CDC.

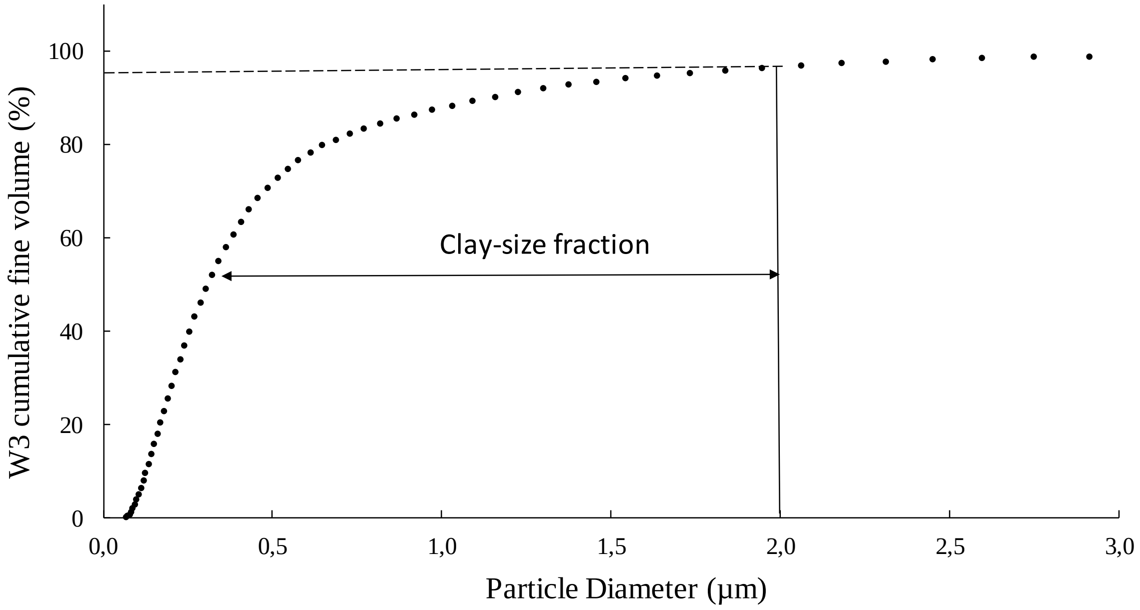

Figure 2-8: Cumulative particle size distribution on the CDC of sample W3, indicating the clay-size fraction (<2 um) obtained after separation by centrifugation

The high efficiency of the CDC fraction extraction using the centrifuge method suggests that, in principle, the reduced sample technique may work, but the physical agitation of the samples is insufficient to extract the WDC. The adjusted PSA method used an electric mixer for physical agitation, while the centrifuge method used reciprocal shaking. Although these two agitation methods are used interchangeably for PSA, the addition of a dispersing agent may reduce the effect of any differences in physical agitation methods. For WDC determination, where no dispersant is added, agitation techniques may have an effect. To establish if the mixing technique was responsible for the lower extraction efficiency of the centrifuge-pipette method, electric mixing and reciprocal shaking, were compared for three soils using the adjusted PSA method (Figure 2-9). These results show there is no significant difference (p=0.66) between the two agitation methods for either CDC or WDC (Figure 2-9 a and b). This suggests that the agitation technique is not responsible for the difference in the WDC extracted in the centrifuge-pipette and the sedimentation method. Which implies that the low extraction efficiency of the centrifuge-pipette method may be due to the incomplete agitation of the suspension rather than using a different agitation type. Agitation by shaking has numerous advantages over the electric mixing such as, small sample volumes can be used, and multiple samples can be prepared simultaneously. Thus, improving the agitation effectiveness of the reciprocal shaker would be required in order to develop a reduced sample WDC extraction technique. The next chapter aims at improving the reduced sample, centrifuge-pipette method to better the WDC extraction efficiency compared to sedimentation-pipette method.

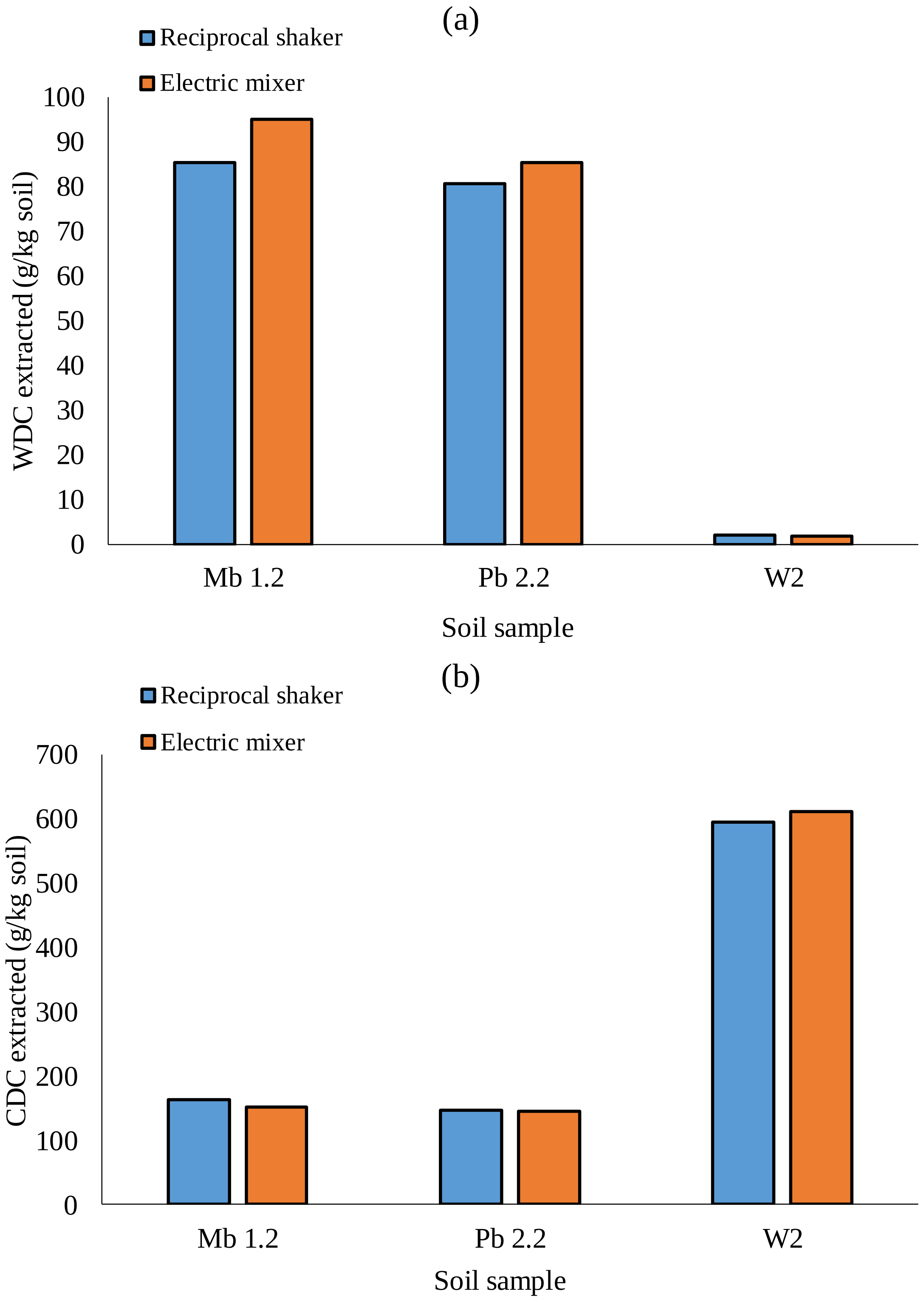

Figure 2-9: (a) WDC and (b) CDC measured after agitating soils using a reciprocal shaker and an electric mixer

2.4 Conclusions

An investigation of the extraction efficiency of different methods commonly used to determine the water dispersible clay (WDC) and chemically dispersible clay (CDC) in soils was compared to the sedimentation-pipette method. Two sedimentation methods (pipette vs hydrometer) and two simple, reduced sample centrifuge methods (pipette vs decanting) were evaluated. As expected, there were no substantial differences in the WDC extraction efficiency for the two sedimentation methods, but the sedimentation-pipette is more sensitive and accurate in determining WDC and therefore used as the adjusted PSA method. The relationship between WDC and CDC determined using the adjusted PSA method and total clay determined in the same manner after removal of all cementing and binding agents revealed a non-consistent trend between these factors. Water dispersible clay had a poor correlation and extraction efficiency with total clay across all soil samples. The relationship between CDC and total clay was better, however the extraction efficiency of CDC to clay content was only half.

Expressing WDC as a function of CDC was comparable to when it was expressed as total soil, and expressing it over total clay correlated the least in all methods. X-ray diffraction (XRD) patterns revealed that the mineralogy of the WDC and CDC content for all the soils tested was similar and that both fractions are dominated predominately by kaolinite.

In the two reduced sample, centrifuge methods tested against adjusted PSA method; the centrifuge-pipette method had a better extraction efficiency but it was only half to adjusted PSA method. Pipetting rather than decanting suspensions has the advantage of extracting reproducible WDC and CDC contents. The low WDC extraction efficiency of the centrifuge-pipette method was inferred to be a result of incomplete agitation after no substantial differences were observed between reciprocal shaking and electrical mixer (using adjusted PSA method). This meant that the two agitating methods were equivalent to each other and can be used alternatively.

Chapter 3 : Optimisation of the rapid, reduced sample size centrifugation method for WDC measurements

3.1 Introduction

The centrifuge-pipette method has shown potential to extract WDC but its extraction efficiency was only 50% of the sedimentation-pipette method. If this method is to be used in expressing WDC some improvements are necessary to optimise it. Soil physical agitation has been shown to have an integral role in separating and releasing small sized fractions in suspensions (Amézketa, 1999). Therefore, one of the factors which would have to be considered when improving the centrifuge-pipette method is different methods of agitation to maximise the separation of WDC from aggregates.

Physical sample dispersion is fundamental in achieving efficient WDC extraction. The commonly-used mixing technique to disperse soils is the reciprocal shaker. In simple terms, this mixing technique (alongside other factors) imitates field conditions when bare soil is subjected to raindrop impact in severe cases (Le Bissonnais, 2006). Kemper and Rosenau (1986) placed an emphasis that for forces causing disintegration to have any practical significance, it is important that they are related to the forces soils experience under field conditions. Because the mechanical forces that soils experience in the field vary from minor human disturbances to the raindrop effect, there is some degree of flexibility to the borders with which it can be applied. This is usually the reason why mixing methods are not standardised. When stability of soil aggregates are compared for size distribution however, this standardisation of the disruptive forces is crucial (Kemper and Rosenau, 1986). The same would also be true for WDC, which is used in erosion models or as a classification threshold. Although aggressive shaking methods may overestimate WDC, it does help create a standard that can be used for comparative purposes.

Pojasok and Kay (1990), indicated that shaking time and period are important factors affecting dispersible clay. Therefore, more detail should be given to the stirring and mixing procedure to ensure homogenous and reproducible results are obtained. Borja, Mercado and Combatt, (2015) found that a higher content of clay was extracted when soil samples were agitated for 6 hours at 60 rpm compared to 15 minutes at 4000 rpm, thus duration of agitation is as important as energy of agitation. A greater amount of ultrasonication applied to the soil suspension, for a shorter period, is more effective in aggregate disruption and clay recovery (Gregorich, Kachanoski and Voroney, 1988). Table 2-1 indicates a wide variety of shaking times used in WDC extraction procedures. It is not known how agitation time effects WDC but in order to standardise results one would want to establish what the effect of agitation time is on extraction efficiency and establish the minimum agitation time required to achieve maximum efficiency.

Another, less common, physical agitation mechanism is ultrasonic vibrations (sonication). More total clay can be recovered when there is higher input energy applied to soil, because this promotes greater aggregate disruption (Gregorich, Kachanoski and Voroney, 1988). Similar to reciprocal shaking, there is lack of standardisation and assessment of the sonication methods. In addition it has been reported that sonication can result in the fragmentation of clay particles (Gee and Or, 2002). This is in contrast to work done by Gregorich, Kachanoski and Voroney (1988) and Środoń (2006), who demonstrated that using a high input sonication technique do not alter or fragment the clay particles. Środoń (2006) also indicated that sonicating samples for a shorter time in a small volume of water is efficient in disintegrating aggregates, and that this should be done before clay separation is performed. This is in agreement with the work by Gregorich, Kachanoski and Voroney (1988), who found that shaking samples by sonication for a shorter time was effective in decreasing the sand-sized fraction (ultimately increasing total clay in suspension) than dispersing them for 16 hours with reciprocal shaker. How the WDC extraction efficiency improves, compared to the standard sedimentation method, using this agitation procedure has not been looked into. This information would be beneficial to standardising the WDC agitation procedure. Over sonicating samples may lead to spillage and loss of material which would negatively affect the clay recovered. It is therefore important to calibrate soils in order to determine the input energy needed to achieve full dispersion because the texture of the soil can affect the dispersion outcome (Schmidt, Rumpel and Kogel-Knabner, 1999; Yang et al. 2009).

Part of the procedure in WDC determination is the gravimetric determination of the clay content. This procedure is lengthy and decreases productivity when many samples need to be analysed in a day. Several attempts have been made to substitute it, but have not been very successful. Photoelectric procedures, the most common of which are turbidity measurements, has been attempted to substitute gravimetric methods for estimating the clay content in soil. Measuring colloidal particles by turbidity is appealing because this parameter best correlates with suspended particles and is easily measured for routine laboratory analysis (Resler, 2011). Preparation and measurement of clay particles can all be done within 5 minutes compared to gravimetric determination which can take hours before the results are obtained. Anderson (2005) described turbidity as the expression of optical properties of liquid that cause more light rays to be absorbed rather than transmitted by a sample. Suspensions with substantial amounts of clay particles in them have an optical impact on water quality which reduces light attenuation. It would then be expected that the turbidity measurements obtained from those samples is higher than in clearer suspensions, because the optical impact in water would be reduced (Davies-Colley and Smith, 2001).

