

Colloid mobilization and transport in structured soils

The role of colloid dispersion, colloid stability and preferential flow

Ph.D. dissertation

Kolloidmobilisering og –transport i struktureret jord

Effekt af kolloiddispergering, kolloidstabilitet og præferentiel strømning

Ph.D.-afhandling

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Preface

The present dissertation including the enclosed four articles is submitted in partial fulfilment of the requirements for the Doctor of Philosophy (Ph.D.) degree at Aalborg University (AAU). Associate Professor Per Moldrup, Department of Environmental Engineering, Institute of Life Sciences, Aalborg University, and Senior Scientist Lis Wollesen de Jonge, Department of Agroecology, Danish Institute of Agricultural Sciences have been my supervisors.

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Summary

An increasing number of studies have referred to the concept of mobile colloids acting as transport carriers of strongly sorbing environmental contaminants such as pesticides, phosphorus, heavy metals and nonpolar organic compounds. Strongly sorbing contaminants have traditionally been regarded as immobile, but the ability of mobile colloids to facilitate the transport of sorbing contaminants in the vadose zone is now well documented. Studies on model systems and packed soil columns have revealed the importance of physical and chemical perturbations on the mobilization and transport of colloids. At present, however, the available information about the intrinsic and dynamic soil properties controlling *in situ* colloid mobilization and transport in natural structured soil is still insufficient to predict the risk of colloid and colloid-facilitated transport. The main issue to be considered when evaluating *in situ* mobilization and transport in structured soils is first the process of colloid mobilization or colloid dispersion. Once colloids have been mobilized the transport is determined by both the size and stability of the colloids in the soil solution, and by the pore size and geometry of the actively conducting pore system. Results have shown that macropores may provide preferential pathways for water flow and suspended colloids, however, less is known about the actual role of soil structure and preferential flow on the *in situ* mobilization of colloids. The overall purpose of this thesis is to contribute to the understanding of *in situ* colloid mobilization and transport in structured soils, with focus on four aspects: (i) colloid dispersion, (ii) colloid stability, (iii) soil structure and flow behavior in structured soils, and (iv) the overall process of *in situ* mobilization and transport in structured soils. Special emphasis is on investigating the effect of soil clay content (represented by six soils along a natural clay gradient, Lerbjerg, with 12, 18, 24, 28, 37 and 43% clay) and initial matric potential ($\psi = -2.5, -100$ and $-15,500$ hPa) and evaluate the role of colloid dispersion and preferential flow in controlling colloid mobilization and transport.

Measuring the amount of water-dispersible colloids (WDC) reflects the inherent susceptibility of the soil aggregates to disintegrate and release colloids in response to infiltration of water. In order to resemble the natural *in situ* release of colloids, a new low-energy input measurement of WDC (LE-WDC) was developed and compared with measurements of conventional high-energy input WDC (HE-WDC). When investigating colloid dispersion from the Lerbjerg clay gradient, total clay content, initial matric potential and the interacting effect of clay and water turned out to be key properties with respect to predicting colloid dispersion, while the effect of wetting rate was significant only at dry initial conditions (IMP $-15,500$ hPa). Pretreatment and energy input in the measurement procedure significantly affected the amount of WDC, yielding a positive correlation between clay content and HE-WDC, while a negative correlation existed between clay content and LE-WDC. Decreasing the initial matric potential reduced the amount of LE-WDC, and also the dependency of soil clay content. Soils incubated at $-15,500$ hPa released a low amount of LE-WDC independent of clay content. Colloid dispersibility changed as a function of time and moisture status with the main part of the changes in dispersibility occurring during or immediately after adjustment of the moisture content. This study

demonstrated that WDC is a very sensitive and dynamic parameter, which highlights the importance of choosing the estimates of WDC that resemble the relevant conditions for predictive modeling.

The transport of mobilized colloids highly depends on the size and stability of dispersed colloids in the soil solution. This study documented that surface coatings of organic matter increased the suspension stability of natural WDC isolated from a typical Danish Agrudalf. The contribution of organic carbon (OC) to the colloidal stability was inferred from: (i) a low N_2 -adsorption surface area, more negative zeta(ζ)-potential and larger suspension stability of WDC with larger content of OC, and (ii) increased N_2 -adsorption surface area, reduced negative ζ -potential as well as suspension stability after OC removal. The stability behavior of the natural WDC strongly depended on $CaCl_2$ concentration, with a two fold increase of the initial particle diameter occurring at an electric conductivity of $91 \mu S cm^{-1}$ for the least stable colloids and $1023 \mu S cm^{-1}$ for the most stable and OC-enriched colloids. The effect of solution pH on colloid stability was significant only at pH below 4.5. This implies that under the ionic strength conditions observed in the effluent from the Lerbjerg columns ($200-700 \mu S cm^{-1}$) only the most stable OC-enriched colloids will remain suspended, while the least stable colloids will flocculate. This study demonstrated that the average ζ -potential alone could not predict colloid stability, due to the possible effect of heterogeneously charged surface sites and steric repulsion forces.

Both the *in situ* mobilization and subsequent transport of mobilized colloids depends on the pore size and geometry of the actively conducting pore system. In addition, the dynamic properties of the soil and the changes in soil structure may be important with respect to *in situ* mobilization of colloids, as changes in soil structure changes the cohesive forces among colloids, exposes new surfaces and changes the flow pathways. Analysis of the soil (macropore) structure characteristics and the flow behavior of the Lerbjerg clay gradient revealed that the macroporosity (defined as pores $\geq 30 \mu m$) and number of macropores ($\geq 30 \mu m$) decreased with increasing clay content, while all soils exhibited pronounced structural similarity with respect to pore organization index and equivalent macropore diameter. The 12% clay soil exhibited matrix dominated flow behavior, probably attributed to the existence of a large fraction of drained pores at the applied pressure potential which may have resulted in disconnection of part of the rapidly conducting flow pathways. With increasing clay content, up to 24% clay, the degree of preferential transport increased. This was inferred from (i) the shape of the breakthrough curves with rapid breakthrough and pronounced tailing, (ii) the number of pore volumes eluted when 12.5% of the applied tritium had been displaced, and (iii) the estimated amounts of mobile and immobile water demonstrating an increased amount of immobile water with increasing soil clay content. Thus, at higher clay contents only a minor fraction of the pore volume participated in the convective transport, accompanied by diffusive mass transfer between mobile and immobile water regions. Drying to $-15,500 hPa$ and re-wetting significantly reduced the degree of preferential flow probably as a result of closing of

the largest pores following shrinkage and swelling, resulting in matrix dominated flow behavior for soils with 12, 18 and 24% clay.

In situ mobilization and transport of colloids in natural structured soils depends on the complex interaction of both (i) the inherent soil properties controlling the maximum colloid dispersibility, and (ii) the dynamic properties determining the prevailing conditions for mobilization and transport. Two key properties controlling colloid mobilization in structured soils were hypothesized to be the ability of colloids to disperse in response to infiltration of low-ionic strength rainwater, and the degree of preferential flow. The results revealed that (i) accumulated colloid leaching decreased with increasing clay content to a minimum leaching at $\geq 24\%$ clay for the initially wet and moderate wet soils, (ii) colloid leaching from initially dry soils was low and independent of clay content, (iii) initial matric potential affected only accumulated colloid leaching at the lower clay content (12 and 18% clay), and colloid leaching was higher from the initially moderate wet soils than the initially wet soils due to an initially lower ionic strength in the pore water in the moderate wet soil, (iv) accumulated leaching of carbon consisted mainly of DOC and was independent of clay content, and (v) drying to $-15,500$ hPa increased the accumulated amount of carbon leached. The primary factor controlling colloid mobilization seemed to be the ability of colloids to disperse in response to low-ionic strength rainwater. Results indicated that colloid mobilization was limited by colloid dispersion due to either (i) the time-dependent increase in repulsive forces due to continued infiltration of low-ionic strength rainwater, (ii) low diffusive exchange of resident water with low-ionic strength rainwater, or (iii) a combination of low diffusive exchange of resident water with low-ionic strength rainwater, and high colloid cohesive associations due to either a high volume of clay ($\geq 24\%$ clay) or stronger associations upon drying (IMP $-15,500$ hPa). This study highlighted the importance of both colloid dispersibility and the degree of preferential flow as key parameters when predicting *in situ* colloid mobilization.

Dansk resumé (Danish summary)

Et stigende antal undersøgelser refererer til det faktum at mobile kolloider fungerer som transportører af stærkt adsorberende miljøfremmede stoffer såsom pesticider, phosphor, tungmetaller og apolære organiske forbindelser. Stærkt adsorberende forureningsstoffer er traditionelt blevet betragtet som immobile i jord, men mobile kolloiders evne til at facilitere transporten af stærkt adsorberende forureningsstoffer i den umættede zone er nu fuldt dokumenteret. Grundlæggende studier på modelsystemer og pakkede jordkolonner har belyst betydningen af fysiske og kemiske perturbationer på mobilisering og transport af kolloider. På nuværende tidspunkt er den tilgængelige viden omkring de iboende og dynamiske faktorer der kontrollerer *in situ* mobilisering og transport af kolloider i naturlig struktureret jord dog stadig utilstrækkelig til at forudsige risikoen for kolloid- og kolloid-faciliteret transport. De primære forhold, der skal betragtes i forbindelse med evaluering af kolloid mobilisering og transport i struktureret jord, er først og fremmest processen omkring kolloid mobilisering eller dispergering. Når kolloider er mobiliseret vil transporten igennem jorden være bestemt af såvel størrelse som stabilitet af de suspenderede kolloider, samt af porestørrelse og geometri af det aktive strømningssystem. Resultater har vist at makroporer kan fungere som præferentielle strømningssysteme for vand og suspenderede kolloider, hvorimod det er uklart hvilken betydning jordstruktur og præferentiel strømning har på *in situ* mobilisering af kolloider. Det overordnede formål med denne afhandling er at bidrage til en øget forståelse af *in situ* mobilisering og transport af kolloider i struktureret jord, med særlig fokus på at undersøge effekten af lerindhold og initialt matrix potentiale, samt evaluere af betydningen af kolloid dispergering og præferentiel strømning på kolloid mobilisering og transport.

Målinger af mængden af vand-dispergerbare kolloider (VDK) reflekterer aggregaters tilbøjelighed til at nedbrydes og frigive kolloider som respons til infiltration af vand. Med henblik på at efterligne den naturlige *in situ* frigivelse af kolloider, blev der i dette studie udviklet en ny lav-energi dispergeringsmetode til bestemmelse af VDK (LE-VDK). Denne blev sammenholdt med en konventionel høj-energi dispergeringsmetode (HE-VDK). I forbindelse med undersøgelse af kolloid dispergering på en naturligt forekommende tekstur gradient (Lerbjerg) blev lerindhold, initialt matrix potentiale (IMP) og vekselvirkningseffekten mellem ler og vand fundet at være nøglefaktorer, mens effekten af opfugningshastighed kun var signifikant under tørre initiale betingelser (IMP -15,500 hPa). Forbehandling og energitilførsel i målingsproceduren påvirkede bestemmelsen af VDK signifikant og resulterede i en positiv korrelation mellem lerindhold og HE-VDK, hvorimod der blev observeret en negativ korrelation mellem lerindhold og LE-VDK. Reduktion af det initiale matrix potentiale reducerede mængden af LE-VDK, samt afhængigheden af lerindhold hvor udtørring til IMP -15,500 hPa resulterede i en lav mængde LE-VDK der var uafhængig af lerindholdet. Mængden af dispergerbare kolloider varierede som funktion af tid og vandstatus, hvor den primære variation i mængden af dispergerbare kolloider forekom under eller umiddelbart efter justering af vandindholdet. Dette studie demonstrerede at VDK er en meget følsom og

dynamisk parameter, hvilket fremhæver betydningen af at vælge relevante VDK-estimer i forbindelse med risikovurdering og prediktiv modellering.