The size composition of the particle, its distribution and concentration in suspension are important contributors to light attenuation in water (Davies-Colley and Smith, 2001; Resler, 2011). Finely-grained, highly concentrated clay particles have a low settling rate and thus these particles remain longer in suspension according to Stokes' Law. The turbidity measurement from these suspensions would typically be higher because of the high concentration of finely suspended sediments (Resler, 2011). Measuring turbidity may possibly be more practical in determining colloids in suspension compared to the time-consuming gravimetric weighing process currently used. However, there has been very little work looking at using turbidity to measure clay contents in suspensions. Such a technique would provide a huge advantage in terms of time saving.

From the above it is clear that there is an opportunity to standardise and optimise WDC extraction techniques. The centrifuge-pipette method shows promise for WDC on small sample sizes, however it requires optimisation to increase its extraction efficiency compared to the adjusted PSA method. Any measures to reduce the time of analysis would also be valuable in method development. This chapter sets out to: (i) improve the WDC extraction efficiency of the centrifuge-pipette method by assessing the effects of headspace, sonication and shaking time on WDC extraction and (ii) explore using turbidity as an alternative to the oven-drying procedure used to measure WDC.

3.2 Materials and Methods

3.2.1 Soil samples

Most of the optimisation in this chapter was done on the subsoil sample W3 due to the abundance and easy access of the sample (collected from the Stellenbosch research farm). The effect of shaking time and sonication on the WDC and CDC extraction efficiency were evaluated using this sample. To examine whether ultrasonication did not result in physical fragmentation of soil particles, the particle size distribution of sonicated and non-sonicated samples from W3 was measured. A calibration curve between the CDC measured gravimetrically using sedimentation method and turbidity was also conducted using this sample.

Nine from the ten soil samples used in chapter 2 were used in improving the centrifuge-pipette method. Due to limited availability of archive sample (Bp 3.2) this sample was excluded in this chapter. The WDC and CDC extraction efficiency of the centrifuge-pipette method was compared to adjusted PSA method, after increasing the headspace in the centrifuge tube was conducted on these nine samples.

3.2.2 Optimisation of agitation

The headspace in the centrifuge tubes was increased in an attempt to improve the physical agitation of the soil. This was achieved by only adding 30 ml liquid (deionised water or deionised water plus chemical dispersant) and shaking (using reciprocal shaker) at the maximum possible speed (ca. 148

rpm) for 20 hours, thereafter another 20 ml added and the samples agitated for a further 4 hours. The addition of liquid creates a larger column of water above the sediments in an attempt to reduce the possibility of extracting unwanted sediments (i.e. sand and silt) from the bottom of the centrifuge tubes. The effect of agitation time was assessed using the same process described above, but increasing the initial shaking time incrementally from 1 to 30 hours. After the respective hour-intervals 20 ml deionised water was added to both WDC and CDC and the samples agitated further for 30 minutes. A fixed 42.5 ml was extracted using a Lowy pipette, oven dried at 105 ˚C (overnight) and weighed. The effect of ultrasonication and shaking time was investigated by repeating the time series procedure after samples had been sonicated for 1 minute. An overhead probe-type sonicator (Qsonica) was used to disperse the soil in the centrifuge tubes at 30 % amplitude. The probe was immersed to the same depth (roughly 7 cm from the bottom of the centrifuge tubes) in all the tubes to avoid air injected into the soil and to decrease biased dispersion. Thereafter, samples were shaken incrementally as described above. All time series experiments were conducted in duplicates.

The particle size distribution of the sonicated and non-sonicated samples agitated for the same period was determined following the extraction procedure in centrifuge-pipette using CDC extracts from W3. The particle size distribution was determined using a Micromeritics Saturn DigiSizer 5200 high definition digital particle size analyser (Micromeritics, USA) to identify the WDC treated with chemical dispersant.

3.2.3 Turbidity, gravimetric clay content determination and particle size analysis

The use of turbidity was explored as a mechanism to measure clay content by setting up a calibration with a representative soil (similar in mineralogy to all soils under investigation). The adjusted PSA method, as described in Chapter 2 was used to separate and extract the clay. A range of soil masses were added to the cylinders to generate an absolute CDC range of between 4.01 and 35.36 g/L. The extracted clay suspensions were thoroughly mixed to ensure that they were homogenous and representative, thereafter a 1 ml aliquot was extracted to determining turbidity and the remaining 24 ml oven dried at 105 ºC (overnight). Each 1 ml clay aliquot was added to 700 ml deionised water and vigorously stirred for approximately 1 minute by hand. Thereafter the turbidity was measured using a turbidimeter (HACH Co. model 2100P). This data were used to set up a calibration curve for clay content (g/L). The calibration was tested on four samples Mb 1.2, Pb 2.2, Br 1.2, W2 (refer to Table 2-2 in chapter 2). All four samples were dominated by kaolinite and showed a range of CDC contents. The CDC was measured gravimetrically and using the turbidity calibration curve. To establish if mineralogy has an effect on turbidity, a range of suspensions of reference kaolinite (KGa-11) and smectite(STx-1b) obtained from Source Clay Repository of The Clay Mineral Society, Purdue

University were also prepared in various concentrations following the centrifuge pipette method and analysed as described above.

3.2.4 Particle density and Particle size analysis (PSA)

The particle size of the suspensions extracted using the centrifuge-pipette method from the reference clays and W3 were analysed to assess whether the particles in suspension were <2 µm. Particle size analysis was also conducted on sonicated and non-sonicated samples on the CDC extract from W3. When the reference clays yielded different turbidity measurements, the mean particle density of these colloids was determined using the standard pycnometer method. This involved carefully weighing 3g clay and filling the pycnometer with deionised water so that pore space are excluded. The density was determined by weighing the pycnometer before and after any additions were made, by using the density of water at the observed temperature.

The complete reduced-sample size centrifuge method for WDC and CDC determination is included in Appendix A.

3.3 Results and Discussion

3.3.1 Importance of head space to improving extraction efficiency

Increasing the headspace in the centrifuge tube resulted in substantial improvements in extraction efficiency specifically for the WDC treatment (Figure 3-1). Over all the samples the WDC extraction efficiency improved from 49% to 81% (Figure 3-1 a). There were minor positive changes in the CDC extraction efficiency with only 4% increase compared to unimproved method (Figure 3-1 b). A strong correlation (R^2=0.95) is observed between WDC and the adjusted PSA method. Similarly, significant correlations (R^2=0.81) were obtained between CDC and adjusted PSA . The standard errors (SE) for WDC (0.07 g/kg) and CDC (0.18 g/kg) are low, indicating less variability and more certainty in the improved centrifuge-pipette method. The background noise (y-intercept) for CDC is lower when headspace is improved and not significantly different ($p<0.05$) from point of origin. Increasing the headspace in the centrifuge tube has the effect of increasing agitation energy, which confirms the conclusions of the previous chapter that physical agitation was the main constraint on WDC extraction efficiency. The relatively small improvement in the CDC demonstrates the fact that chemical dispersion dominates mechanical dispersion of colloids. This was also observed by Dourado, Da Silva and Marinho (2012) who found that low speed shaking dispersed different PSA textural classes satisfactory in the presence of a dispersing agent.

Despite the improved extraction efficiency of the above method, if a reduced sample centrifuge technique is to replace the adjusted PSA method, a higher efficiency is required. In addition, establishing the minimum time required to mechanically disperse samples can be useful in optimising the extraction technique. Both aspects will be dealt with in the following section.

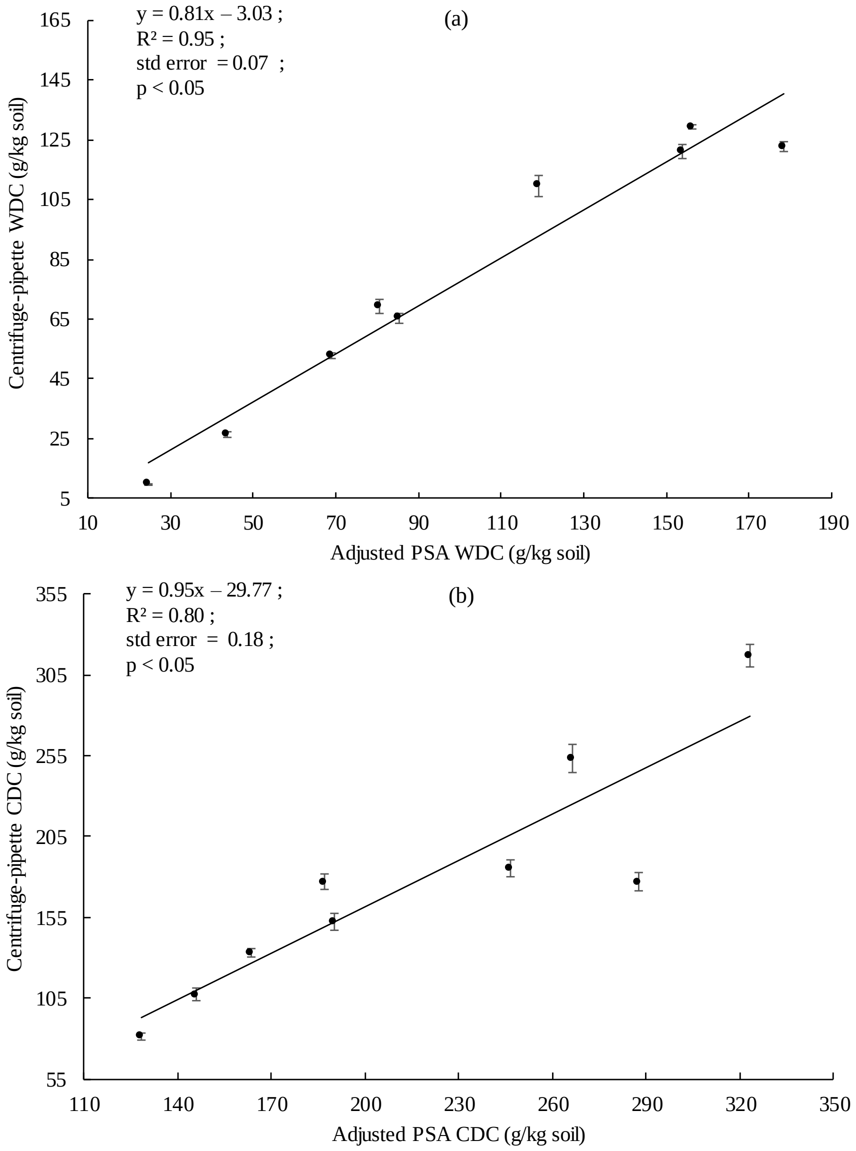

Figure 3-1: (a) WDC and (b) CDC extraction efficiency of the centrifuge-pipette method compared to adjusted PSA method, after increasing the headspace in the centrifuge tube. The error bars indicate standard error (SE) of the means

3.3.2 The effect of shaking time and sonication on WDC and CDC extraction efficiency

Figure 3-2 indicates the effect of shaking time, with and without prior sonication, on the extraction efficiency (as compared to the adjusted PSA method) for the subsoil of W3. In the absence of sonication there was little to no WDC extracted during the first three hours, after which extraction efficiency incrementally increases until around 22 hours (Figure 3-2). A similar trend was observed for the CDC treatment but, there was already 14.77% clay extracted in the first hour (Figure 3-2 b). This demonstrates the ability of the chemical dispersant to disperse clay in addition to the effect of agitation. Both the WDC and CDC treatments were conducted in duplicates for each hour with similar results. The extraction of both WDC and CDC improves considerably during the first 16 hours in the sonicated compared to the non-sonicated samples. After just 1 hour, the WDC extraction improved by 56.43% reaching 98.81% at 24 hours in the sonicated samples (Figure 3-2 a). A similar trend was observed for CDC (Figure 3-2 b). Interestingly sonicating does not reduce the time to the maximum WDC or CDC extraction with both methods reaching a plateau in extraction efficiency after 22 hours. It also only slightly increases the WDC efficiency from 96.16 to 98.81% during the 22nd hour.

These results demonstrate that agitation time is a critical consideration when extracting WDC. Previous WDC studies used different agitation techniques that are often not calibrated with sedimentation method. De azevedo and Schulze (2007) studying oxisols in Brazil, found that WDC release was optimal after 7.5 hours of shaking with horizontal shaker because large aggregates disintegrate and they are the main source of WDC release. The study by Gregorich, Kachanoski and Voroney (1988) demonstrated that a short (time was varied to produce a range of ultrasonic energies) sonication period was equivalent to 16 hours of agitation, but these workers were interested in the sand-size fraction and therefore did not quantify the WDC content. Work by Watson (1971) and Christensen (1985) showed that ultrasonication as a method of dispersing soil did not yield consistent results. The WDC extraction efficiency after dispersing soil using ultrasonication is also not standardised and this would help for comparative purposes.

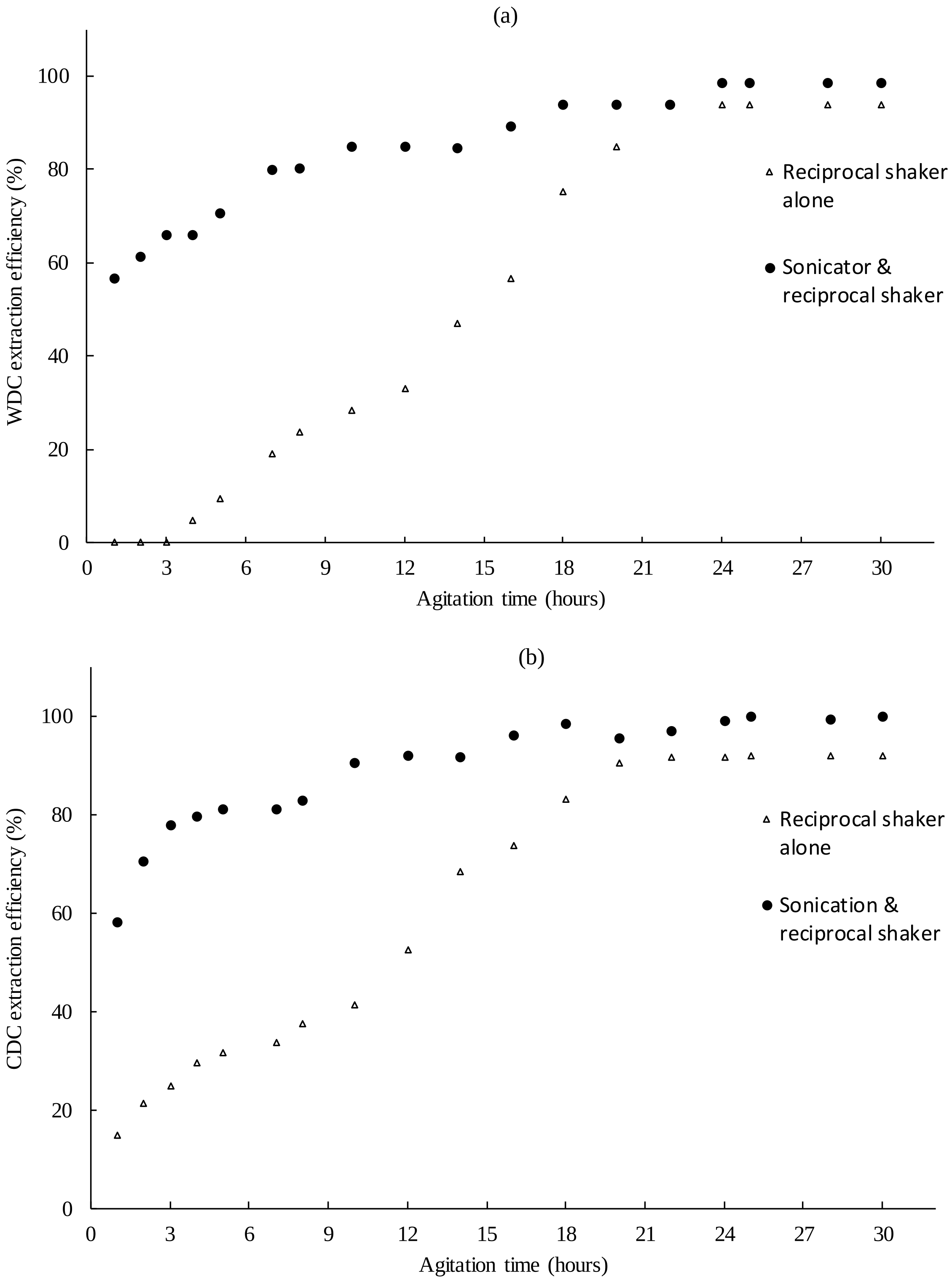

Figure 3-2: a) WDC and b) CDC extraction efficiency after physical agitation using a reciprocal shaker with and without prior sonication, expressed as a percentage of clay extracted using the adjusted PSA method.

Sonication prior to agitation for 24 hours gave the highest WDC extraction efficiency (Figure 3-2). This method was further tested on nine other soils (Figure 3-3). There is a very good correlation ($R^2 = 0.97$) between the extractions of the centrifuge-pipette method and the adjusted PSA method after sonication. The average efficiency measured over 9 samples increased from 81% (Figure 3-1 a) to 92% with the addition of a sonication step. Adding this short sonication step improved the intercept the most for both fractions and was not significantly different ($p<0.05$) from the point of origin. Expressing the WDC as a proportion of CDC improves the extraction efficiency to 99% with an R^2 of 0.97 (Figure 3-3 b).

To verify that ultrasonication did not result in a physical shattering of soil particles, as warned by Gee and Or (2002), particle size distribution of sonicated and non-sonicated samples (using CDC extracts from W3) were measured (Figure 3-4). There is little change in the shape of the particle distribution curve or the total clay extracted after sonication, confirming the findings by Poli et al. (2008) and Środoń (2006) that sonication for short periods does not result in clay fragmentation.

These results suggest that sonicating samples seems to be a significant contributor to releasing clay content into suspension and sonication should be included in the reduced sample centrifuge method to achieve maximum extraction efficiency. Expression of WDC as a proportion of CDC gives an extremely high extraction efficiency. Not only does expressing WDC as a percentage of CDC, reduce error involved in incorrect clay determination, it is also relatively quicker (than PSA) and can be conducted alongside the WDC extraction and under the same experimental conditions. Using such a divisor would make WDC results significantly more reliable and transferable. This parameter will be different to WDC normalised to clay content and new thresholds would need to be determined on this measure. In order to reduce confusion, it is proposed the divisor of WDC should be given as a subscript. For a CDC divisor a subscript of *h* (hexametaphosphate) should be used. Such a fraction would be calculated as:

$$\mathrm{WDC_h} = \frac{\mathrm{WDC\ (g\ kg^{-1})}}{\mathrm{CDC\ (g\ kg^{-1})}} \times 100$$

Where $\mathrm{WDC_h}$ = the WDC fraction expressed as a function of CDC; WDC and CDC = water dispersible clay and chemically dispersible clay respectively, both measured as a fraction of total soil ($\mathrm{g\ kg^{-1}}$)

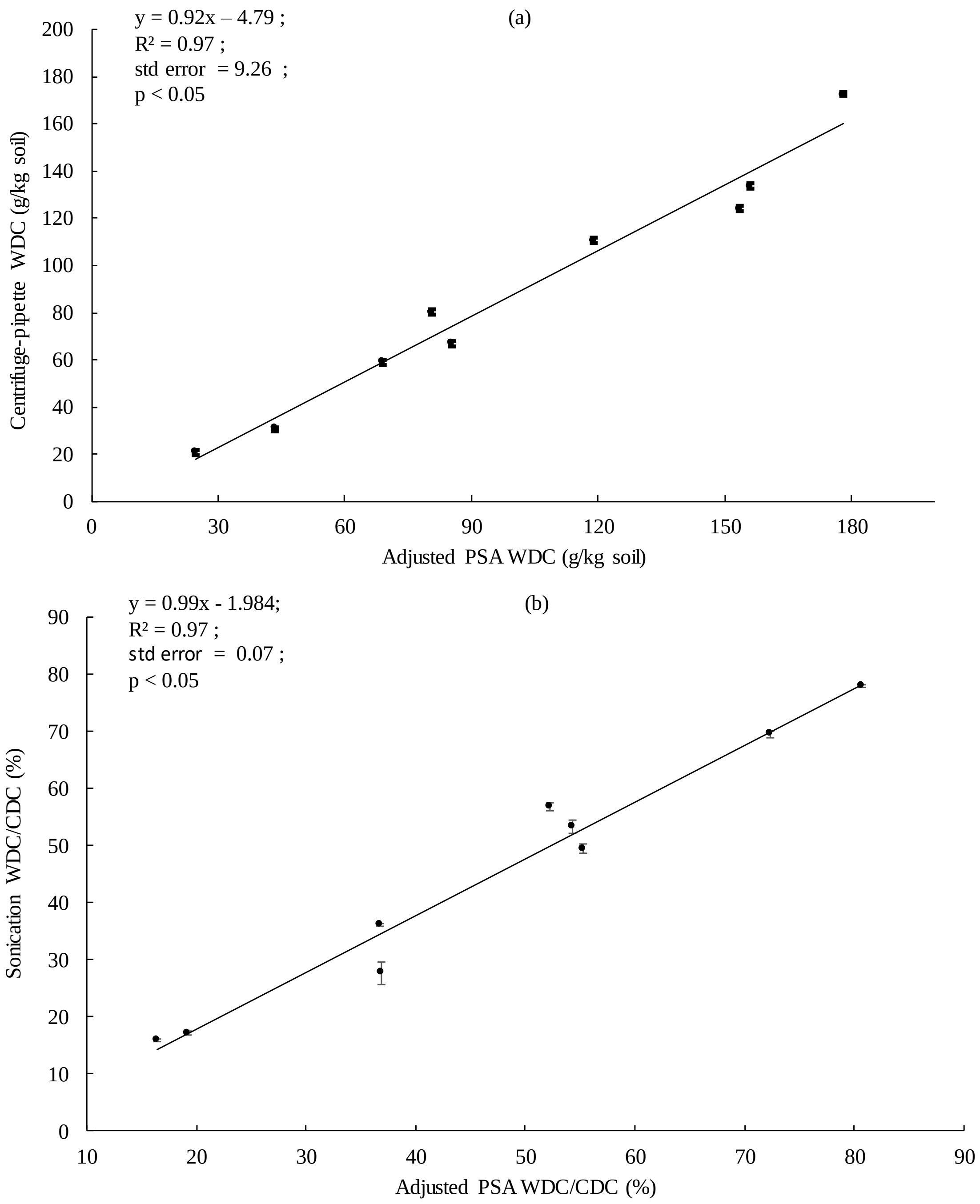

Figure 3-3: WDC extraction efficiency expressed as (a) g/kg soil and (b) as a function of CDC compared to adjusted PSA method after mixing soils with a combined agitation of sonication and reciprocal shaker over nine samples. Error bars indicate standard error of the means

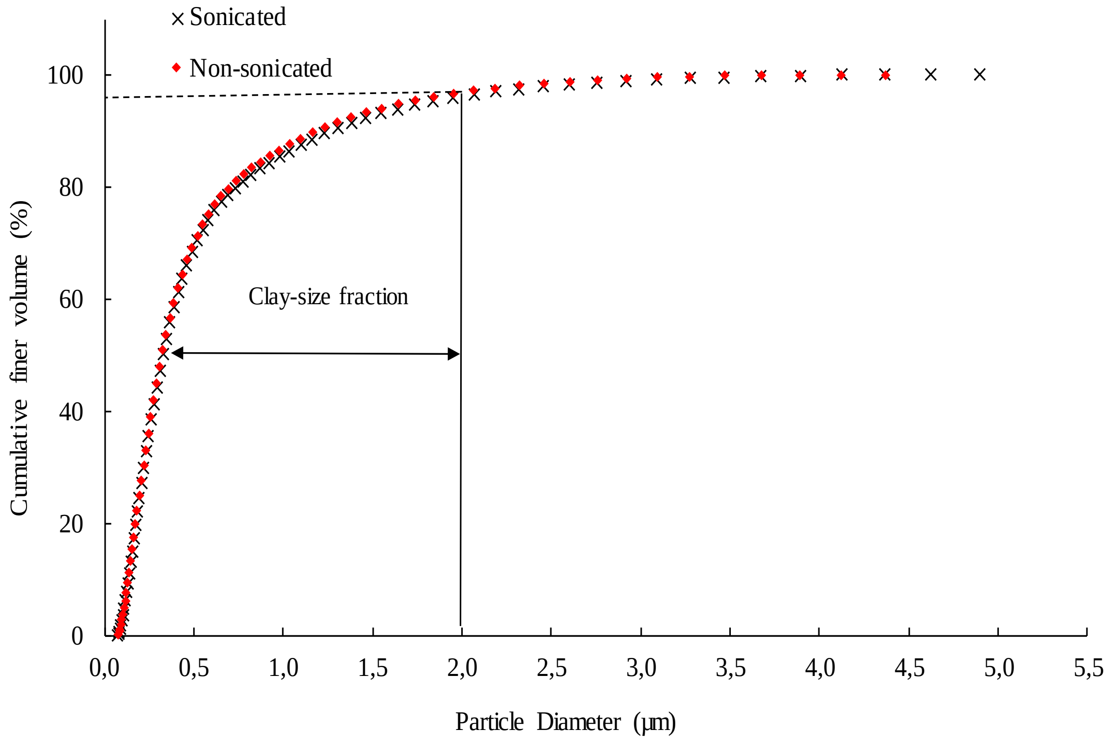

Figure 3-4: Particle distribution curve obtained from CDC suspensions extracted from W3 after agitation with sonication and without sonication.

3.3.3 Measurement of clay using turbidity

In order to establish if turbidity can be used to replace the time-consuming gravimetric clay determination, a calibration curve between CDC content and turbidity was constructed (Figure 3-5). The calibration curve has an excellent correlation coefficient ($R^2 = 0.999$) and a background limit of 1.45 NTU. The standard error (0.03) is low and the coefficient of variation (CV) is 1.04%.

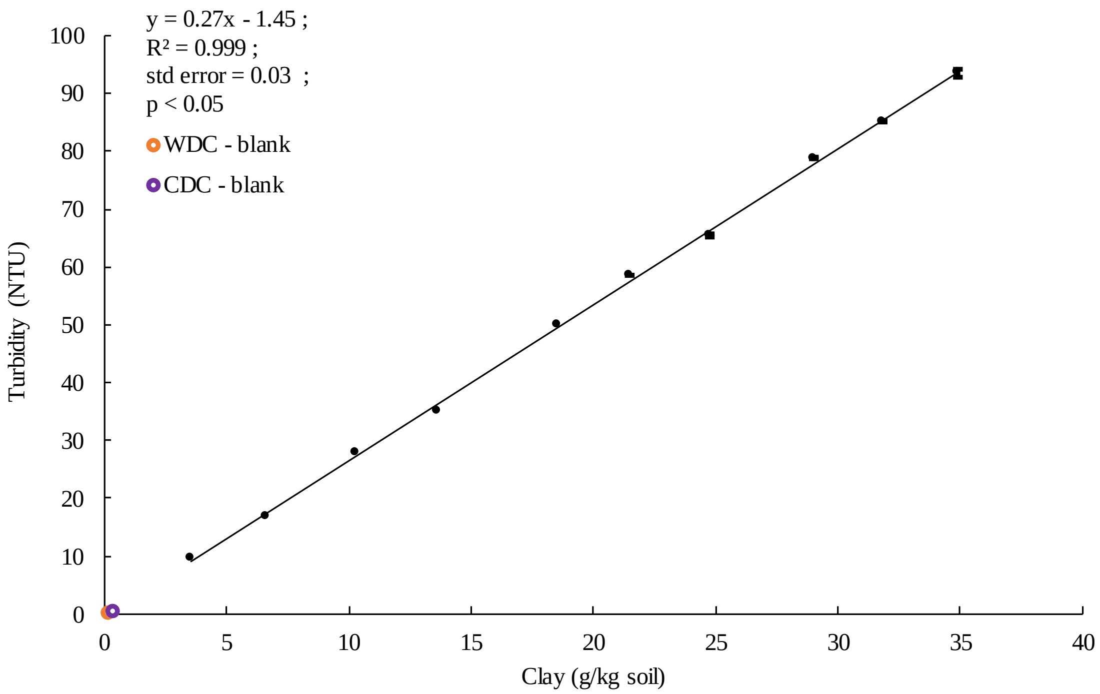

Figure 3-5: Calibration curve between CDC measured gravimetrically (after adjusted PSA method) and turbidity for W3. The circles indicate water samples with (CDC) and without chemical dispersant (WDC) and the standard error bars are indicated but not visible on the Figure

The calibration curve above was tested on CDC extracts of four soils. The clay estimated using the calibration curve and determined gravimetrically is shown in Figure 3-6. Although the slope gradient is close to 1 (0.82) the R^2 is 0.80 suggesting there is not a prefect correlation between the two techniques. The intercept is significantly different ($p<0.05$) to the point of origin, and this could be a result of overestimation of background sample by turbidity readings.