Transporten af mobiliserede kolloider afhænger af størrelse og stabilitet af dispergerede kolloider i jordvæsken. Dette studie dokumenterede at overfladeassociationer af organisk materiale forøgede suspensionsstabiliteten af naturlige VDK isoleret fra en typisk dansk Agrudalf (Flakkebjerg). Betydningen af organisk carbon (OC) på kolloidstabiliteten blev antydnet på basis af: (i) lavt N_2 -adsorptions overfladeareal, mere negativt zeta(ζ)-potentiale og større suspensionsstabilitet af VDK med større indhold af OC, og (ii) forøget N_2 -adsorptions overfladeareal, reduceret negativt zeta(ζ)-potentiale og reduceret suspensionsstabilitet efter fjernelse af OC. Suspensionsstabiliteten af naturlige VDK afhang markant af $CaCl_2$ koncentrationen, med en fordobling af den initiale partikeldiameter ved en elektrisk ledningsevne på $91 \mu S cm^{-1}$ for de mindst stabile kolloider og $1023 \mu S cm^{-1}$ for de mest stabile og OC-berigede kolloider. Effekten af jordvæskens pH på kolloidstabiliteten var kun betydelig ved pH under 4.5. Dette indebærer at kun de mest stabile OC-berigede kolloider vil vedblive at være suspenderede, mens de mindst stabile vil flokkulere under de ionstyrke forhold der blev observeret i effluenten fra Lerbjerg-kolonnerne ($200-700 \mu S cm^{-1}$). Dette studie demonstrerede at det gennemsnitlige ζ -potentiale ikke kunne bruges til at forudsige kolloidstabiliteten, som følge af den mulige effekt af heterogent ladede overflader og steriske frastødningskræfter.

Såvel *in situ* mobilisering og efterfølgende transport af mobiliserede kolloider afhænger af porestørrelse og geometri af det aktive strømningssystem. Desuden kan ændringer i jordstruktur være en væsentlig faktor i forbindelse med *in situ* mobilisering af kolloider, idet ændringer i jordstruktur påvirker bindingskræfterne mellem kolloider, eksponerer nye overflader og påvirker det aktive strømningssystem. Analyse af jord(makropore)struktur karakteristika og strømningforhold i jorde fra Lerbjerg teksturgradienten belyste at makroporøsiteten (defineret som porer $\geq 30 \mu m$) og antallet af makroporer ($\geq 30 \mu m$) aftog med stigende lerindhold. Derimod udviste samtlige jorde en strukturel lighed med hensyn til poreorganisationsindeks og ækvivalent makroporediameter. Jorde med 12% ler udviste matrix-dominerede strømningforhold. Dette var formodentligt resultatet af en stor fraktion af afdrænede porer ved det pågældende trykpotentiale, hvilket kan have resulteret i afkobling af dele af det hurtigt ledende strømningssystem. Graden af præferentiel strømning blev forøget med stigende lerindhold op til 24% ler. Dette blev udledt af (i) gennembrudskurvens form med hurtigt gennembrud og udpræget asymmetri, (ii) antal udvaskede porevolumener efter udskiftning af 12.5% af det tilførte tritium, og (iii) den estimerede mængde af mobilt og immobilt porevand, med en stigning i mængden af immobilt vand ved stigende lerindhold. Ved højere lerindhold bidrog således kun en mindre fraktion af porevolumenet i konvektiv transport, ledsaget af diffusiv transport mellem mobilt og immobilt porevand. Udtørring til $-15,500$ hPa og genopfugtning reducerede graden af præferentiel strømning signifikant. Dette var sandsynligvis et resultat af lukning af de største porer som følge af skrumpning og kvældning, og resulterede i matrix-domineret strømning for jorde med 18 og 24% ler.

In situ mobilisering og transport af kolloider i naturlig struktureret jord afhænger af den komplekse vekselvirkning af såvel (i) de iboende jordegenskaber der kontrollerer den maksimale mængde dispergerbare kolloider, og (ii) de dynamiske egenskaber der definerer de aktuelle forhold for mobilisering og transport. To centrale egenskaber der kontrollerer kolloid mobilisering i struktureret jord blev antaget at være kolloiders dispergerbarhed som respons til infiltration af lav-ionstyrke vand, samt graden af præferentiel strømning. Resultaterne viste at: (i) Den akkumulerede kolloidudvaskning blev reduceret med stigende lerindhold til en minimums udvaskning ved $\geq 24\%$ ler for den initialt våde (IMP -2.5 hPa) og moderat våde (IMP -100 hPa) jord. (ii) Udvasningen af kolloider fra den initialt tørre jord (IMP -15,500 hPa) var lav og uafhængig af lerindholdet. (iii) Det initiale matrix potentiale påvirkede kun den akkumulerede kolloidudvaskning ved lavere lerindhold (12 og 18% ler). Kolloidudvasningen var højere fra den initialt moderat våde jord sammenlignet med den våde. Dette var en følge af en lavere ionstyrke i porevandet i den moderat våde jord. (iv) Den akkumulerede udvaskning af carbon bestod primært af opløst organisk carbon og var uafhængig af lerindholdet. (v) Udtørring til -15,500 hPa forøgede den akkumulerede udvaskning af carbon. Den primære faktor der kontrollerede mobiliseringen af kolloider syntes at være kolloidernes dispergerbarhed ved infiltration af lav-ionstyrke vand. Resultaterne indikerede at kolloidmobiliseringen var begrænset af dispergering som følge af enten: (i) den tidsafhængige forøgelse i den elektrostatiske frastødning, som følge af fortsat infiltration af lav-ionstyrke vand, (ii) en lav diffusiv udveksling af høj-ionstyrke intraaggregat vand med lav-ionstyrke infiltrations vand, eller (iii) en kombination af lav diffusiv udveksling af høj-ionstyrke intraaggregat vand med lav-ionstyrke infiltrations vand, og stærke kolloidassociationer som følge af enten et højt indhold af ler ($\geq 24\%$ ler) eller stærkere associationer efter udtørring (IMP -15,500 hPa). Dette studie fremhævede betydningen af såvel kolloid dispergering samt graden af præferentiel strømning som centrale parametre i forbindelse med prediktering af *in situ* kolloid mobilisering.

List of supporting papers

- I. C. Kjaergaard, L.W. de Jonge, P. Moldrup and P. Schjønning. 2004. Water-Dispersible Colloids: Effects of Measurement Method, Clay Content, Initial Soil Matric Potential and Wetting Rate. *Vadose Zone Journal* 3:403-412.
- II. C. Kjaergaard, T.G. Poulsen, P. Moldrup and L.W. de Jonge. 2004. Colloid Mobilization and Transport in Undisturbed Soil Columns. I. Pore Structure Characterization and Tritium Transport. *Vadose Zone Journal* 3:413-423.
- III. C. Kjaergaard, P. Moldrup, L.W. de Jonge and O.H. Jacobsen. 2004. Colloid Mobilization and Transport in Undisturbed Soil Columns. II. The role of Colloid Dispersibility and Preferential Flow. *Vadose Zone Journal* 3:424-433.
- IV. C. Kjaergaard, H.C.B. Hansen, C.B. Koch and K.G. Villholth. 2004. Properties of Water-Dispersible Colloids from Macropore Deposits and Bulk Horizons of an Agrudalf. *Soil Sci. Soc. Am. J.* 68:1844-1852.

In this thesis the papers will be referred to by their Roman numerals.

List of abbreviations

BTC:	Breakthrough curves
CBD:	Citrate-bicarbonate-dithionite
CFC:	Critical flocculation concentration
DOC:	Dissolved organic carbon
EC:	Electrical conductivity
EDL:	Electrical double layer
EM:	Electrophoretic mobility
HE-WDC:	High-energy water-dispersible colloids
IMP:	Initial matric potential
LDV-PCS:	Laser Doppler Velocimetry – Photon Correlation Spectroscopy
LE-WDC:	Low-energy water-dispersible colloids
NOM:	Natural organic matter
MM:	Macropore matrix
MP:	Macropore deposits
OC:	Organic carbon
PCS:	Photon correlation spectroscopy
PMP:	Pretreatment matric potential
POC:	Particulate organic carbon
PZC:	Point of zero charge
SAR:	Sodium adsorption ratio
TOC:	Total organic carbon
WDC:	Water-dispersible colloids
WSA:	Water-stable aggregates

List of symbols

a_i	Activity of ion species (i) in the double layer	-
$a_{i\infty}$	Activity of ion species (i) in bulk solution	-
A	Cross section area	m^2
C	Solute concentration	$mg\ m^{-3}$
C_m	Solute concentration in the mobile water phase	$mg\ m^{-3}$
C_{im}	Solute concentration in the immobile water phase	$mg\ m^{-3}$
d	Separation distance between colloids	m
d	Equivalent pore diameter	μm
d_H	Hydrodynamic particle diameter	m
D	Hydrodynamic dispersion coefficient	$m^2\ s^{-1}$
D_{mec}	Mechanical dispersion	$m^2\ s^{-1}$
D_e	Effective diffusion coefficient	$m^2\ s^{-1}$
D_{Col}	Colloid diffusion coefficient	$m^2\ s^{-1}$
D_a	Air diffusion coefficient in soil air	$m^2\ s^{-1}$
D_0	Air/water diffusion coefficient in free air/water phase	$m^2\ s^{-1}$
E	Electric field	$V\ m^{-1}$
J_a	Diffusive air flow	$kg\ m^{-2}\ s^{-1}$
k_a	Air permeability	μm^2
k_{att}	First-order rate coefficient of colloid attachment	s^{-1}
k_{det}	First-order rate coefficient of colloid detachment	s^{-1}
k_{diff}	First-order rate coefficient of colloid diffusion	s^{-1}
L	Length	m
L_S	Sample length	m
M	Molar concentration	$mol\ L^{-1}$
n	Number	-
n_i	Number of ion species (i) at the surface	m^{-3}
$n_{i\infty}$	Number of ion species (i) in the bulk solution	m^{-3}
P	Air pressure	$kg\ m^{-1}\ s^{-2}$
q	Darcy flux velocity	$m\ s^{-1}$
q_a	Convective air flow	$m\ s^{-1}$
r	Particle radius	m
R	Retardation factor	-
t	Time	h
T	Temperature	K
z	depth	m
x	Distance	m
z	Ion valence	-
α	Diffusional mass transfer coefficient	h^{-1}
δ	Stern layer	m^{-1}