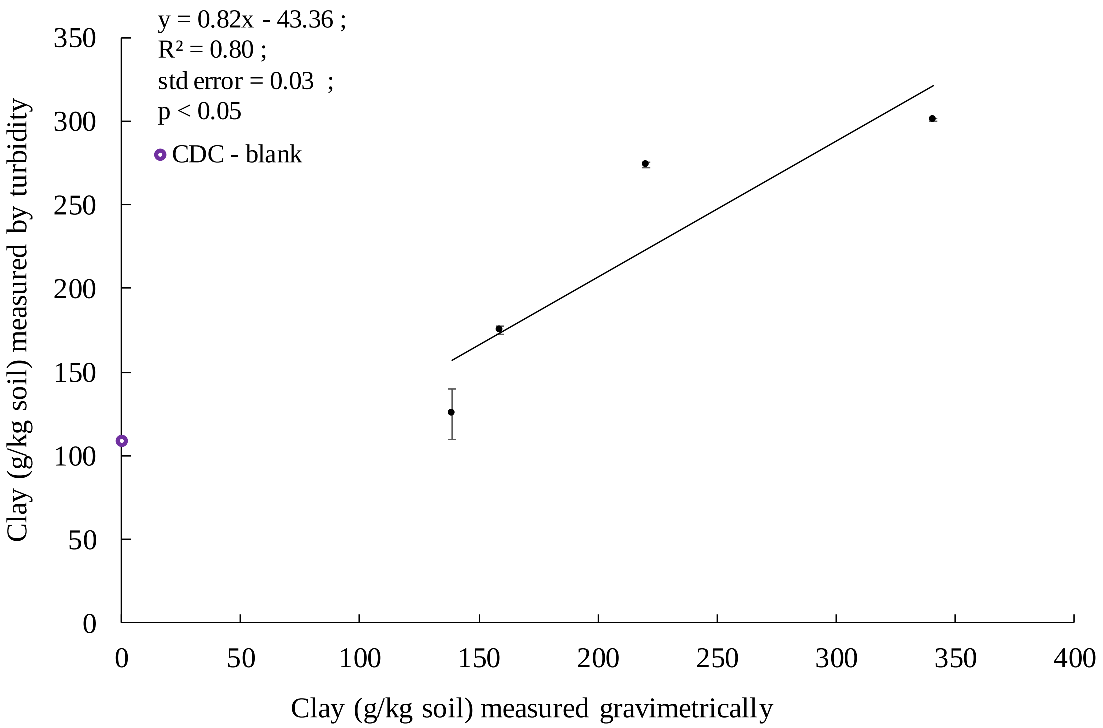

Figure 3-6: The relationship between CDC measured by turbidity and obtained gravimetrically after suspensions were extraction using centrifuge-pipette method. The circle indicates the turbidity reading and gravimetric water samples solution with 10% chemical dispersant

In order to establish how turbidity curves are affected by different mineralogies, calibration curves were constructed using kaolinite (KGa-1) and montmorillonite (STx-1b) reference material (Figure 3-7 a and b, respectively) dispersed using a mixture of sodium hexametaphosphate and sodium carbonate. The calibration curves for both clays gave excellent R^2 values (0.97), but their slopes differed substantially from each other. Interestingly the slope of the kaolinite curve (2.9) corresponded quite closely with the slope of the W3 calibration curve (2.7), but the slope of the smectite curve was 5 times lower (Figure 3-7 a and b). This extreme difference between the curves of kaolinite and smectite was unexpected. To understand the results better a particle size analysis of two extracts was conducted using a particle size analyser (Figure 3-7 c and d). Despite both clays being treated in the same fashion and the colloidal phase being separated by centrifugation, the particles in the smectite are much larger than what they should be given the separation procedure. While the kaolinite showed good separation of the clay phase (99.4% particles < 2µm) the smectite showed only 37% of particles were smaller than 2 µm. This result is quite surprising considering both minerals were present in a stable colloidal suspension. This suggests the smectite samples are somehow more buoyant than they should be or generate short-lived aggregates.

The former was discarded based on the particle size density of the smectite being 2.29 g/cm^3 which is typical of soil particles. To assess if this phenomenon was just related to STx-1b, a self-mulching vertic

A horizon from desolation pan in Botswana was also separated and the particle size measured. A similar pattern is observed, with only 60 % of the clay in suspension being clay size (<2 µm) (Figure 3-8). This result is not easy to explain, as such particles should be too large to exist in a stable colloidal suspension. One possibility is that short-lived aggregates are forming between smectite particles, however there is no evidence of this. For the purposes of this study an important conclusion can be reached from this finding and that is turbidity cannot be used as an alternative for the oven-drying procedure given the effect mineralogy has on turbidity measurements. If turbidity were to be used, other soil-water properties, such as mineralogy would have to be examined alongside it as suggest by Meozzi (2011).

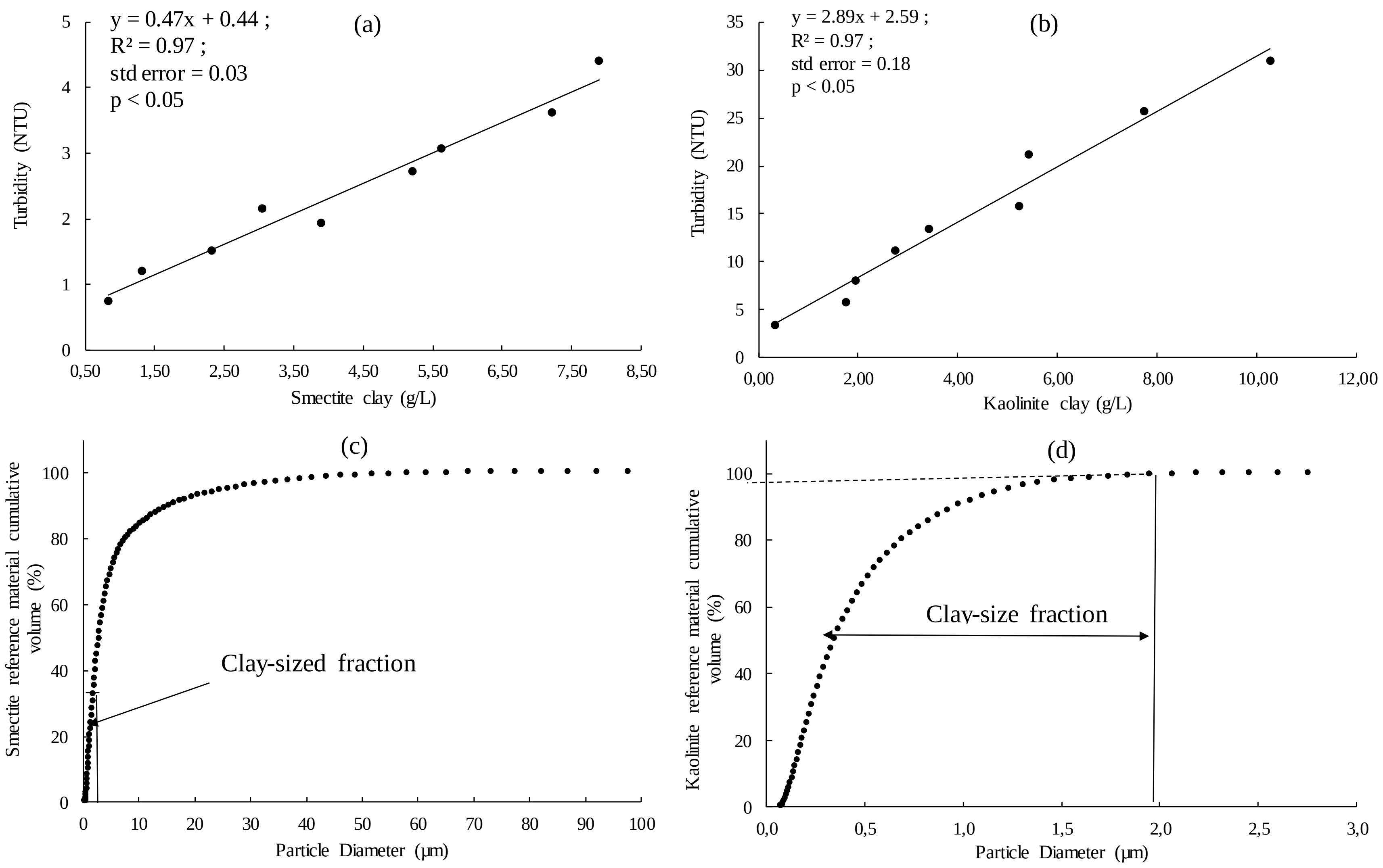

Figure 3-7: Relationship between turbidity and gravimetric clay content for (a) smectite and (b) kaolinite reference material, dispersed using a chemical dispersant and their respective particle size distribution (c and d) for these two clay minerals after separation by centrifuge-pipette method

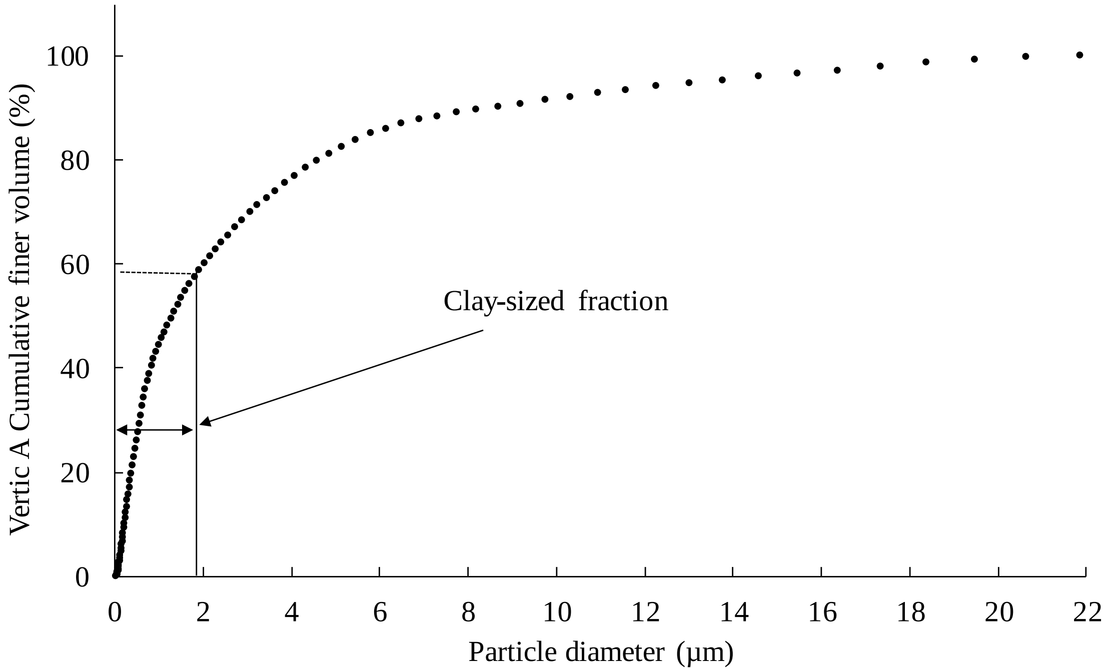

Figure 3-8: Particle size distribution of a self-mulching vertic A horizon from Desolation pan in Botswana

3.4 Conclusions

Increasing the headspace, and thereby the agitation energy, in the centrifuge tube and including a sonication step drastically improved the WDC extraction efficiency, as compared to the adjusted PSA method. Clay extraction efficiency increases with increasing extraction time up until 22 hours after which no change is detected. Sonicating the sample prior to agitation had no effect on the time required to reach maximum extraction. However, on average, sonicating the samples prior to agitation increased the efficiency from 82% to 91%. Particle size analysis, conducted on sonicated and non-sonicated CDC treated samples, showed no fragmentation to clay particles.

Expressing WDC as a fraction of CDC improved the extraction efficiency to 97%. It is proposed that WDC should be expressed as fraction of CDC. This would negate the need for a texture analysis and would serve to standardise the expression of WDC. To avoid confusion, it is proposed that a subscript *h* be used to indicate that WDC is expressed as a fraction of CDC.

Despite the promising relationship between gravimetrically determined clay content and turbidity measurements for kaolinitic rich soils, this trend was not observed for soils with smectite mineralogy. Surprisingly, a smectite reference material clay differed from the kaolinitic clay samples in that it apparently had particles larger than 2µm in suspension after they were separated in the same manner. This was not easy to explain as such particles should be too large to exist in stable colloidal suspensions. For the scope of this study, it was concluded that mineralogy had an effect on turbidity readings and is therefore not a good substitute for gravimetric clay determination.

Chapter 4 : Application of a reduced sample centrifuge method on archived samples to discriminate between cutanic and apedal soil horizons

4.1 Introduction

Apedal (red and yellow-brown apedal B) horizons are well-developed subsoils, and often some of the oldest subsoils in South Africa, they are uniform in colour and typically manifest themselves topographically, however there are some exceptions (Fey, 2010). The red variants are typically found on the crest where it is drier and the yellow-brown apedal horizons occupy the moister midslope (Fey, 2010). These diagnostic horizons are usually enriched in Fe and Al which stabilises the clay fraction therefore dispersion of clay by water is expected to be limited. Neocutanic horizons are similar to the red and yellow-brown apedal horizons, in terms of structure, but are more youthful as indicated by their incipient soil development (Fey, 2010). They must contain signs of cutans which attributes to the colour variegation in the subsoil horizon (Soil Cassification Working Group, 1991), the presence of cutans could also be a sign that the clay fraction is less stable which would make them prone to dispersion. Therefore, clay movement and clay instability is expected to be higher in these horizons compared to apedal horizons. Clay enrichment can also be a result of topsoil erosion which would result in the formation of binary profiles. For these reason Fey (2010) mentions that a bleached topsoil can often be present above a neocutanic B horizon. Although many pedologists, recognise that neocutanic horizons often have a less stable clay phase compared to red and yellow-brown apedals, this largely appears to tacit knowledge as there is no literature to support this.

Due to yellow-brown apedal, red apedal and neocutanic horizons all having an apedal structure, it is often non-uniform colour (as an indicator of clay cutans) which is used to differentiate neocutanic horizons from red and yellow-brown apedal horizons (Soil Cassification Working Group, 1991). Colour variation is a subjective measure and debate often exists as to whether the degree of non-uniformity is sufficient to warrant the horizon being in the neocutanic class. A case in point is the classification of the red, weakly structured subsoil horizons in the Western Cape. Some classifiers claim sufficient colour variation to qualify as a neocutanic designation while others prefer a red apedal classification. These red, weakly structured, horizons often display hardsetting properties in the dry summer months and can be overlain by bleached dispersive topsoils (Le Roux, 2015). It is often these negative physical properties that lead to local surveyors preferring to classify these subsoils as neocutanic horizons rather than the more physically favourable red apedal B horizon. Similar borderline red apedal/neocutanic soils were also debated in a 2016 Soil Surveyors meeting just outside Bloemfontein. Again, the degree of colour variation was subjectively interpreted. These soils were also hardsetting and showed severe erosion (large erosion gullies; Clarke pers. comm). Given that scientific and technical classification systems should be based on objective and measurable properties it is better to assess if the behavioural properties of these horizons can be encapsulated in a measurable attribute.

In the WRB system, Ferralic horizons resemble the apedal profiles but represent a more restricted physciochemical range and typically develop under intense weathering conditions compared to the wide range of climatic conditions under which apedal horizons develop (Fey, 2010; IUSS Working Group WRB, 2015). Many luvic apedal profiles would also classify as argic horizons, however Fey (2010) observes the clay increase is often gradual. Neocutanic horizons should typically be classified as cambic horizons, however, many neocutanic horizons can also be classified as argic horizons which are characterised by clay illuviation (IUSS Working Group WRB, 2015). The WRB deals with argic and ferralic horizons that have similar properties, by the addition of a diagnostic criteria which states a ferralic horizon should have less than 10% WDC or geric properties, or a soil organic carbon (SOC) content of 1.4% or greater. Given the wide variety of mineralogy's and SOC content permissible in neocutanic and red/yellow-brown apedal soils, only the WDC would hold any promise as a physical discriminator between these horizons. This is based on the notion that neocutanics are have a less stable clay phase compared to apedal horizons. Therefore firstly, it would be useful to determine if neocutanic soils do show a higher WDC than red/yellow-brown apedal horizons. Secondly, given the use of WDC as one of the criteria used to classify Ferralsols, it would also be instructive to determine if WDC is a good discriminator between neocutanic horizons and red and yellow brown apedals and in particular between borderline red apedal and red neocutanic soils. To achieve this, this chapter aims to: i) apply the improved centrifuge method to archived samples to assess whether neocutanic horizons have a higher WDC content compared to red and yellow brown apedal horizons; ii) determine if WDC can be used as a discriminator between cutanic and apedal horizons and finally iii) determine the best classification for borderline red apedal and neocutanic soils

4.2 Materials and methods

4.2.1 Soils

Archived samples of neocutanic B, red and yellow-brown apedal B1 horizons from the Weatherly catchment in the Eastern Cape, Boland region of the Western Cape, Mpumalanga Highveld, KwaZulu-Natal midlands and the central Free Sate were selected (Table 4-1). In total 39 soils were used. The WDC_h was determined using the improved centrifuge-pipette method specified in Chapter 3.

Table 4-1: Number of selected neocutanic, yellow-brown and red apedal horizons in each region

Location	**Number of profiles**	**Number of subsoil horizon**
Weatherly (EC)	6	ne = 2 ye = 2 re = 2
Boland (WC)	15	ne/re = 13 ye = 2 re = 0
Middleburg (MP)	13	ne = 2 ye = 7 re = 4
Greytown (KZN)	2	ne = 1 ye = 1 re = 0
Bloemfontein (FS)	3	ne/re = 3 ye = 0 re = 0

EC: Eastern Cape, WC: Western Cape, MP: Mpumalanga, KZN: KwaZulu Natal, FS: Free State
ne: neocutanic, ye: yellow-brown apedal and re: red apedal horizon.

4.2.2 Data analysis and statistical methods

The WDC content of the three horizons, red apedal yellow-brown apedal and neocutanic were compared and statistical significance tested using either a Students t-test or a one-way analysis of variance (ANOVA) followed by a Tukey post hoc test. Outliers were tested for using Chi-squared test. The above was processed with the R environmental software (R Core Team, 2014). For the initial comparison, all borderline red apedal/neocutanic samples were omitted from the dataset. These borderline samples were used to test the various groupings of these horizons.

4.3 Results and Discussion

4.3.1 Discriminating between neocutanic and red and yellow-brown apedal horizons using WDC

The WDC extracted from neocutanic and red and yellow-brown apedal subsoil groups, expressed as a percentage of CDC (WDC_h) is presented in Figure 4-1. Borderline neocutanic/red apedal soils were not included in this dataset. The average WDC_h for neocutanic horizons is 55.80%, 48.48% for yellow-brown apedal and 31.04% for red apedal horizons (Figure 4-1). The WDC_h for red apedal is highly variable compared to the neocutanic and yellow-brown apedal horizon. Neocutanics are distinguishable from red apedal horizons at a 95% confidence level when expressed as WDC_h, but cannot be distinguished from yellow-brown apedals. The WDC_h for neocutanic > red apedal implying that in general the apedal subsoils are less dispersive than neocutanic horizons, however a clear distinction between neocutanic and yellow-brown apedals is not that clear. Although this is not an exhaustive data set, it does add some evidence to support the notion that neocutanic horizons have a less stable clay phase than red and yellow-brown apedal soils.

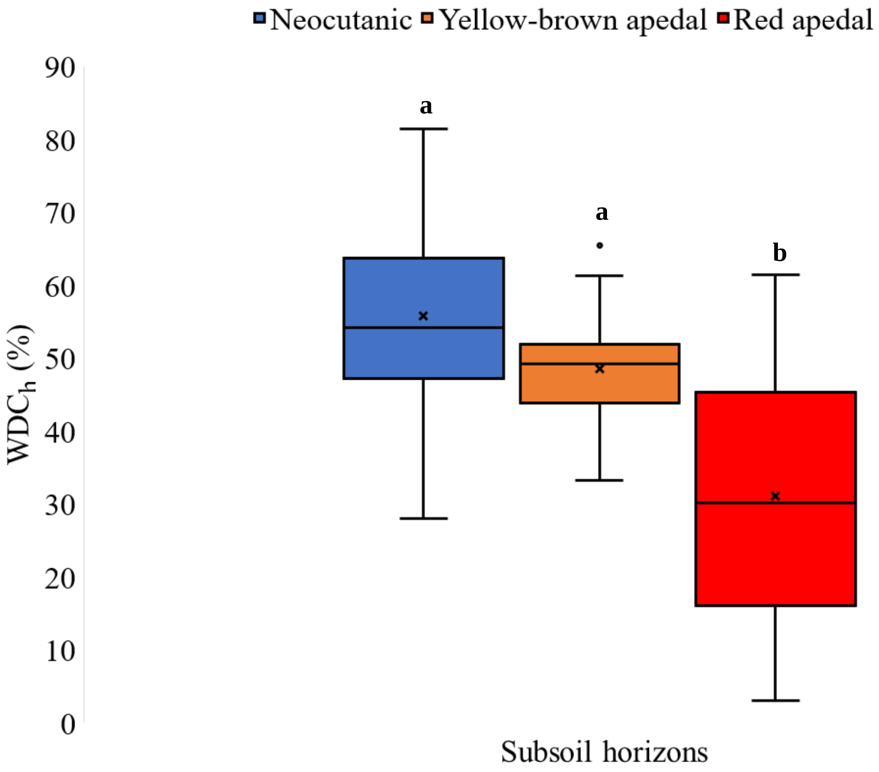

Figure 4-1: WDC expressed as a function of CDC (WDC_h) percentage for a group of neocutanic, yellow-brown apedal and red apedal subsoil groups when the borderline red apedal/neocutanic horizons are omitted.

One problem facing research on classification categories is the subjective nature of the classification category in the first place. For example, including the borderline neocutanic/red apedal horizons in either the neocutanic or the red apedal class would profoundly affect the outcome of the results shown in Figure 4-2. The objective of a classification system is to group soils with like properties and separate soils with unlike properties. One of the fundamental properties of red apedal B horizons is their stable clay phase (Soil Cassification Working Group, 1991; Fey, 2010) therefore, given the WRB approach for ferralsols, WDC may be an important property to focus on. To assess the different classification approaches to the borderline red apedal/neocutanic horizons found in the Western Cape and Bloemfontein, a grouping experiment was conducted. In one instance the borderline cases were included into the dataset as neocutanics (Figure 4-2 a) and in the other instance they were included as red apedal (Figure 4-2 b). It is clear that the neocutanic assignment creates a significant difference between the red apedals and neocutanics (p=0.01), while when the borderline cases were classified as red apedals there is no significant difference (p=0.21) between the two groups (Figure 4-2 a and b).

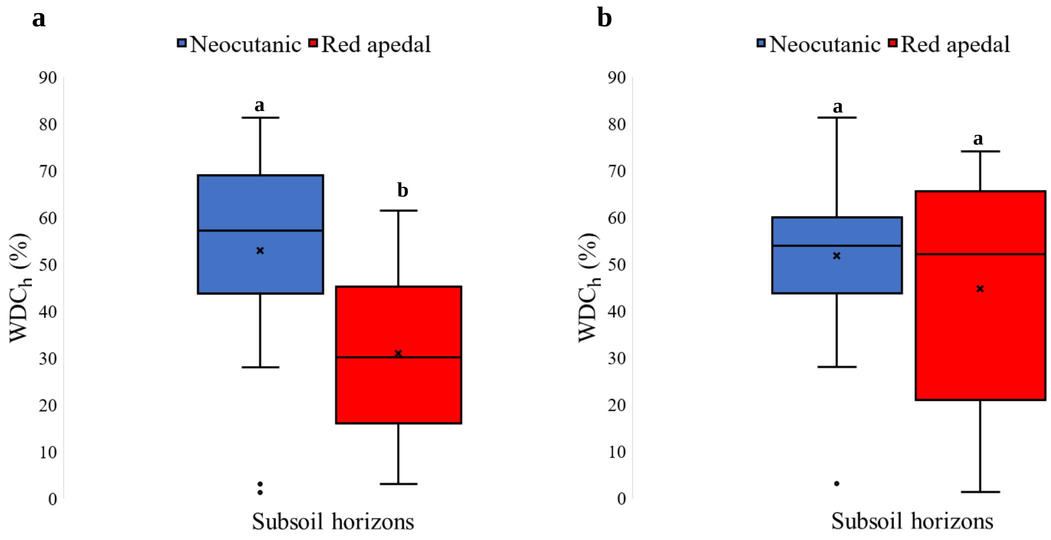

Figure 4-2: Grouping experiment where borderline neocutanic/red apedal horizons were included into the original dataset either as a) neocutanic or b) red apedal horizon. Same letters above whiskers indicate no significant difference at the $p<0.05$ significance level

The results in Figure 4-1 show that neocutanic soils generally have a higher WDC$_h$ than red apedals. The borderline samples were therefore compared (as a group on their own) to typical neocutanic and red apedal horizons in the original dataset. The results are presented in Figure 4-3. No significant difference (p=0.34) is observed between the borderline and neocutanic horizons. While there is a significant difference ($p<0.05$) between borderline and red apedal horizons. Figure 4-2 shows that not much change in WDC$_h$ is noted when borderline soils are classified as neocutanics but including them in red apedal horizons causes them to have positively skewed WDC$_h$. Given the importance of clay stability in red apedal horizons, it is recommended that the borderline neocutanic/red apedals are classified as neocutanics because of they have high WDC$_h$.

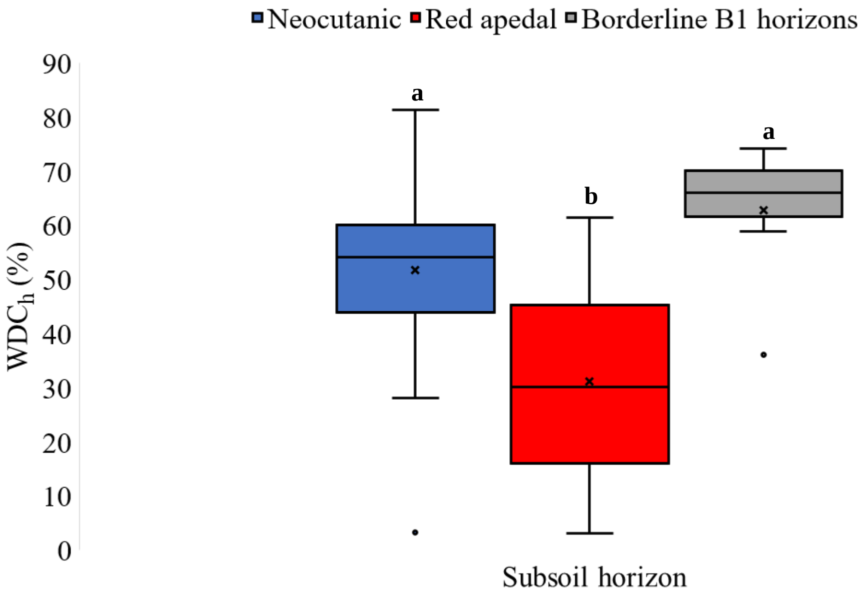

Figure 4-3: The borderline neocutanic/red apedal horizons compared to typical neocutanic and red apedal horizons from the rest of the country. Same letters above whiskers indicate no significant difference at the $p<0.05$ significance level.

The average WDC$_h$ of subsoils from different regions is presented in Figure 4-4. These results cannot be used as a generalization for each region as certain areas only had samples collected from one or two locations, and only should be used to understand the samples used in this study. The regions showed no significant differences ($p=0.08$) in terms of WDC$_h$ content (Figure 4-4). Boland and Middleburg soils had highly variation WDC$_h$ compared to the Bloemfontein, Weatherly and Greytown soils. The variation is attributed to the fact that the Boland and Middleburg soils were taken from a larger geographic area compared to the other regions. Nonetheless, the average WDC$_h$ decreased in the following order Bloemfontein > Greytown > Boland > Weatherly > Middleburg. Le Roux (2015), using these Boland and Middleburg soils, also noted that profiles in the Western Cape were more dispersive than those in Mpumalanga.