ε	Dielectricity constant		$C^2 J^{-1} m^{-1}$
ε_a	Air-filled porosity		$m^3 m^{-3}$
Φ	Total interaction energy between colloids		J
Φ_A	Attractive energy		J
Φ_R	Repulsive energy		J
η	Viscosity		$kg m^{-1} s^{-1}$
$1/\kappa$	Doublelayer thickness		m
λ	Tortuosity		-
μ	Electrophoretic mobility		$m^2 V^{-1} s^{-1}$
v	Pore water velocity / Particle velocity		$m h^{-1}$
θ	Volumetric water content		$m^3 m^{-3}$
θ_{m1}	Water region with rapid water flow		$m^3 m^{-3}$
θ_{m2}	Water region with moderate water flow		$m^3 m^{-3}$
θ_{im}	Immobile water region		$m^3 m^{-3}$
ρ_b	Dry bulk density		$g m^{-3}$
τ	Dispersivity		m
ψ	Electrical potential		V
ψ	Soil matric potential		hPa
ζ	Zetapotential		V

Physical constants

N_A	Avogadros number	6.023×10^{23}	mol^{-1}
k_B	Boltzmanns constant	1.3804×10^{-23}	$J K^{-1}$
ε_0	Dielectricity constant in vaccum	8.85×10^{-12}	$C^2 J^{-1} m^{-1}$
ε	Dielectricity constant in water (25°C)	78.54	-
e	Elementary charge	1.6021×10^{-19}	C
F	Faradays constant	96490	$C mol^{-1}$
R	Gas constant	8.3143	$J mol^{-1} K^{-1}$

1. Introduction

The presence of fertilizers, pesticides and other environmental contaminants in surface and groundwater has led to public concern about the quality of drinking water, and large monitoring programs has been initiated to evaluate the content of environmental contaminants in groundwater. The occurrence of environmental contaminants in groundwater reveals the limitation of our current understanding of transport processes in soils. Traditional approaches to describe and predict the movement of non-volatile contaminants treat soil and groundwater as a two-phase system in which contaminants partition between immobile solid constituents and the mobile water phase. Contaminants that are sparingly soluble in water, and have a strong tendency to bind to the solid phase, are assumed to be retarded in the soil. Many contaminants readily sorb to the soil solid phase and are therefore considered to present little danger in risk assessments concerning surface water or groundwater pollution. However, based on the extend of contaminants found in groundwater, it has become evident, that predictions and results obtained in laboratory batch systems may not always be applied to the field situation. Spatial variability or preferential flow phenomena have been hypothesized to be responsible for some of the inconsistencies between predictions and actual leaching of contaminants (Jury and Flühler, 1992). In addition, colloids in the solid phase may be mobile and can therefore act as a third phase increasing the extent of transport of strongly sorbing contaminants (McCarthy and Zachara, 1989).

The tendency of soil colloids to disperse from soil aggregates in response to infiltration of water (water-dispersible colloids, WDC) is a natural phenomenon, which results in the development of illuvial subsurface horizons with higher contents of clay compared to the upper eluvial horizons. Furthermore, micromorphological features showing deposits of clay skins on ped faces and at the interface of water conducting pores represent evidence of colloid translocation (Buol and Hole, 1961). Dispersion of colloids has also been suspected to be responsible for affecting soil physical properties such as surface crusting, surface erosion, water infiltration, and hydraulic conductivities (e.g. Miller and Baharuddin, 1986; Shainberg *et al.*, 1992). Leaching of suspended colloids has been documented in several laboratory experiments and field studies (see review by Kretzschmar *et al.*, 1999). The source of mobile colloids in the vadose zone is generally considered to be the *in situ* release of water-dispersible colloids. Colloids are operationally defined as particles between 1-10 nm and 2-10 μm in diameter (e.g. Stumm, 1992; Buffle and Leppard, 1995), and include layer silicates, sesquioxides (Fe- and Al-oxyhydroxides), organic macromolecules, bacteria and viruses (Figure 1). Owing to their high specific surface area colloids have a high sorptive capacity and can be effective sorbents of low solubility, strongly sorbing contaminants. Transport of colloids through the vadose zone hereby causes an increased risk of leaching of contaminants generally regarded as relatively immobile.

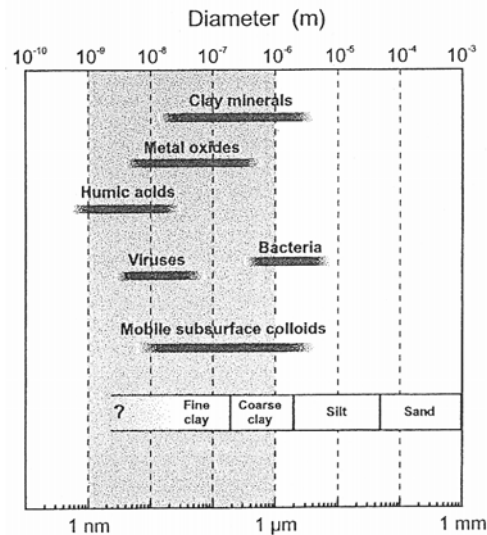


Figure 1. Size range of soil colloidal particles. (From Kretzschmar *et al.*, 1999).

Several experimental investigations have suggested that colloids may influence the transport of contaminants in the vadose zone. Laboratory column studies have demonstrated cotransport of contaminants sorbed to suspended colloids, or contemporary leaching of *in situ* colloids and contaminants, and field studies have demonstrated the association of contaminants with colloids in drain or groundwater. Using homogeneously packed soil columns Vinten *et al.* (1983) demonstrated vertical transport of DDT adsorbed to suspended montmorillonite colloids. Grolimund *et al.* (1996) demonstrated that suspended *in situ* mobilized colloids provided a pathway for rapid transport of Pb. Williams *et al.* (2000) found evidence that napropamide was transported through packed soil columns complexed to dissolved organic matter. Experiments with undisturbed soil columns have documented that suspended colloid-contaminant complexes may facilitate the transport of atrazine (Seta and Karathanasis, 1997b), and Cu and Zn (Karathanasis, 1999). In addition it was demonstrated that *in situ* mobilized colloids was able to facilitate the transport of prochloraz (de Jonge *et al.*, 1998) and glyphosate (de Jonge *et al.*, 2000) in undisturbed macroporous soil columns. In the field Jørgensen and Frederecia (1992) found indications of transport of DDT adsorbed to clay minerals in a fractured clayey till. In roadside soils receiving deicing salts Amrhein *et al.* (1993) found effluent concentrations of Cu, Pb, Ni, Cr in the colloidal size fraction. Grant *et al.* (1996) found significant drainage loss of particulate phosphorus from arable catchments. Laubel *et al.* (1999) observed significant loss of particulate matter and particulate phosphorus in both field plot experiments and tile-drained catchment studies. Sprague *et al.* (2000) found that a measurable amount of total atrazine transport in a field lysimeter occurred in association with mobile soil colloids. Villholth *et al.* (2000) found evidence of colloid-facilitated transport of prochloraz to subsurface drains. Uusitalo *et al.* (2001) observed that most of the phosphorus leached as drainflow occurred as particulate phosphorus. Petersen *et al.* (2003) observed a positive correlation between drainage water concentration of strongly sorbing Pendimethalin and

particle turbidity, whereas concentrations of weakly sorbing ioxynil and turbidity were uncorrelated. The authors concluded, that the strong positive correlation between pendimethalin concentration and turbidity suggested, but did not prove, that pendimethalin transport was facilitated by colloids. Experimental evidence demonstrating the phenomenon of colloid-facilitated transport of contaminants exist, however, at present we are still not able to predict the quantitative importance of this phenomenon, or make priori predictions of the risk of colloid-facilitated transport of contaminants under field conditions. Understanding the processes controlling *in situ* mobilization and transport of colloids in the vadose zone is a prerequisite for predicting the risk and quantifying the importance of colloid-facilitated transport of contaminants.

A comprehensive amount of literature exists on theories describing colloid mobilization, transport or deposition, and laboratory experiments using model systems or packed soil have been applied to test these theories (e.g. Swanton, 1995; Roy and Dzombak, 1996; Ryan and Elimelech, 1996; Kretzschmar *et al.*, 1999). These studies have revealed the importance of physical and chemical perturbations on the mobilization and transport of colloids. In contrast to the vast majority of studies on model systems or packed soil columns, only few studies have investigated colloid mobilization and transport in natural structured soils (Kaplan *et al.*, 1993; Jacobsen *et al.*, 1997; Seta and Karathanasis, 1997a; de Jonge *et al.*, 1998, 2000; Ryan *et al.*, 1998; Karathanasis, 1999; Lægdsmand *et al.*, 1999; El-Farhan *et al.*, 2000; Villholth *et al.*, 2000; Schelde *et al.*, 2002; Petersen *et al.*, 2003). At present the available information about the intrinsic and dynamic soil properties that control *in situ* colloid mobilization and transport in natural structured soil are still insufficient to predict the risk of colloid leaching.

In situ mobilization and transport of colloids in natural structured soils depend on the complex interaction between the inherent soil characteristics controlling the maximum colloid dispersibility, and the dynamic properties determining the prevailing conditions for colloid mobilization and transport. Three main issues should be considered when evaluating the overall process of *in situ* colloid mobilization and transport (Figure 2). The first issue to be considered involves (i) dispersion or release of *in situ* colloids. Once the colloids have been mobilized, they can be transported through the vadose zone, the transport being determined by both (ii) the size and stability of the dispersed colloids in the soil solution, and by (iii) the pore size and geometry of the actively conducting pore system. A variety of soil properties influence the amount of colloids that disperse in water, however, several studies have identified clay content and soil-water content as two of the most important properties determining the amount of water-dispersible colloids released in response to low-ionic strength solution (Pojasok and Kay, 1990; Brubaker *et al.*, 1992; Rasiah *et al.*, 1992). Clay content affects colloid mobilization directly due to the influence on colloid cohesion and aggregate stability, and indirectly through the effect on soil structure and structure stability. The initial soil water content is of significant importance both with respect to the dispersibility of colloids, as well as the soil structure (e.g. shrinkage-swelling phenomena) affecting the actively conducting flow system.

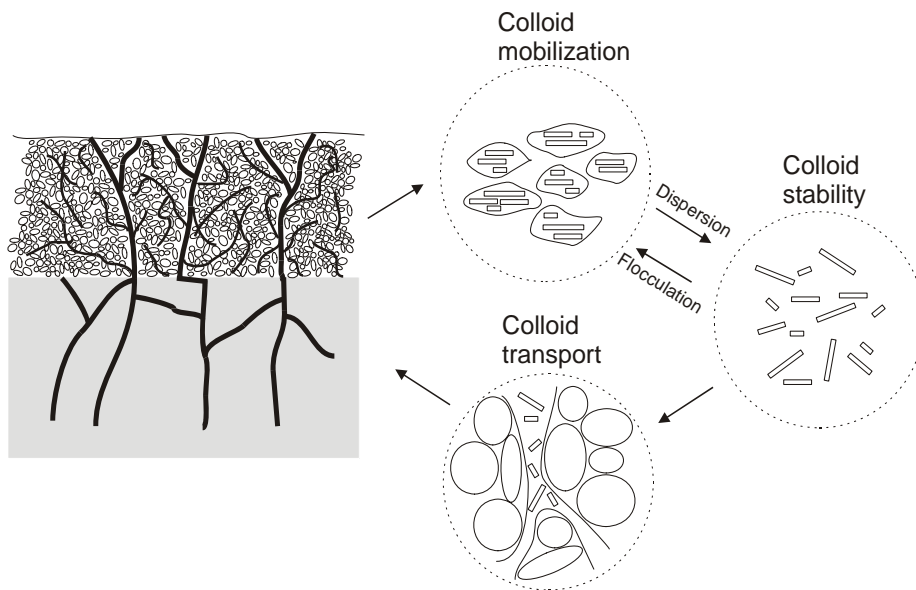


Figure 2. Conceptual illustration of the main issues to be considered when investigating the process of *in situ* colloid mobilization and transport.