The samples from Greytown were collected from neocutanic and yellow-brown apedal subsoils under a Humic A horizon. The WDC$_h$ for these samples (60 and 52%, respectively, Figure 4-4) plotted close to the average values for these two groups (56 and 48%, respectively) suggesting that these WDC$_h$ relationships may also hold for Humic soils although more samples would be required to confirm this.

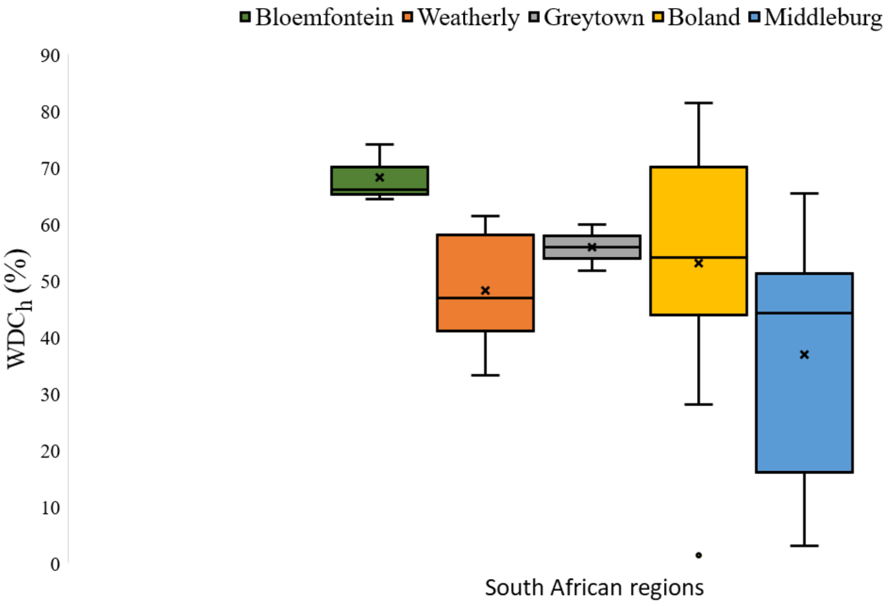

Figure 4-4: The average percentage WDC_h for subsoil horizons from selected regions in South Africa.

The results presented here suggest that WDC_h may be able to differentiate neocutanic and red apedal horizons with fairly high confidence, but it cannot be used to differentiate between yellow-brown and neocutanic horizons. Interestingly, yellow-brown and red apedal horizons could also be differentiated by WDC_h with 95% confidence. This may be attributed to yellow-brown soils often containing less Fe that red apedal B horizons (Fey, 2010). An ROC (receiver operating characteristics) test was conducted to determine a potential threshold WDC_h between red apedal and neocutanic groups. The results showed the threshold level to split the groups with a sensitivity of 0.71 (i.e. a 29% chance of a false positive) is 47% WDC_h. Analysis of more soils would be required to improve this threshold but it does show that, although WDC_h is not an absolute discriminator, it can be used as an aid to split borderline horizons into neocutanic or red apedal groups.

4.4 Conclusions

Omitting borderline neocutanic/red apedal from the dataset showed that neocutanics generally have higher WDC_h that the apedal groups and are distinguishable from red apedals at a 95% confidence level but not distinguishable from yellow-brown apedals. This evidence adds to the tacit knowledge that neocutanics have a less stable clay phase than red apedal soils and may explain the hardsetting nature often observed in these soils. When borderline neocutanic/red apedal horizons were treated as a group on their own, the results showed that they had comparable WDC_h to neocutanics but not red apedal horizons. The threshold level for distinguishing neocutanics and red apedals in borderline cases is 47% WDC_h with 71% sensitivity, indicating there is a low (29%) chance of a false positive.

The WDC_h relationships also held promise for soils with different topsoils (Humics and Orthics) across locations but with the current limited dataset it can be concluded that WDC_h is not a good enough parameter to serve as a diagnostic criterion but could be useful as an aid to distinguish between neocutanic and red apedal horizons.

Chapter 5 : Study conclusions and recommendations for further work

5.1 Study conclusions

Water dispersible clay is regarded as the clay fraction found when the sample is dispersed in water without any pre-treatment to remove the binding or cementing agents and without the use of a dispersing agent. The overall aim of this study was to develop, test and optimise a simple, reduced sample centrifuge method for determining WDC in order to allow analysis of archive samples and assess the use of WDC as a soil classification discriminator.s The following conclusions were reached from this study:

- Centrifugation achieves complete separation of the colloidal phase, and is effective in causing faster sedimentation which reduces the need for gravimetric sedimentation. This meant that analysis of archived samples could be generated using a simple, reduced sample method. This also has the benefit of reducing the extraction time and increasing the number of samples that can be analysed at one time
- The extraction efficiency is highly dependent on the physical energy exerted on samples. It was demonstrated that shaking time has a major influence on the WDC extraction efficiency and a short sonication step improves the extraction efficiency to over 90%
- It was proposed that WDC should be expressed as fraction of CDC because this would negate the need for texture analysis and would serve to standardise the expression of WDC. To avoid confusion, the subscript *h* was suggested to indicate that WDC is expressed as a fraction of CDC.
- Turbidity was not a reliable method to measure clay in suspension, due to the profound effect of clay mineralogy on turbidity readings. It was concluded that the gravimetric method could not be substituted.
- Neocutanic horizons tended to have WDC_h contents higher than the red apedal horizons, and were distinguishable at a 95% confidence level. However, WDC could not be used to distinguish neocutanic from yellow-brown apedals. This supported the tacit notion that neocutanic horizons have a less stable clay phase than red apedal soils, but not necessarily yellow brown apedals.
- Borderline red apedal/neocutanic horizons and typical neocutanics from around the country proved to have similar WDC_h. Given the importance of clay stability in red apedal horizons, it was recommended they are classified as neocutanics rather than red apedals and that a tentative threshold of 47% WDC_h be used to differentiate between horizons. This may be useful as a classification aid but due to the limited number of samples used it cannot be a discriminating criterion.

5.3 Recommendations for further work

- Given that WDC was highly dependent on agitation energy, standardising this step is ideal to maximising the extraction efficiency. It is therefore suggested that different agitation techniques (individual or mixed) are explored and compared to the adjusted PSA method. The effect of shaking speed and time on WDC can be assessed for these techniques incrementally in order to select a technique with maximum extraction efficiency at a reduced time period.
- The mechanism causing the larger particles to remain in suspension in the smectite clay after centrifugation can be investigated as such particles should be too large to remain in suspension.
- The WDC_h needs to be determined on numerous B1 horizons with different physicochemical properties and overlaid by different topsoils to increase the confidence of WDC_h as a classification aid. This parameter could also be related to properties like hardsetting.
- The new WDC_h parameter could be testing to determine if it correlates to properties such as hardsetting and aggregate stability.

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APPENDICES

Appendix A: Summary of the reduced sample-size centrifuge method for WDC and CDC

The adjusted particle size analysis (PSA) method is used as the benchmark method for WDC and CDC. The method is the same as particle size analysis (PSA), however there is no removal of binding agents. The reduced-sample centrifuge method is based on the centrifugation method of Seta and Karathanasis, (1996) but modified in terms of sample size and extraction procedure. Two treatments were used for the centrifuge method, namely water dispersible clay (WDC) and chemically dispersible clay (CDC). The CDC samples were treated with a mixture of sodium hexametaphosphate and sodium carbonate made up using the guidelines specified by the Soil Classification Working Group (1991), whereas WDC had no chemical dispersant added.

Water dispersible clay and calgon dispersible clay extraction methods

Adjusted PSA method

A.1. For WDC, 40 g soil and approximately 150 ml deionised (DI) water were agitated on an electrical mixer (Hamilton Beach HMD200 Single-Spindle Drink Mixer 120V) for 5 minutes. The same procedure was followed for the CDC treatment, however 10 ml (10%) calgon was added prior to shaking. The sand fraction was separated from silt and clay using a 2 mm sieve and both WDC and CDC were extracted by pipette following Stokes' Law.

Reduced sample size centrifuge method

A.2. A mixture of 2.5 g soil and 30 ml liquid was added into a 50 ml centrifuge tube. A mixture of 0.5 ml (10%) sodium hexametaphosphate and sodium carbonate aliquot was added to the CDC treatment and only deionised water added to WDC.

A.3. Samples were agitated for 1 minute (with 30% amplitude) on an overhead probe-type sonicator (Qsonica) immersed to the same depth (roughly 7 cm from the bottom of the centrifuge tubes). The samples were immediately placed on a reciprocal shaker at the maximum possible speed (ca. 148 rpm) for 24 hours. Thereafter another 20 ml deionised water was added and agitated for 30 minutes.

A.4. All samples were centrifuged (Sigma 2-16P) at 800 rpm for 3.5 minutes as described by Le Roux (2015)

A.5. A fixed 42.5 ml was extracted using a Lowy pipette. The extracted fraction was oven dried at 105 ˚C (overnight) and weighed using a 0.001 g decimal place scale.

A.6. Three replicates were extracted for both WDC and CDC. The WDC was expressed as a function of CDC.

Appendix B: Supplementary information for Chapter 2

Profile: Bp 1.2

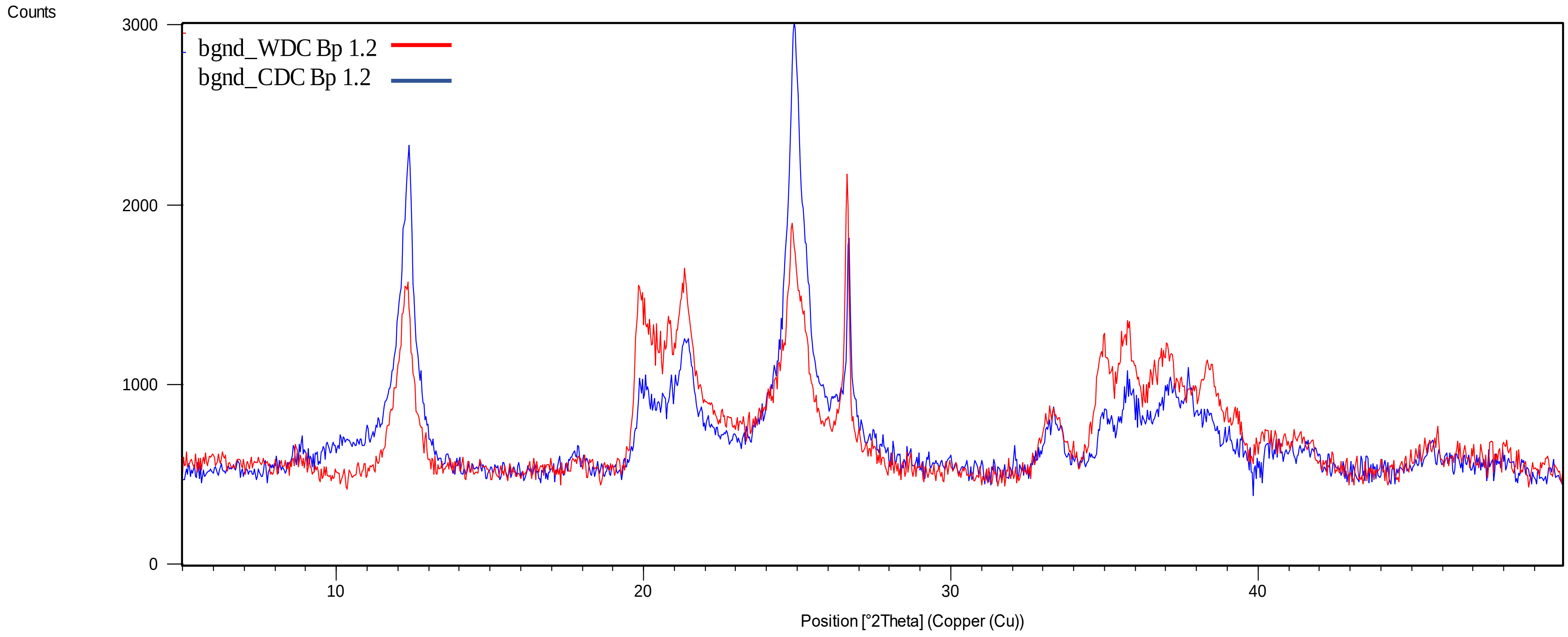

Figure B-1: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (neocutanic B1 horizon) of profile Bp 1.2 found in these two treatments.