In this project it was hypothesized that two key properties controlling colloid mobilization in natural structured soils were: (i) the ability of colloids to disperse in response to infiltration of low-ionic strength rainwater, and (ii) the degree of preferential flow. The ratio between soil volumes conducting water versus soil volumes bypassed by water-flow, defining the degree of preferential flow, may be an important property influencing both *in situ* colloid mobilization and the subsequent translocation. Preferential flow may accelerate the transport of externally applied colloid-contaminant complexes or colloid-contaminants complexes located close to the preferential pathways, but decrease the *in situ* mobilization and leaching of colloids located at some distance from the preferential flow paths. At present no studies have systematically investigated the role of preferential flow on colloid mobilization.

1.1 Objectives

The general objective of this study is to increase the understanding of the processes controlling colloid mobilization and transport in natural structured soils. Focus is on four aspects influencing colloid mobilization and transport: (i) colloid dispersion, (ii) colloid stability, (iii) soil structure and the susceptibility for preferential flow in structured soils, and (iv) the overall process of *in-situ* colloid mobilization and transport in structured soils. Special emphasis is placed on investigating the effect of soil clay content and initial matric potential on *in situ* colloid mobilization and transport, and evaluating the role of colloid dispersion and preferential flow.

i. Colloid dispersion

Measuring the amount of water-dispersible colloids reflects the inherent susceptibility of the soil aggregates to disintegrate and release colloids in response to infiltration of low-ionic strength rainwater. Key properties determining the amount of WDC is hypothesized to be soil clay content, initial matric potential and wetting rate. Traditional methods for measuring WDC involve air-drying and mechanical shaking, but air-drying may introduce changes that alter colloid cohesion, and application of high energy inputs during the shaking may break up aggregates and increase colloid dispersion. In order to resemble the natural *in situ* mobilization of colloids better, a new low-energy input measurement of WDC was developed and compared with measurements of conventional high-energy input WDC. The objectives of this study were:

- to evaluate the results from the low-energy input measurement of WDC against a conventional high-energy input measurement using air-dry soil.
- use the low-energy input WDC measurement to determine the influence of clay content, initial matric potential, and wetting rate on colloid dispersion in response to infiltration of low-ionic strength water.

ii. Colloid stability

To be mobile over significant distances colloids must be stable in the soil solution, i.e. resistant to flocculation with other colloids or attachment to the matrix surfaces. Transport of colloids through soil is thus enhanced by conditions promoting colloid stability. Experimental evidence suggest that natural organic matter adsorbed to soil colloids stabilizes colloid suspensions, and thereby control the stability behavior of natural soil colloids. This has also raised doubt about the direct importance of the clay mineralogy on the stability behavior of natural soil colloids. The objectives of this study were:

- to characterize the mineralogy and physico-chemical properties of WDCs separated from bulk soil horizons and from macropore deposits of a Typic Agrudalf, a typical Danish clayey soil in which dispersion and translocation of clay colloids are key phenomena.
- to evaluate the effect of solution pH, ionic strength and the role of colloid associated organic matter and sesquioxides on the stability behavior of natural WDCs.

iii. Soil structure and preferential flow

Both the *in situ* mobilization and subsequent transport of mobilized colloids depend on the contact area between the infiltrating water and the colloids, and the pore size and geometry of the actively conducting pore network. In order to investigate the role of soil

structure and flow behavior on *in situ* colloid mobilization and transport an analysis of the soil structure characteristics and flow-behavior was carried out on soils from the Lerbjerg clay gradient. The objectives of this study were:

- to examine the influence of varying clay content (along a natural soil texture gradient) on the soil (macropore) structure, and evaluate the effect of initial matric potential (predrying) on the soil structure.
- to examine the influence of soil structure, as determined by clay content and initial matric potential (predrying), on tritium transport under steady unsaturated flow conditions

iv. Colloid mobilization and transport in structured soils

In situ mobilization and transport of colloids in natural structured soils depend on the complex interaction of both (i) the inherent soil properties controlling the maximum colloid dispersibility, and (ii) the dynamic properties determining the prevailing conditions for colloid mobilization and transport. At present the available information about the inherent and dynamic soil properties that control colloid mobilization and transport in natural structured soils are insufficient to predict the risk of colloid leaching. Two key properties controlling colloid mobilization in structured soils may be the ability of colloids to disperse in response to infiltration of low-ionic strength rainwater, and the degree of preferential flow. The objectives of this study were:

- to investigate the effect of soil clay content and initial matric potential on mobilization and leaching of colloids and organic carbon from unsaturated structured soils in response to infiltration of low-ionic strength rainwater.
- to evaluate the role of colloid dispersibility and preferential flow in controlling colloid mobilization and transport in unsaturated structured soils.

2. Colloid dispersion

The fraction of colloids that disperse in water – water-dispersible colloids – is recognized as an important property with respect to predicting soil erosion (e.g. Miller & Baharuddin, 1986; Brubaker *et al.*, 1992), colloid leaching (Jarvis *et al.*, 1999) and colloid-facilitated transport (Villholth *et al.*, 2000). However, different mechanisms and soil properties may influence the release of WDC in different soil types and to understand why and how these differences arise we must first consider the mechanisms involved in aggregate breakdown and colloid release.

2.1 Processes of aggregate breakdown

In general most of the particles in soils are compound particles or aggregates which maintain their structure because of associations between colloids and the larger particles present. Soil aggregates are formed by both physical and biological processes. The major abiotic forces involved in soil aggregation result from the cohesive nature of clays and the shrink-swell capacity associated with the colloids. The greater the clay content the more important is the abiotic forces in soil aggregation (Oades, 1993). These interactions can be influenced by the presence of bonding components such as sesquioxides (Fe- and Al-oxyhydroxides) and organic matter. Such material may influence the surface properties of the clay minerals, thus controlling the interparticle forces. In general particulate organic matter and sesquioxides are expected to increase the strength and stability of aggregates due to the cementing effect of these components. The influence of organic matter on aggregate stability and clay dispersion has, however, been subject to much discussion since it has been found that organic matter may both promote aggregation and dispersion (Shanmuganathan & Oades, 1983; Durgin & Chaney, 1984; Barzegar *et al.*, 1997). The stabilizing effect of soil organic matter has been attributed to the role that roots and hyphae have in stabilizing macroaggregates and thereby preventing clay dispersion. When these bonds are broken by mechanical disturbance and macroaggregates are destroyed, the dispersive effects of organic matter predominate (Goldberg *et al.*, 1990; Nelson *et al.*, 1998).

Colloids are released in the process of aggregate breakdown. In a literature review Le Bissonnais (1996) distinguished four main mechanisms of aggregate breakdown: (i) Slaking; breakdown caused by compression of entrapped air during wetting, (ii) Breakdown by differential swelling; internal pressure by clay differential swelling; (iii) Rain-drop impact; breakdown by external pressure caused by rain-drop impact; and (iv) Physical-chemical dispersion; caused by alteration of the double-layer forces acting between electrically charged colloids. As discussed by Le Bissonnais (1996) these processes, however, differ in the intensity of disaggregation and the size of the resulting fragments. The direct effect of slaking and differential swelling is the breakdown of larger (macro)-aggregates to minor (micro)-aggregates and subsequent changes in the soil structure. In contrast, raindrop impact and physical-chemical dispersion may result in release of clay particles. Dispersion may also be initiated by slaking or differential swelling. As it will be discussed in the following sections the soil properties controlling the mechanism of breakdown depend on the type of forces involved.

2.1.1 Slaking and differential swelling

The breakdown of aggregates by slaking is caused by compression of entrapped air when dry aggregates are wetted rapidly. The *matric potential of the aggregates* and the *rate of wetting* are thus critical factors in the extent of disruption. Maximum disruption of aggregates occurs when very dry aggregates are wetted quickly due to entrapment of air and unequal swelling as water enters coarse pores rapidly. The influence of entrapped air has been illustrated by the greater stability of aggregates which are wetted under vacuum or wetted very slowly on ceramic suction plates (Oades, 1986).

Since the influence of wetting on the resulting slaking depends on the rate of wetting, the extent of slaking will be influenced by the *porosity of the soil aggregates*, which in turn depends on the associations of particles and the *swelling potential* of the minerals. The associations of clay particles are mainly dependent on their mineralogy and the ionic composition of the exchange complex (Rengasamy *et al.*, 1984). Association of clay particles can occur via face-to-face and edge-to-edge interactions (van Olphen, 1977). Results have shown that the proportion of air and water in an aggregate varies according to the type of clay (Tessier *et al.*, 1990). Aggregates dominated by kaolinite and illite have higher air-filled porosity than aggregates dominated by smectite. These differences arise as a result of the interdependency between particle morphology and particle associations in aggregates (Oades, 1986; Oades & Waters, 1991). Kaolinites are large blocky-rigid particles and associations of kaolinite particles results in structures with minimal degree of ordering. The associations of the smaller platy-rigid Ca-illite particles in domains have some degree of parallel stacking in which there is sufficient orientation of the particles to allow close contact of a part of the surface area, while Ca-smectites are associated in parallel flexible sheets creating a stable but expansible structure of a number of basic units in close contact with each other. Tessier *et al.* (1990) investigated the influence of wetting on micro-structural changes of kaolinite, illite and smectite. For smectite, due to the parallel association (face to face and continuous overlapping of crystals) pores were mainly isolated. The hydraulic conductivity was very low, the cohesion was extremely high and the material was able to maintain its cohesion even after complete re-hydration. In contrast, the wetting was very rapid for kaolinite and illite, and entrapment of air resulted in slaking. In general, entrapped air is most important in aggregations of large blocky particles because of the larger pore sizes. Aggregates containing smectite are therefore more resistant to slaking than those containing illite and kaolinite because water only enters the small pore slowly (Oades, 1986).

In the field, when the immediate surface soil is wetted, the underlying soil may also slake if the wetting is sufficient and the soil is sufficiently dry. At depth, when drying of the soil is caused only by plant roots severe slaking would be restricted to kaolinitic soils (Emerson & Greenland, 1990). In natural soils a mixture of different minerals such as kaolinite, illite, smectite, vermiculite and interstratified minerals may associate in aggregates through a combination of electrostatic forces and various bonding agents, affecting both the internal cohesion between colloids and the porosity of the aggregates. In addition organic matter in soil

aggregates may also promote aggregate stability by reducing wettability and swelling of the aggregates, since some of the organic materials are hydrophobic or may become so as they dehydrate, thereby reducing the affinity for water. These properties all add to the complexity in the process of aggregate breakdown by slaking and swelling. In **Paper I** the importance of colloid release as a result of aggregate breakdown by slaking and/or swelling following fast wetting was evaluated on the Lerbjerg clay gradient soils at different initial matric potentials.

2.1.2 Raindrop impact

Mechanical breakdown of aggregates by raindrop impact usually occurs in combination with the other mechanisms if the kinetic energy of the raindrops is great enough (Abu-Sharar *et al.*, 1987; Sharma *et al.*, 1995). The importance of raindrop impact has been demonstrated by the role of vegetation cover which protects the soil surface against such impact. Mechanical breakdown by raindrop impact plays a dominant role on wet soils because the aggregates are weaker when the soil is wetter. The fragments resulting from aggregate breakdown by raindrop impact are generally small being either elementary particles or small microaggregates (Le Bissonnais, 1996). Modeling particle mobilization and transport in the field Jarvis *et al.* (1999) applied the traditional soil erosion modeling approach where the rate of soil detachment is a function of the rainfall intensity and kinetic energy in rain (which is an exponential function of the rainfall intensity). In this approach they assumed that the effect of slaking and dispersion was lumped into the soil detachability coefficient. The effect of raindrop impact on colloid mobilization was not investigated in the present study.

2.1.3 Physical-chemical dispersion

Dispersion is the ultimate state of breakdown that results in release of colloids as a consequence of expanding electrical double layers and dominating repulsive forces between electrically charged colloids. Colloidal particles possess surface charge due to either (i) isomorphic substitution or crystal lattice defects in the internal structure of the minerals (layer silicates), (ii) ionic dissolution on surfaces of mineral soil colloids (oxides and edge of layer silicates), and (iii) ionization of active organic functional groups. Colloids possessing electrical charge will accumulate counter charge in order to preserve electrical neutrality. The counter charge is subject to two opposing forces: electrostatic attraction tending to localize the counterions close to the colloids and the tendency of ions to diffuse randomly throughout the solution due to their thermal energy. The counter charge may consist simply of a diffuse atmosphere of counter ions or it may take the form of a compact layer of bound charge and a diffuse atmosphere as well, both giving rise to an electrical double layer (EDL). This topic has been the subject of several reviews e.g. van Olphen (1977), Hiemenz (1986), Singh and Uehara (1986), and only a brief introduction of the main issues will be presented here.

The diffuse electrical double layer

Several formulations of the electrical double layer exist. Originally, the double-layer was assumed to be built up by a monoionic layer of opposite point charges approaching the surface without limit. Gouy (1910) and Chapman (1913) independently described the diffuse

distribution of point charges accumulated near an electrical surface from such an assumption. The basis of the EDL-theory is presented by the basic Poisson-Boltzmann differential equation, describing the variation in electrical potential (ψ) in direction x from a planar surface across the electrical double-layer:

$$\frac{d^2\psi}{dx^2} = -\frac{e}{\varepsilon} \sum_i z_i n_{i\infty} \exp\left(\frac{-z_i e \psi}{k_B T}\right) \quad [1]$$

where e is the elementary charge, ε is the dielectric constant, z_i is the valence of ion species i , $n_{i\infty}$ is the number of ion species i in the bulk solution, k_B is the Boltzmann's constant, and T is the absolute temperature. At low electrical potential, when $z_i e \psi < k_B T$, the Poisson-Boltzmann equation reduces to:

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi \quad [2]$$

If the electrical potential in the bulk solution (ψ) is defined such that $\psi = 0$ when $x = \infty$ and $d\psi/dx = 0$, and the electrical potential at the colloid surface (ψ_0) is defined such that $\psi = \psi_0$ when $x = 0$, integration of Eq. [2] gives the Debye-Hückels approximation:

$$\psi = \psi_0 \exp(-\kappa x) \quad [3]$$

where κ is the Debye-Hückel parameter expressed as:

$$\kappa^2 = \frac{e^2 \sum_i z_i^2 n_{i\infty}}{\varepsilon k_B T} \quad [4]$$

where $n_{i\infty} = 1000 \times C_i \times N_A$, and C is the molar concentration. Equation [4] presents an exponential reduction of the electrical potential with distance from the surface. The Debye-Hückel parameter has the dimensions of reciprocal length, and κ^{-1} is a characteristic length, which determines the extent of the diffuse layer. The length κ^{-1} is often referred to as the "thickness" of the double layer. The Debye-Hückel parameter reveals that the double layer extension varies inversely with the solution ionic composition (z) and concentration ($C^{1/2}$). Values of κ^{-1} vary from about 1 μm in pure water to less than 1 nm in concentrated electrolyte solutions (Gregory, 1989).

Stern (1924) refined the Gouy-Chapman theory, recognizing that counterions are unlikely to approach the surface closer than the radius of the ion species. They also introduced the concept of binding energy for specific adsorption. According to the modified Stern concept the EDL is composed of (i) a layer of counterions located close to the surface (Stern-layer), through which

the electrical potential declines linearly with distance from the surface, and (ii) a Gouy-layer with diffuse ion distribution, through which the electrical potential declines approximately exponential with distance from the boundary of the Stern-layer (δ) (Figure 3). The boundary of the Stern-layer is generally considered to be at a distance of about 0.3 to 0.5 nm from the colloid surface corresponding to the diameter of a hydrated counterion (Gregory, 1989). When describing the variation in electrical potential across the EDL the surface potential in Eq. [3] is considered to be the potential at the Stern surface (ψ_δ). There is no direct experimental method for determining the Stern potential but the zeta (ζ)-potential is assumed to be in the same order of magnitude (Hiemenz, 1986). The ζ -potential is an experimentally determined electrokinetic potential at the plane of shear between a particle and a fluid, when there is relative motion between them. The exact location of the shear-plane is unknown but it is generally assumed to be located close to the boundary between the Stern-layer and the diffuse layer as illustrated in Figure 3.

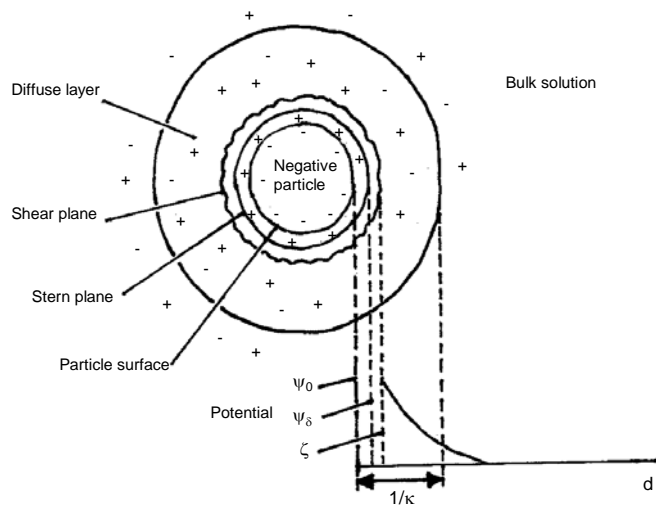


Figure 3. Conceptual illustration of the location of the Stern plane, the shear plane and the diffusive layer with separation distance (d) from a negatively charged particle. ψ_0 is the surface potential, ψ_δ the Stern potential, ζ is the zeta-potential at the shear plane, and $1/\kappa$ represents the double-layer thickness.

DLVO theory of colloid stability

Dispersion of colloids is caused by alteration of the interparticle forces between the colloids. Comprehensive amounts of literature exist on the subject of colloid stability and only a brief introduction of the theory of colloid stability will be presented here. For further details please consult textbooks and papers, e.g. van Olphen (1977), Hiemenz (1986), Gregory (1989), Swanton (1995), Ryan and Elimelech (1996). According to the DLVO theory of colloid stability proposed by Derjaguin and Landau (1948) and Verwey and Overbeek (1948) the total interaction energy (Φ_T) between colloids is the sum of attractive (Φ_A) and repulsive (Φ_R) forces:

$$\Phi_T = \Phi_A + \Phi_R \quad [5]$$

where Φ_A is van der Waals attractive forces between atom pairs in adjacent particles and Φ_R the electrostatic repulsion between particles.

van der Waals attraction

An expression for Φ_A based on size, shape and distance between colloids was introduced by Hamaker (Hiemenz, 1986):

$$\Phi_A = -\left(\frac{A_{212}}{12\pi}\right) \times d^{-2} \quad [6]$$

where Φ_A is the attractive energy between two blocks separated by distance d , and A_{212} is the Hamaker constant that depends on the properties of the interacting colloids (phase 2) and the medium (phase 1). The Hamaker constant for most aqueous colloidal suspensions lies in the range $0.3-10 \times 10^{-20}$ J, with dense mineral colloids having high values and organic material with low density having low values (Gregory, 1989). As revealed from Eq. [6] the attractive energy is inversely proportional to the second power of the distance separating the particles. In principle, the attractive energy should become very strong on close approach. However, short-range repulsive forces work at short distances keeping the attraction finite.

Electrostatic interaction

When two charged colloids approach each other their diffuse double layer overlap and in case of identical charged colloids electrostatic repulsion will repel the colloids while opposite charged colloids will attract each other. An expression for the repulsive energy (Φ_R) between two blocks is given by the approximation (Hiemenz, 1986):

$$\Phi_R = \frac{64n_\infty k_B T}{\kappa} \left[\frac{\exp(ze\psi_0 / 2kT) - 1}{\exp(ze\psi_0 / 2kT) + 1} \right] \exp(-d\kappa) \quad [7]$$

where Φ_R is reduced when the distance between particles increases, the “thickness” of the EDL decreases or the surface potential decreases. Since the interaction between charged colloids is governed primarily by the overlap of diffuse layers Gregory (1989) considered the Stern-potential to be more relevant for interactions between colloids, rather than the potential at the colloid surface. Roy and Dzombak (1996) also found that the measured ζ -potential was more appropriate for predictions of the electrostatic repulsion between natural and latex colloids than the surface potential obtained from the Gouy-Chapman theory.

Energy barrier approach for colloid dispersion

The repulsive and attractive energies can be summed over the separation distance to give the resultant potential interaction energy between colloids as illustrated in Figure 4. In the classical DLVO approach particles attached in the primary minimum of potential energy would need an infinite amount of energy to disperse. However, to account for the reversibility of colloid

dispersion and flocculation, the DLVO theory has been modified to include short-range Born repulsion giving a finite energy minimum, and additionally it is assumed that two particles cannot get any closer than the diameter of a hydrated counterion giving a finite minimum (e.g. review by Ryan and Elimelech, 1996). With these modifications the DLVO profile provides an estimate of the energy barrier required to mobilize colloids.

In the case of low electrolyte concentration (Figure 4a) the repulsive energy dominates resulting in a very large energy barrier. When two colloids approach each other as a result of Brownian motion they would have to overcome the energy barrier during collision in order to flocculate, and only few collisions would result in colloids being attached in the primary minimum where attraction is very strong. This would result in a dispersed and stable colloidal suspension. In the case of medium concentration an energy barrier still exists, however, more collisions will result in colloids being attached in the primary minimum. The system will be less stable and slow flocculation will take place. In case of high concentrations (Figure 4b) the attractive energy dominates resulting in most collisions being attached in the primary minimum. Under such conditions, rapid flocculation takes place and the colloidal suspension is very unstable. The secondary minimum in the potential energy curve is a consequence of the different distance dependencies of the electrical interaction with exponential decay and van der Waals interactions with power law decay, which gives a slower decrease at large separation distance. This means that attraction dominates at some separation distance. However, this phenomenon however is only of significance for relatively large particles and moderately concentrated solutions (Gregory, 1989).