Profile: Bp 3.2

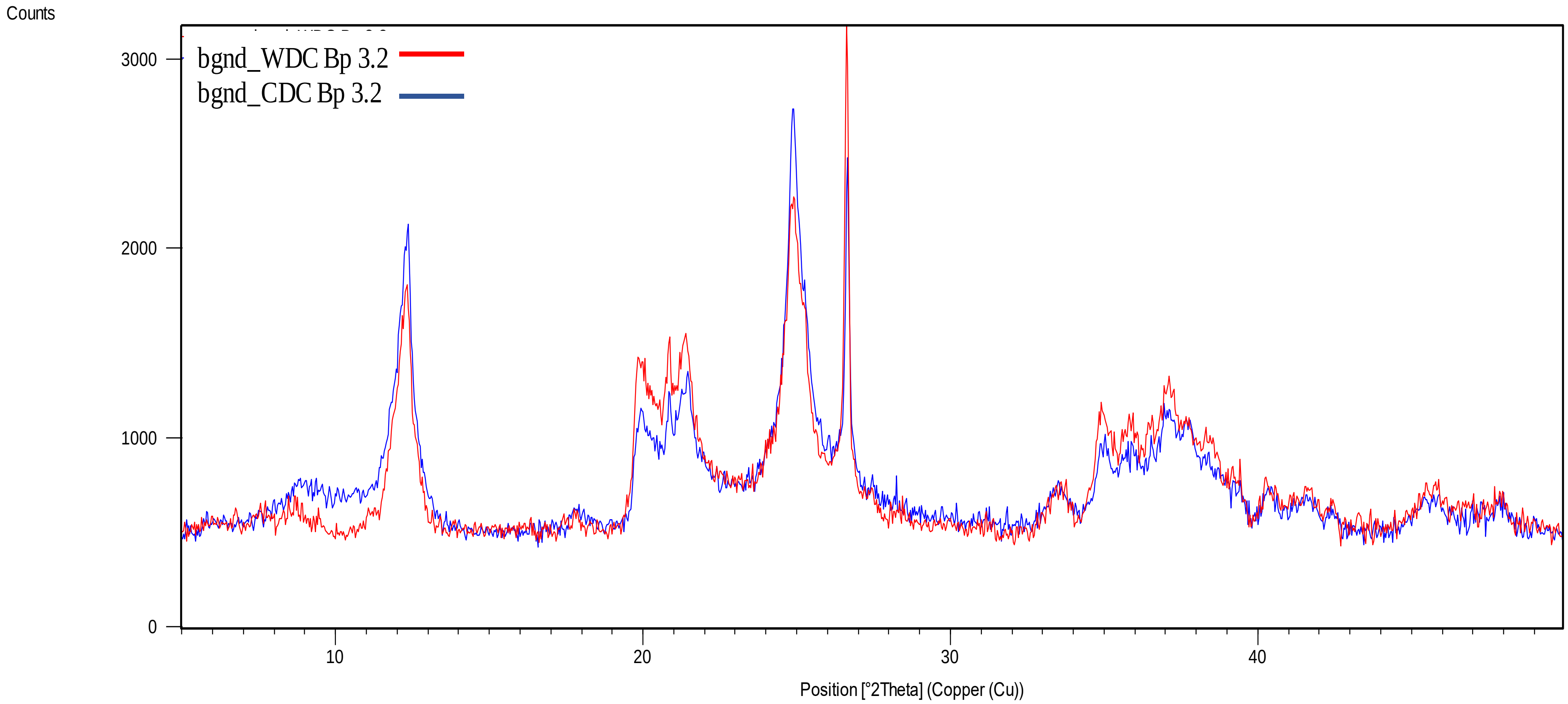

Figure B-2: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (yellow-brown apedal B1 horizon) of profile Bp 3.2 found in these two treatments.

Profile: Br 1.2

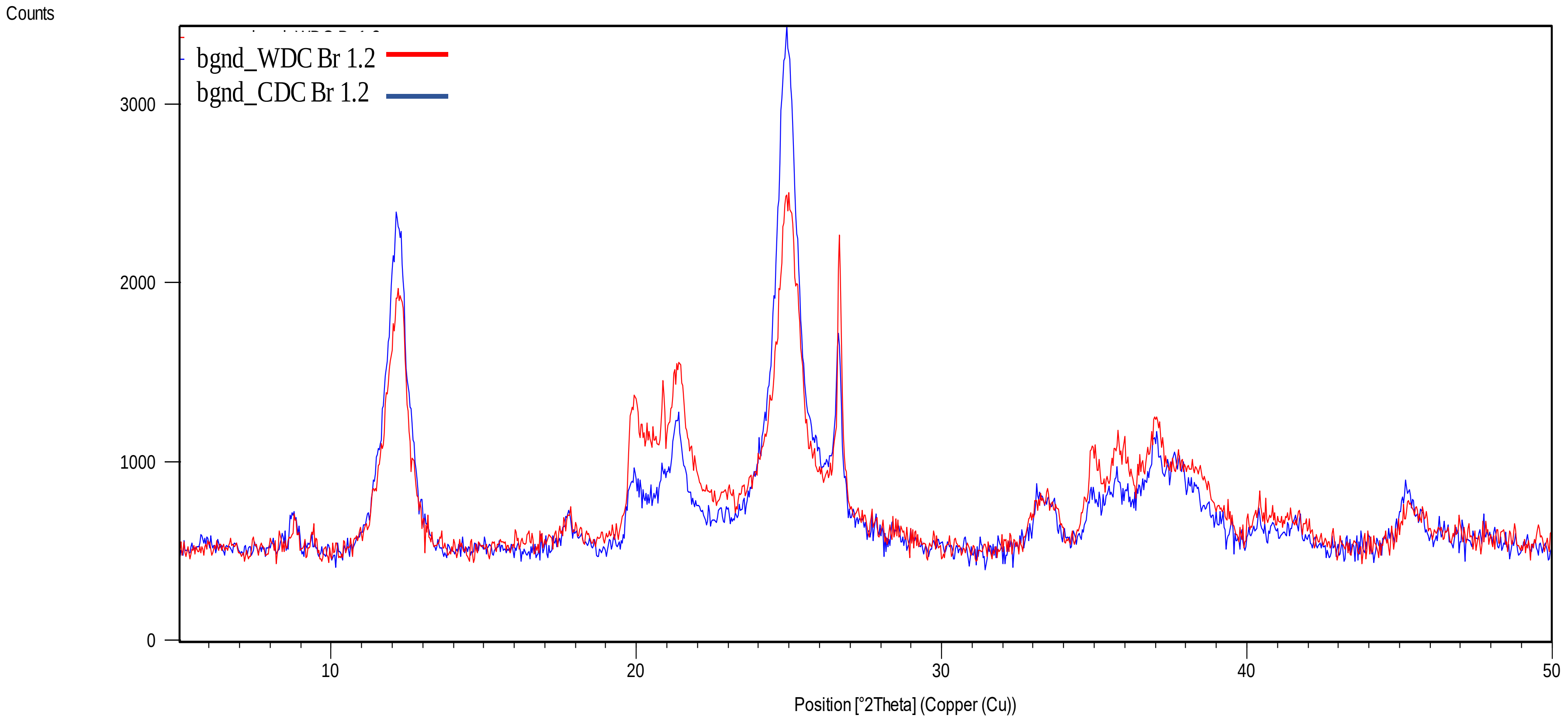

Figure B-3: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (red apedal B1 horizon) of profile Br 1.2 found in these two treatments.

Profile: Hh 1.2

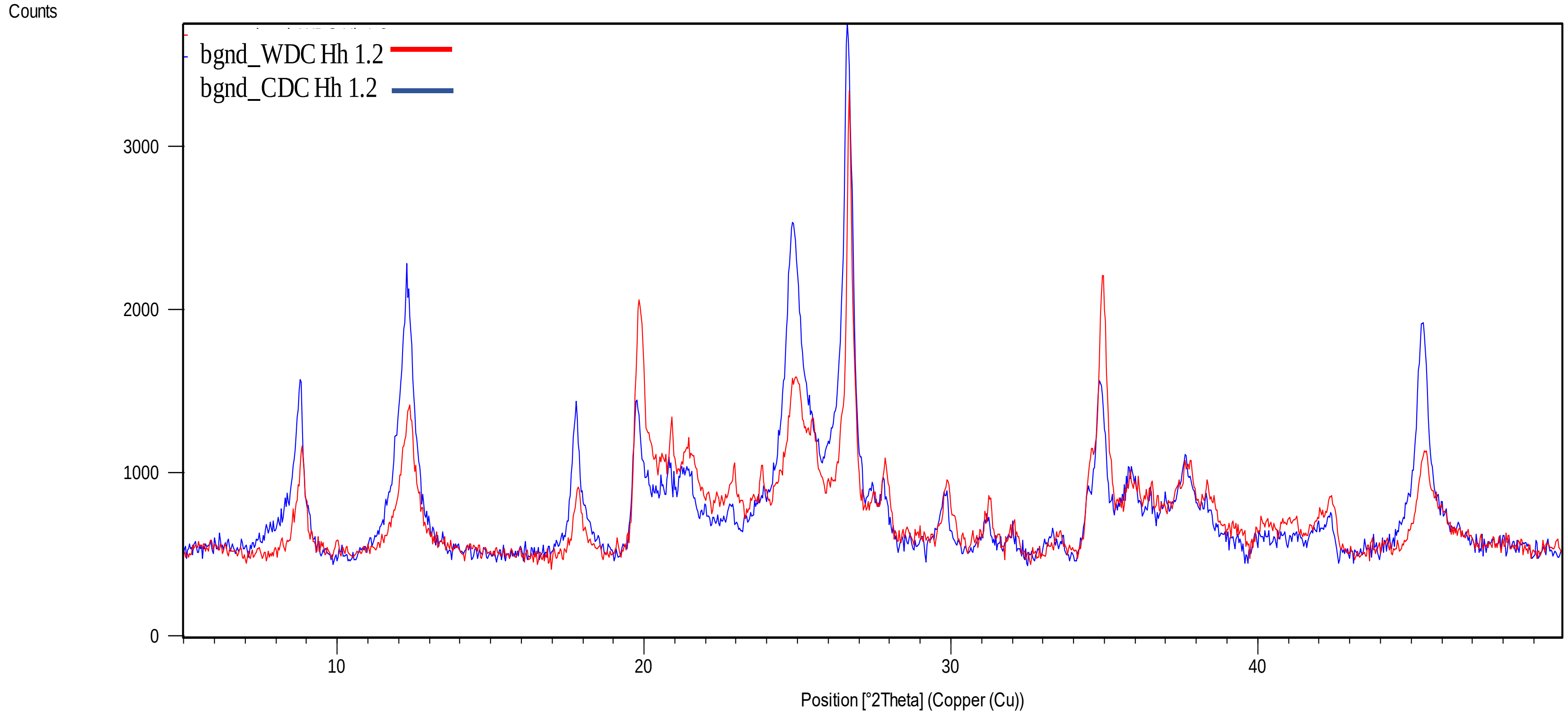

Figure B-4: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (neocutanic B1 horizon) of profile Hh 1.2 found in these two treatments.

Profile: Hh 3.2

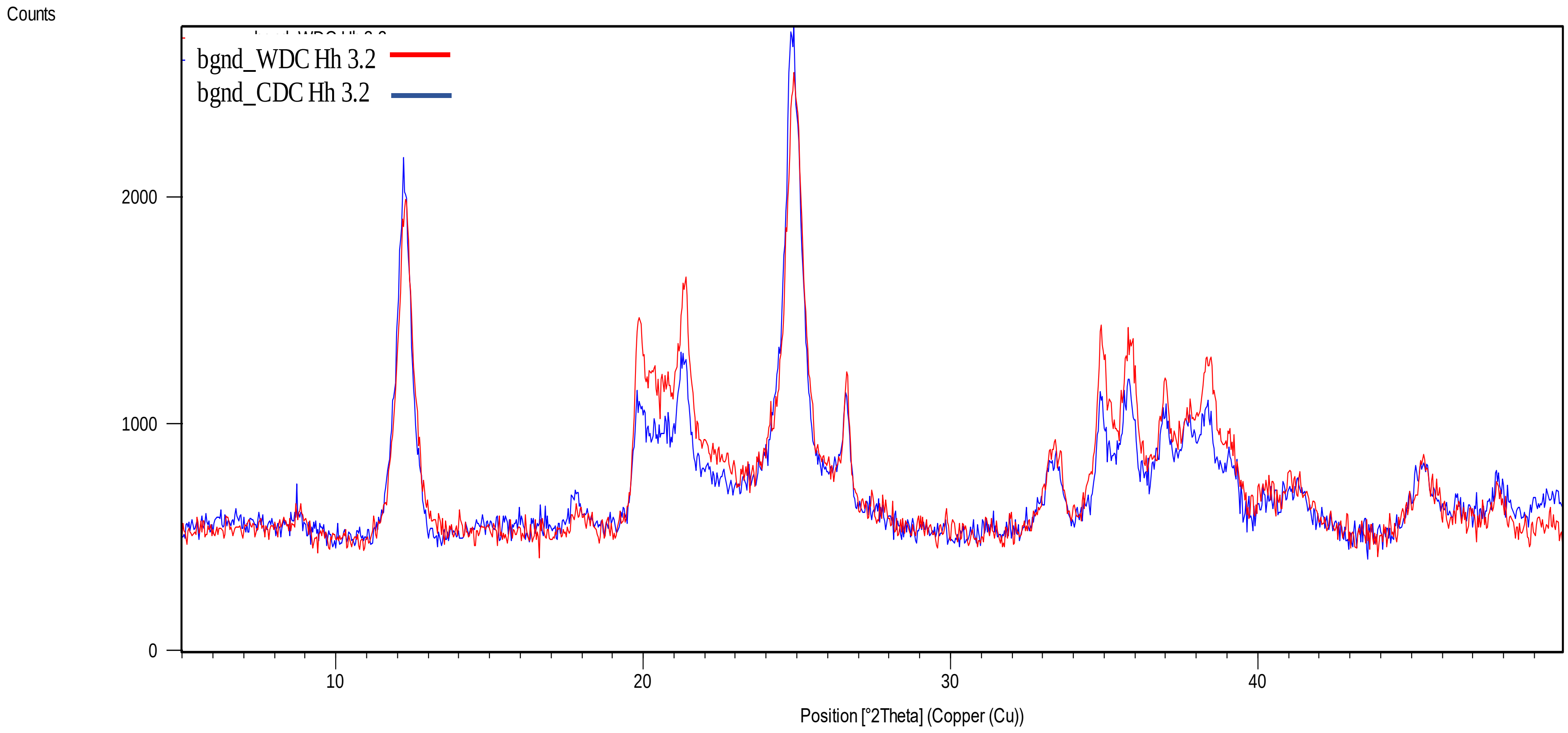

Figure B-5: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (neocutanic B1 horizon) of profile Hh 3.2 found in these two treatments.