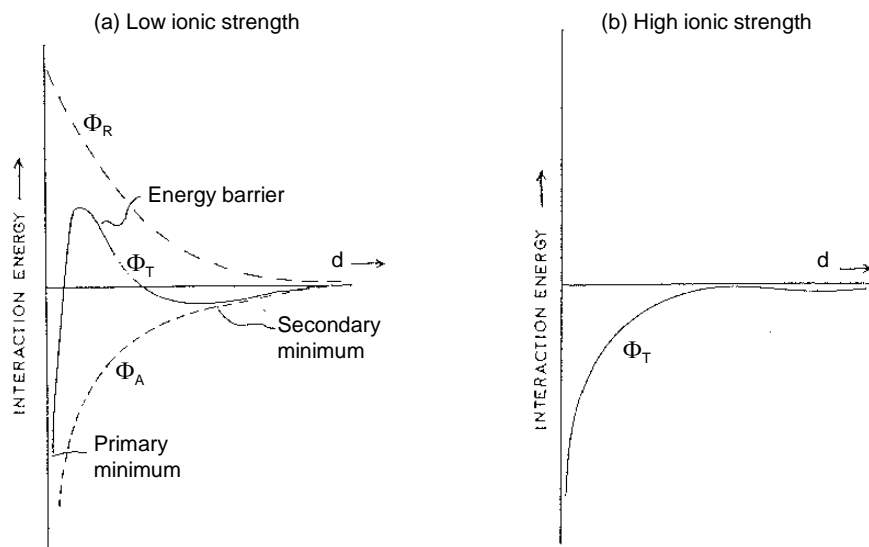


Figure 4. Potential interaction energy between colloids showing the van der Waals attraction (Φ_A), electrostatic repulsion (Φ_R) and the total interaction energy (Φ_T) as a function of the particle separation at (a) low ionic strength with an energy barrier, and (b) at high ionic strength when the energy barrier is absent. (Modified from Gregory, 1989).

Non-DLVO forces

A range of non-DLVO forces, such as hydration repulsive forces, hydrophobic attraction, polymer bridging or steric repulsion also contributes to the overall stability behavior of colloids (Gregory, 1989). The hydration repulsive forces are a consequence of the repulsive energy arising when two particles approaches each other because of the need for ions to loose their water of hydration if actual contact between particles is to be achieved. Gregory (1989) refers to these repulsive forces as quite appreciable relative to double layer repulsive forces, especially at high ionic strength. In effect, they serve to reduce van der Waals attractive forces at close distance and prevent particles from coming into actual contact. Hydration repulsive forces play an important role in colloid mobilization because they define a primary minimum of finite depth. Without these short-range repulsive forces the propability of colloid escape from the deep primary minimum would be zero.

Organic matter may affect colloid stability by hydrophobic attraction, polymer bridging and/or electrostatic and steric repulsion. Hydrophobic attraction is a consequence of the attraction of hydrophobic colloids or colloids having surface areas with hydrophobic character. According to Gregory (1989) these forces of attraction are stronger than van der Waals forces and extend to a distance of about 80 nm in pure water. In addition organic matter may become hydrophobic as it dehydrates reducing the wettability. Colloids may also be bound together through polymer bridging. According to Gregory (1989) bridging flocculation can result in much stronger flocs or aggregates than flocs formed as a result of the DLVO forces. Adsorbed organic matter may also increase colloid stability as a consequence of electrostatic and / or steric repulsion. The stabilizing effect of adsorbed organic matter is a consequence of repulsion from the overlap of the hydrophilic chains when colloids approach each other. The stability of colloids with adsorbed layers of natural organic matter is often higher than expected using the DLVO approach. This has been attributed to the effect of steric stabilization forces where adsorbed macromolecules may displace the shear plane away from the surface (Gregory, 1989). Experimental evidence suggest that natural organic matter adsorbed to soil colloids stabilizes dispersed colloids due to both electrostatic and steric mechanisms (O'Melia, 1989; Kretzschmar *et al.*, 1993; Kaplan *et al.*, 1997; Kretzschmar *et al.*, 1998),

2.2 Soil properties influencing colloid dispersion

As indicated by the different processes influencing aggregate breakdown and colloid dispersion a variety of intrinsic and dynamic soil properties affect colloid dispersion. These include electrolyte concentration and composition (Rengasamy, 1983; Rengasamy *et al.*, 1984), pH (Suarez *et al.*, 1984), clay mineralogy (Frenkel *et al.*, 1978; Seta and Karathanasis, 1996), Fe and Al oxides (Goldberg *et al.*, 1988; Seta and Karathanasis, 1996), exchangeable sodium (Levy *et al.*, 1993), organic carbon (Goldberg *et al.*, 1988; Pojasok and Kay, 1990), soil-water content (Pojasok and Kay, 1990; Rasiah *et al.*, 1992), and total clay content (Pojasok and Kay, 1990; Brubaker *et al.*, 1992; Rasiah *et al.*, 1992; Levy *et al.*, 1993; Curtin *et al.*, 1994). Generally, in soils dominated by permanently charged layer silicates, colloid dispersion is promoted by decreasing ionic strength, increasing pH and increasing sodium adsorption ratio

(SAR) in qualitative agreement with the double-layer theory. The existence of sesquioxides promotes flocculation, while organic matter may either induce dispersion or flocculation dependent on the type of organic matter. In addition to these inherent soil characteristics, management in terms of crop sequence, application of organic manures, soil tillage and field traffic have been shown to significantly affect clay dispersion (e.g. Watts *et al.*, 1996, Watts and Dexter, 1997; Schjønning *et al.*, 2002). From regression analysis several studies have identified soil clay content as one of the most important properties determining WDC (Pojasok and Kay, 1990; Brubaker *et al.*, 1992; Rasiyah *et al.*, 1992; Levy *et al.*, 1993; Barzegar *et al.*, 1994). On one hand the soil clay content constitutes the pool of potentially mobile colloids, however, as mentioned earlier the clay content also affects colloid cohesion and the aggregate stability. While the process of physical-chemical dispersion is affected by the ionic strength of the water phase, the soil matric potential affects the state of colloid cohesion and the breakdown of aggregates due to slaking and differential swelling. To the knowledge of the author, no studies have systematically investigated the interacting effect of clay content, initial matric potential and wetting rate on release of WDC in response to infiltration of low-ionic strength rainwater. This was accomplished in **Paper I**.

2.3 Measuring colloid dispersion

Measurement of water-dispersible colloids by simple batch experiments is a frequently used and easily accessible index for evaluating the potential amount of dispersible colloids. In general, measurements of WDC involve modified versions of the standard procedure for particle-size analysis. Numerous methods have been used to determine WDC differing in initial conditions of the soil samples (air-dry, sieved, moist), the type of pretreatment (wetting conditions, solution type, soil:water ratio) and the dispersion procedure (shaking time and intensity) (Table 1). This adds to the complexity in interpreting the results of WDC measurements. Traditionally, measurements of WDC have involved the use of air-dry soil. Air-drying is meant to standardize initial conditions, but air-drying may introduce changes in chemical or physical characteristics that can alter stability (Alderfer, 1946; Reid and Goss, 1981). These changes are further increased due to swelling or air entrapment when rewetting the samples (Panabokke and Quirk, 1957). Kay and Dexter (1990) found that the amount of both spontaneously and mechanically dispersed clay significantly depended on sample rotation and antecedent soil-water potential. Pojasok and Kay (1990) demonstrated that values of aggregate stability and dispersible clay significantly depended on sample pretreatment, initial moisture content, length of time aggregates were allowed to wet up and equilibrate and length of the shaking period. Based on these results Pojasok and Kay (1990) recommended that aggregate stability and dispersible clay should be measured using field-moist soils.

2.3.1 Development of a low-energy input dispersion procedure

In this study, the objective was to acquire an estimate of the fraction of potentially mobile colloids released during the infiltration of low-ionic strength rainwater, due to the combined effect of (a) physico-chemical dispersion, (b) differential swelling, and (c) slaking in response to fast wetting of dry soils. This was accomplished by subjecting packed field-moist aggregates

to two pretreatment procedures: (i) saturation and drainage of the packed soil columns to pre-defined matric potentials ($\psi = -2.5, -100$ and $-15,500$ hPa) covering the moisture conditions from near saturation to the crop wilting point, by slow capillary infiltration on tension tables, and (ii) re-saturation after 14 days of equilibration with either slow wetting with controlled tension over 7 days or fast wetting within 4 hours. The colloid fraction (≤ 2 mm) was separated by one-step gravity sedimentation after quantitative transfer of the soil samples to sedimentation bottles and 10-times manually turning the soil suspension up-side-down. This fraction is referred to as low-energy water-dispersible colloids (LE:WDC) (Figure 5). The estimates of LE:WDC were referenced by WDC obtained by a conventional, high-energy input measurement based on air-dried soil (HE-WDC) (consult **Paper I** for further details).

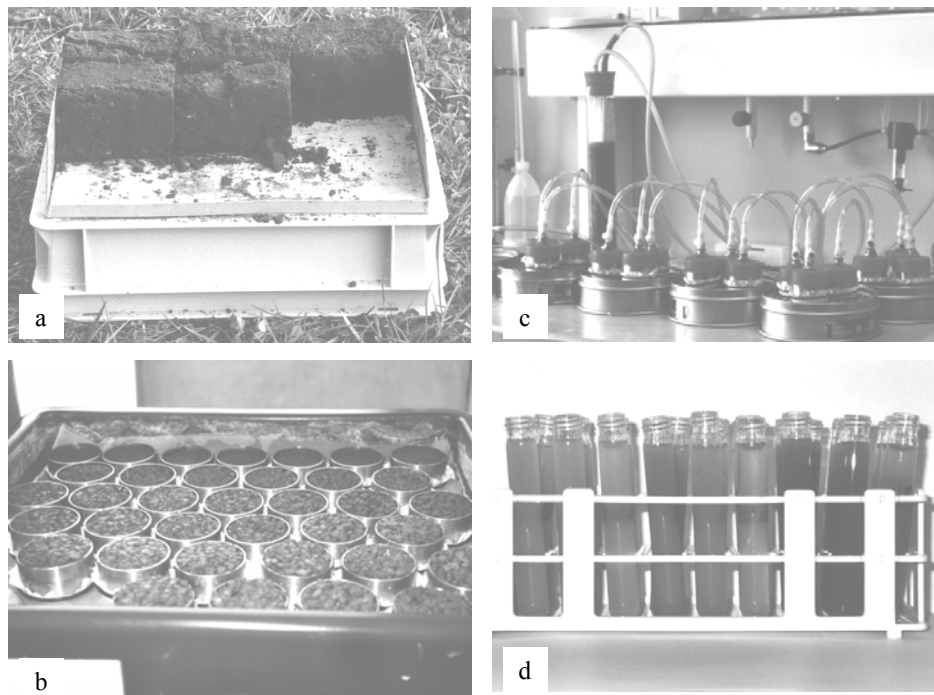


Figure 5. Illustrations of some procedures involved in the measurements of low-energy water-dispersible colloids (LE-WDC) (a) Sampling intact soil cubes, (b) saturation and drainage of packed field-moist aggregates on tension table, (c) drying to initial matric potential (IMP) of $-15,500$ hPa with dry air, and (d) suspensions of LE-WDC.

The quantification of WDC in this study was based on suspensions derived from one-step gravity sedimentation. This inevitably will underestimate the clay dispersed from the sample. A total recovery of dispersed clay would require repeated sedimentations, but this would induce extra dispersion of clay. This deviation from full recovery will depend on soil type due to differences among soils in the particle size distribution of clay particles. Hence, in the present study we obviously did not recover all dispersed clay and we also anticipate some difference in the degree of recovery among the six soils, but consider this error not to compromise the issues addressed.

Table 1. Methods used for measuring water-dispersible colloids (WDC) as a function of total clay content.

Form of sample	Wetting conditions	Suspension type	Soil:water ratio	Type of dispersion	Dispersion time	WDC-determination	Relation between WDC and clay	Total clay content	Reference
Field-moist aggregates	Slow wetting	DI-water	?	Mechanical shaking end-over-end: 0.8 m diam. rotation, 25 rpm	?	Light transmission	Positive correlation	4 - 58	Pojasok & Kay, 1990
Air-dry soil	†	†	†	Mechanical shaking	Overnight	†	Positive linear correlation	5 - 50	Brubaker <i>et al.</i> , 1992
Air-dry soil <2 mm	Directly immersed	DI-water	1:15	Mechanical shaking horizontal shaker: 125 rpm	5 min, 15 min or 60 min	Gravimetrically after sedimentation	Positive logarithmic correlation	5 - 45	Levy <i>et al.</i> , 1993
Field-moist aggregates	Slow wetting	DI-water	?	Mechanical shaking end-over-end: 0.8 m diam. Rotation, 25 rpm	3 min	Light transmission	Positive correlation	6 - 71	Rasiah <i>et al.</i> , 1992
Air-dry soil <0.38 mm	Directly immersed	DI-water	1:10	Mechanical shaking end-over-end	4 hours	Optical density at 641 nm	Positive correlation	20 and 63	Curtin <i>et al.</i> , 1994
Air-dry soil <1 mm	Directly immersed	DI-water	1:5	Undisturbed for 12 h + stirring (0.16 rev s ⁻¹) Mechanical shaking end-over-end (0.5 rev s ⁻¹)	30 sec. 1 hour	Turbidity after sedimentation	Positive correlation	9 - 55	Barzegar <i>et al.</i> , 1994
Moist soil	Directly immersed	DI-water	1:20	Mechanical shaking	Overnight	Gravimetrically after centrifugation	No correlation	21 - 75	Seta & Karathanasis, 1996
Air-dry soil <2 mm	Directly immersed	Electrolyte solution‡	1:8	Mechanical shaking Reciprocal shaker: 0.5 diam. rotation, 29 rpm	16 hours	Gravimetrically after sedimentation	Positive correlation	11 - 43	Kjaergaard <i>et al.</i> , 2003 (present paper)
Field-moist (field capacity)	Slow wetting on tension tables	Electrolyte solution‡	1:8	Manually turning up side down: 10 times	1 min	Gravimetrically after sedimentation	Negative correlation	11 - 43	Kjaergaard <i>et al.</i> , 2003 (present paper)

† NSSL, Lincoln, NE, modified version of the standard particle-size analysis (Soil Survey Staff, 1984)

‡ Electrolyte solution corresponding to natural rainwater with EC 0.025 mS cm⁻¹ and SAR 0.736

2.3.2 High- versus low-energy dispersible colloids as affected by total clay content

The estimates of WDC obtained in this study were significantly affected by the energy application. A positive correlation was obtained between total clay content and HE-WDC (Figure 6a), while employing a low-energy input in the dispersion procedure resulted in a negative and pretreatment dependent relation between total clay content and LE-WDC (Figure 6b). The interpretation of these contrasting results is straightforward. As the clay content increases, the size and stability of the aggregates also increases as a consequence of increasing cohesive strength, since more clay particles are able to make increasing contacts (consult **Paper I** for further details). The positive correlation between clay content and water-stable aggregates (WSA) has been reported in several studies (e.g. Kemper *et al.*, 1987; Pojasok and Kay, 1990). The increase in aggregate size and stability consequently results in a decline in the amount of dispersible colloids released following a low-energy input, which does not break up the aggregates. In contrast, the application of high-energy input in the dispersions procedure breaks up the aggregates and thereby increases the surface area, which consequently increases the dispersion of clay. These results agrees with the conclusions from Kay and Dexter (1990), documenting that the amount of mechanically dispersed clay increases with increasing aggregate size, while the amount of spontaneously dispersed clay increases with increasing surface area, which require initial aggregate breakdown.

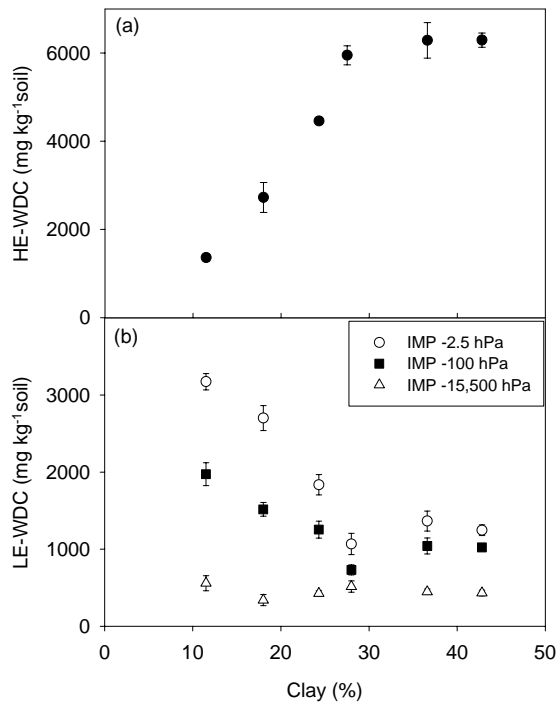


Figure 6. Amount of (a) high-energy water-dispersible colloids (HE-WDC) as a function of clay content, and (b) low-energy water-dispersible colloids (LE-WDC) as a function of clay content and initial matric potential (IMP). Error bars: \pm SE. (Figure from **Paper I**).

The influence of total clay content on the release of water-dispersible colloids has been measured using very different approaches, but all applying mechanical energy (shaking or stirring) in the measurement procedure (Table 1). These studies have found mainly positive correlations between total clay content and WDC, in agreement with the findings of HE-WDC in this study. When comparing Ultisols with Alfisols and Mollisols, Seta and Karathanasis (1996) found that the kaolinite, Fe and Al content accounted for most of the variability in soil dispersibility. In the present study a non-linear relation was observed between HE-WDC and total clay while other studies have found both linear correlations (Brubaker *et al.*, 1992) and logarithmic relations (Levy *et al.*, 1993) between WDC and total clay. The non-linear relation observed in the present study may be explained by a combination of several factors: (i) the samples with 37 and 43% clay also contained small amounts of calcite (1 to 1.7%) which may reduce the dispersibility of the soil, (ii) more energy is probably required to break down aggregates when the clay content increases, and (iii) even though aggregates do break down at first, the volume of clay is so large that shaking without any dispersion agent probably results in production of new aggregates. The inconsistencies observed among positive relations between total clay and mechanically dispersible colloids, may be a consequence of differences in the input of mechanical energy in the dispersion procedure.

The results from the present study points out the importance in choice of dispersion procedure, especially the application of energy. When estimates of WDC are used as input parameter for modeling colloid mobilization and transport one should be aware of the coherence between energy input and the result of the WDC measurement. The application of mechanical energy by the shaking procedure may resemble “worst case” scenarios, where storm flow events or soil tillage increases dispersion by breaking down aggregates, while the use of low-energy input dispersion measurements may resemble the *in situ* release of colloids from surface horizons during average precipitation events.

2.3.3 Effect of initial soil matric potential on LE-WDC

Several studies have documented that colloid cohesion increases upon drying. Drying forces clay particles into close contact, and with increasing proportions of the clay surfaces in close contact a greater resistance against dispersion would be expected (Kay and Dexter, 1992). The results from this study (**Paper I**) revealed that besides a strong dependency of initial soil matric potential on LE-WDC, the effect of initial matric potential additionally depended on clay content (Figure 6b). Three important results should be highlighted from this study: (i) the amount of LE-WDC was reduced with decreasing initial matric potential, (ii) the initially wet (IMP -2.5 hPa) and moderate wet (IMP -100 hPa) soils displayed a negative correlation between LE-WDC and soil clay content, while soils incubated at low water content (IMP -15,500 hPa) released a low amount of LE-WDC, which was independent of clay content, and (iii) the effect of initial soil matric potential declined with increasing clay content, which is probably a consequence of small water-filled pores constituting an increasing fraction of the pore volume with increasing clay content, thereby minimizing the influence of initial soil matric potential. In this study no effect of clay content on LE-WDC was evident after drying to -15,500 hPa, while other studies have observed greater cohesion in higher clay soils after air-drying (Kemper and Rosenau, 1984). The reason that no effect of clay content was observed in this study might be that the cohesive forces created during the drying of low-clay soils was sufficient to withstand dispersion under the mild stresses applied by the low-energy input.

An important feature of the effect of drainage and drying on LE-WDC release revealed from the present study, was that the soil-water effect was evident even after one week of complete rewetting. In the field, the soil is subjected to drying and wetting events that continuously change the moisture status of the soil and thereby the dispersibility as illustrated by the previous. This may have important perspectives with respect to modeling *in situ* colloid mobilization and clearly raises a question about the time dependency of colloid dispersion. The results from the present study revealed that colloid dispersion at 12% clay changed as a function of time and the rate of change depended on the moisture status of the soil (Figure 7).

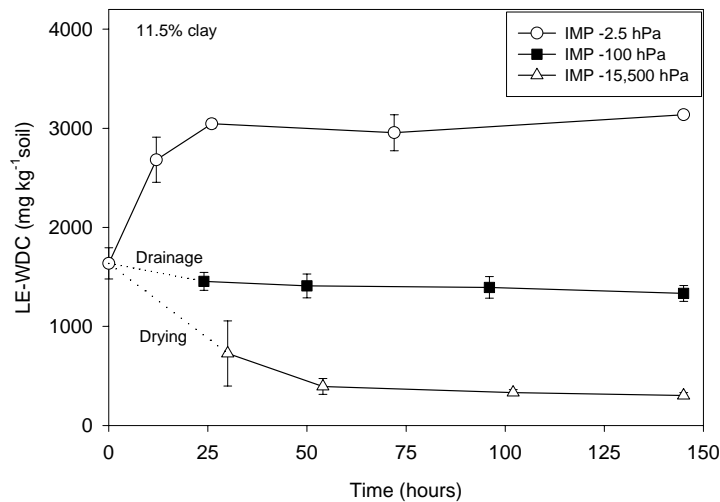


Figure 7. Amount of low-energy water-dispersible colloids (LE-WDC) as a function of time and initial matric potential (IMP) at 11.5% clay. Error bars: \pm SE. (Figure from **Paper I**).

From this study it seemed like the main part of the changes in dispersibility occurred during or immediately after adjustment of the moisture status. The increase in dispersibility at -2.5 hPa occurred within the first 26 hours and the decrease in dispersibility at -100 and -15,500 hPa occurred primarily during the change in moisture status. However, the dispersibility at -100 and -15,500 hPa continued to decrease with time. This is consistent with the results of Kemper and Rosenau (1984) who found an increase in cohesive strength with time of storage, and suggested that the increase in cohesion under air-dry conditions indicate that migration of bonding components continue even when there is as little as one molecular layer of water on the mineral surfaces.