Profile: Hh 4.2

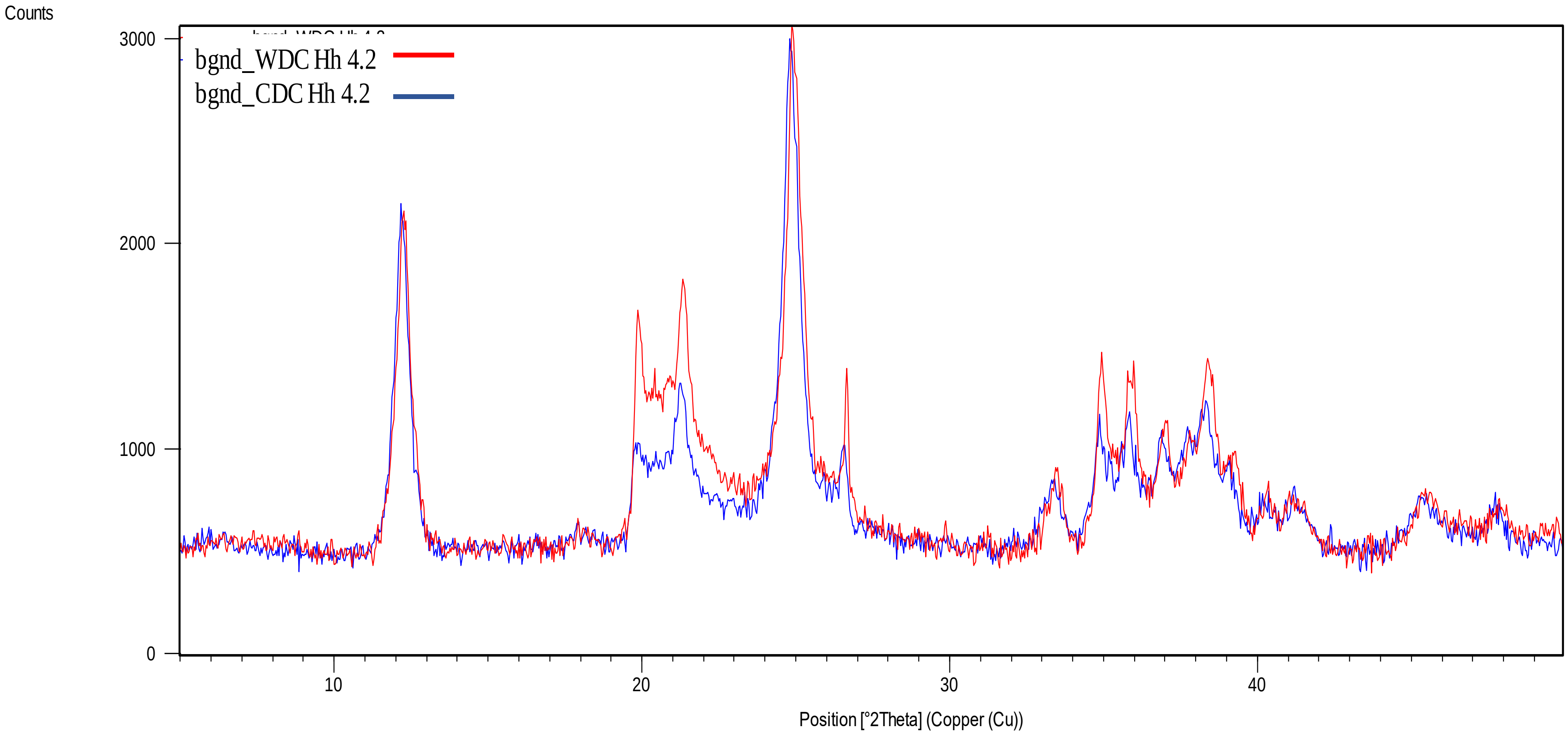

Figure B-6: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (neocutanic B1 horizon) of profile Hh 4.2 found in these two treatments.

Profile: Pb 3.2

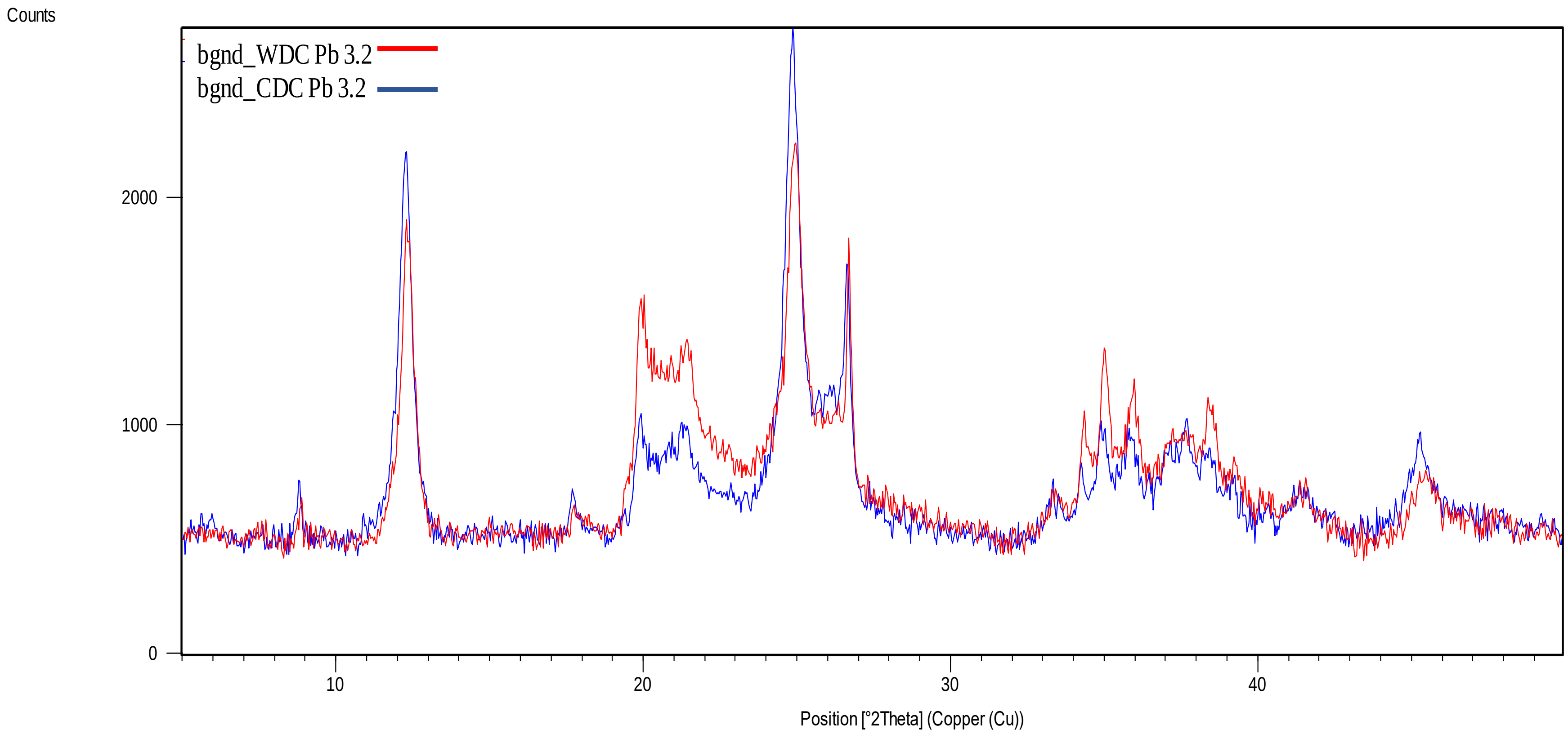

Figure B-7: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (neocutanic B1 horizon) of profile Pb 3.2 found in these two treatments.

Profile: Mb 1.2

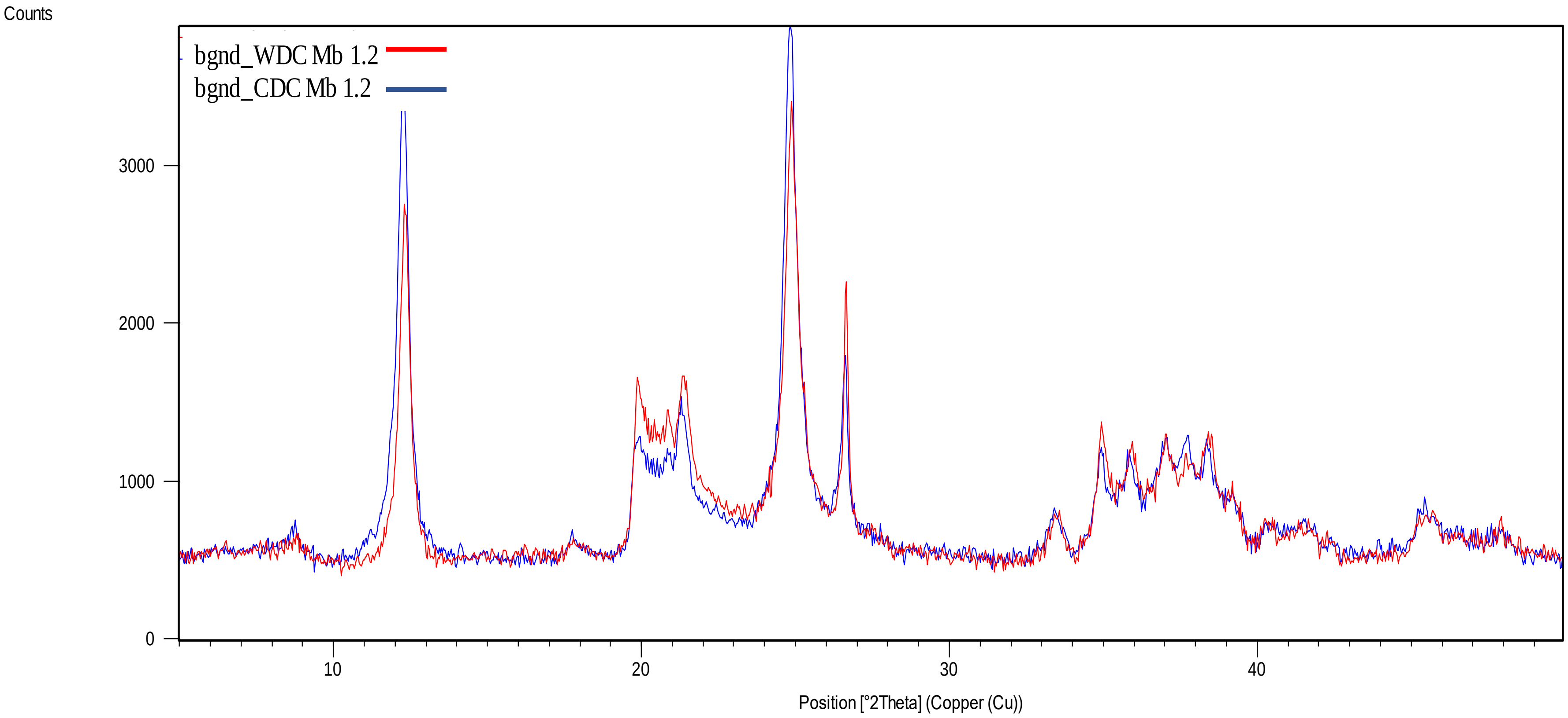

Figure B-8: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (neocutanic B1 horizon) of profile Mb 1.2 found in these two treatments.

Profile: Us 1.2

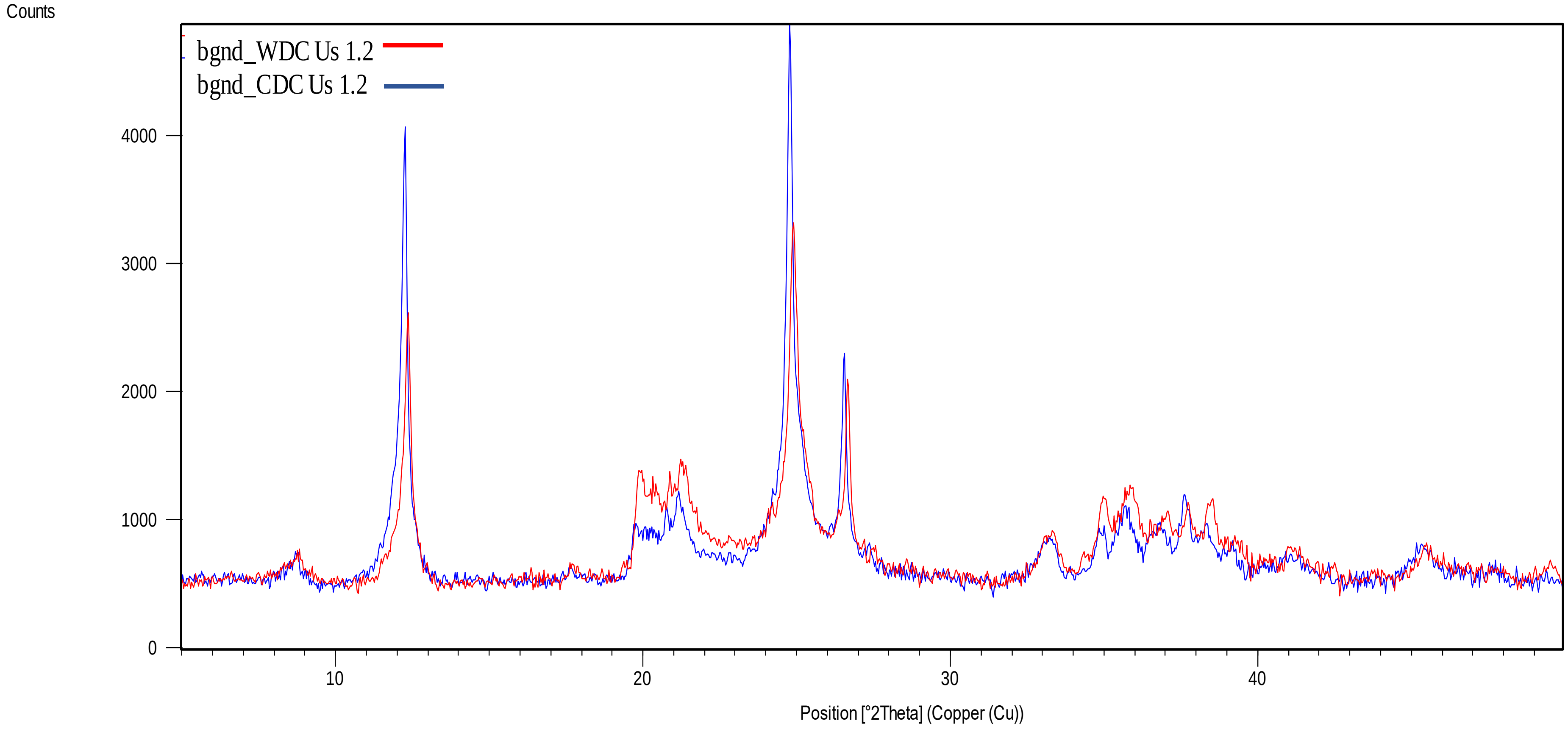

Figure B-9: X-ray diffraction patterns of water dispersible clay (WDC) and chemically dispersible clay (CDC) separated from the subsoil (red apedal B1 horizon) of profile Us 1.2 found in these two treatments.