2.3.4 Effect of wetting rate on LE-WDC

As discussed earlier drying and successive wetting can also cause a decrease in strength as a consequence of slaking and differential swelling when dry aggregates are wetted rapidly (Grant and Dexter, 1989). In this study the sensitivity of LE-WDC released due to slaking and swelling as a consequence of fast wetting was examined using the low-energy input dispersion measurement. The results revealed that the dry soil (IMP -15,500 hPa) reacted to the fast wetting by: (i) an increase in the soil volume indicating swelling and/or slaking, and (ii) a two-fold increase in the amount of LE-WDC (Figure 8). No effect of wetting rate on LE-WDC released from soils incubated at -2.5 and -100 hPa was observed.

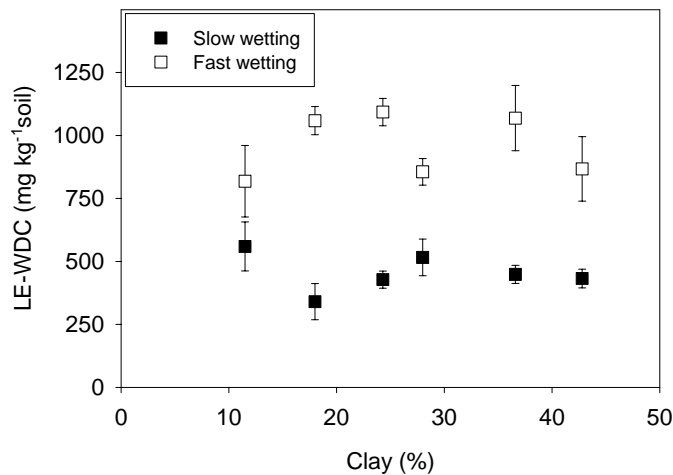


Figure 8. Effect of wetting rate on amount of low-energy water-dispersible colloids (LE-WDC) at an initial matric potential (IMP) of $-15,500$ hPa as a function of clay content. (Modified figure from **Paper I**).

The reason that fast wetting only affected colloid dispersion in the initially dry soils is probably due to the fact that slaking decreases as the initial water content increases until saturation is reached (Panabokke and Quirk, 1957). This is a consequence of the reduction of the volume of air that is entrapped during wetting and also to the reduction of soil matric potential gradients. In addition the upward infiltration applied in the present study probably resulted in some escape of air and thereby minimized the effect of wetting rate compared to a situation with downward infiltration. The reason that no effect of clay content was observed on colloid dispersion after fast wetting may be a consequence of the counteracting effect of swelling and slaking as the clay content increases. According to Le Bissonnais (1996) aggregate breakdown by slaking decreases when clay content increases in the range of 10 to 30%. In contrast to slaking, aggregate breakdown by differential swelling increases with increasing clay content. It is important to recognize that soil dominated by Kaolinite and Illite would be more vulnerable to slaking than Smectitic soils.

2.4 Concluding remarks

This chapter and the present experimental study highlighted that several mechanisms and consequently a variety of inherent and dynamic soil properties may be responsible for the breakdown of aggregates and the mobilization of colloids. When evaluating the susceptibility of a given soil to colloid dispersion it is therefore of great importance to investigate the sensitivity of colloid release in response to the different mechanisms of aggregate breakdown. Obviously different soils may react differently to the different mechanisms of aggregate breakdown.

The results from the present study revealed that:

- Measurements of WDC turned out to be extremely sensitive to pretreatment and energy input in the dispersion procedure:

- The amount of HE-WDC increased with clay content as a consequence of aggregate breakdown by the intensive energy application.
 - The amount of LE-WDC decreased with clay content as a consequence of an increase in the amount of water-stable aggregates.
- Total clay content, initial matric potential and the interacting effect of these turned out to be key properties with respect to predicting colloid dispersion, while the effect of wetting rate was significant only at very dry initial conditions under the given experimental conditions:
 - Decreasing soil matric potential in the period prior to measurement reduced the amount of LE-WDC and the dependency of clay content. A low amount of WDC that was independent of clay content was observed after predrying to IMP $-15,500$ hPa.
 - The main part of the decrease in dispersibility occurred during or immediately after the decrease in soil-water content but dispersibility continued to decrease with time. The effect of decreasing IMP persisted at least for a week after complete rewetting.
 - Fast wetting did only increase the amount of LE-WDC after predrying to IMP $-15,500$ hPa.
 - Practical and environmental implications
 - The sensitivity of the dispersion procedure on the measurement of WDC highlights the importance in choosing estimates of WDC that resembles the relevant conditions when predicting *in situ* colloid mobilization. A low energy input in the dispersion procedure is probably more realistic when evaluating *in situ* mobilization following vertical infiltration of water through the vadose zone.
 - The effect of initial matric potential should be implemented in predictive field models, while the time dynamic and reversibility in colloid dispersion should be explored further. Based on results from this study the quantitative effect of wetting rate was of minor importance as it only increased colloid dispersion from dry soils with already low dispersibility.

3. Stability properties of natural soil colloids

The transport of mobilized colloids depend on the size and stability of dispersed colloids in the soil solution. The transport of colloids through the vadose zone may be limited by sedimentation of large particles and changes in soil solution chemistry may cause flocculation of colloids or favor the attachment to the matrix surfaces. Transport of colloids through soil is enhanced by conditions promoting the stability of the colloids, and understanding the factors affecting the stability behavior of natural soil colloids is therefore a prerequisite for predicting the mobility of colloids through a soil profile consisting of horizons differing in chemistry. The stability behavior of natural soil colloids is, however, complicated by the existence of a mixture of clay minerals with surface properties modified by pedochemical weathering and surface associations of sesquioxides and natural organic matter (NOM), which may mask the direct importance of clay mineralogy on the stability properties of soil colloids. In this thesis a study was carried out in order to identify the surface properties controlling the stability behavior of natural WDC and evaluate the effect of pH and ionic strength on the stability behavior of natural WDC (**Paper IV**).

3.1 Colloid sampling and characterization

Sampling mobile colloids from the vadose zone can be accomplished by sampling drainage water (Øygarden *et al.*, 1997; Uusitalo *et al.*, 2001) or collecting effluent samples from zero-tension lysimeters (Thompson and Scharf, 1994; Biddle *et al.*, 1995). Zero-tension lysimeters are devices designed to collect water, solutes or suspended colloids that move through the soil under influence of gravity. In the present study (**Paper IV**) WDC in size separates <0.2 μm and 0.2-2 μm were separated from bulk soil samples collected from several horizons down through the Flakkebjerg profile and from macropore deposits in the lower soil profile, representing evidence of colloid translocation *in situ* (consult **Paper IV** for further details).

A large variety of techniques are available for characterizing colloids with respect to size and composition (mineralogy, elemental composition, functional groups), concentration (mass, number) and surface characteristics (surface charge density, specific surface area, surface morphology). For review see Buffle and Leppard (1995), Degueldre *et al.* (1996) and Kretzschmar *et al.* (1999). Particle size can be determined by (i) microscopic techniques such as scanning and transmission electron microscopy (SEM, TEM) and atomic force microscopy (AFM), (ii) light scattering techniques (see section 3.2.1), or (iii) size fractionation such as classical sedimentation (**Paper I**), particle centrifugation analysis (**Paper IV**), field flow fractionation (Beckett *et al.* 1990; Chittleborough *et al.*, 1992) or filtration.

Suspended colloid concentration can be determined directly as gravimetric mass concentration (**Paper I, IV**) if the concentration is high or indirectly by turbidity (**Paper I, III, IV**). Turbidity is a measure of the scattering effect suspended particles has on light. The scattering distribution of the incident light is related to the size, shape and composition (refractive index and color) of

the suspended particles and to the wavelength of the incident light (Hach *et al.*, 1987). Based on the multiple factors affecting the intensity of light scattering direct correlation between turbidity measurement and colloid concentration is critical and should be done only if properties such as size distribution, shape, refractive index and absorptive properties remain fairly constant. For measurement of colloid concentration a correlation (calibration) curve should therefore be established for each type of material. Turbidity calibration curves from the Lerbjerg clay gradient were prepared from suspensions of LE-WDC (**Paper I**). A linear correlation existed between colloid concentration and turbidity at turbidity readings <100 NTU, while non-linearity was observed for all clay soils at colloid concentrations >100 NTU. The nonlinear response is due to multiple scattering and greater absorption occurring at the higher concentration. Regression equations were derived from the colloid concentration versus turbidity (<100 NTU) relationship). As revealed from the regression equations the turbidimeter readings at a certain colloid concentration increases with clay content in the sample. This is probably a consequence of the higher TOC:clay ratio in the low clay soils changing the refractive index and the absorptive properties of the sample.

3.2 Methodologies for evaluation of colloid stability

The degree of colloidal stability or instability may be defined or measured in terms of (i) critical coagulation concentrations, (ii) flocculation rates, particle size-distribution and stability ratios, and (iii) measurement of the ζ -potential. Colloid stability has traditionally been inferred from sedimentation experiments, where the critical coagulation concentration (CCC) is the electrolyte concentration defining the threshold value between slow and rapid flocculation (van Olphen, 1977; Hesterberg and Page, 1990a).

The size-dependent ability of colloidal particles to absorb and scatter light have promoted the study of colloid stability or flocculation kinetics by following changes in optical properties such as light scattering intensity (e.g. Anderson and Bertsch, 1993; Kretzschmar *et al.*, 1998). Laser Doppler velocimetry-photon correlation spectroscopy (LDV-PCS) is a dynamic light scattering technique that takes advantage of the Doppler effect, where the movement of particles results in a shift in the frequency of scattered light, which can be used for quantifying both the electrophoretic mobility (ζ -potential) and the particle size on the same sample. LDV-PCS has been widely used for characterization of surface properties by measuring the ζ -potential and studying the coagulation kinetics (particle-size distributions) of both reference colloid suspensions and natural soil colloids (e.g. Novich and Ring, 1984; Anderson and Bertsch, 1993; Kretzschmar *et al.*, 1998; Elimelech *et al.*, 2000). In **Paper IV** colloid stability was evaluated from measurement of particle size-distribution and ζ -potential using LDV-PCS.

3.2.1 Particle-size distribution

Colloids or particles with diameters in the range from 1 nm to 5000 nm can be measured using the method of photon correlation spectroscopy (PCS). The principle of PCS is based on the fact that colloids are in constant random thermal or Brownian motion. The thermal motion of the colloids causes the intensity of light scattered from the particles to form a moving speckle

pattern. This movement can be detected as a change in intensity over time. Large particles move more slowly than small particles so the rate of fluctuation of the light scattered from them is also slower. PCS uses the rate of change of these light fluctuations to determine the diffusion coefficient (D_{Col}) of the particles. From the diffusion coefficient the average hydrodynamic particle diameter (d_H) was calculated using the Stokes-Einstein equation:

$$d_H = \frac{k_B T}{3\pi\eta D_{Col}} \quad [8]$$

where η is the viscosity of the medium. In **Paper IV** the stability behavior of natural WDC was evaluated by measuring the changes in the average hydrodynamic particle diameter with changes in pH and ionic strength.

3.2.2 Zeta (ζ)-potential

Determination of the ζ -potential have practical significance when evaluating colloid stability. Even though the exact location of the shear-plane is unknown, the ζ -potential may provide information about the double-layer structure and properties. In cases where there is no specific adsorption ($\zeta = 0$ when $\psi_0 = 0$) measurement of ζ allows identification of the point of zero charge (PZC) of the system. Since double-layer interactions depend on the potential at the Stern plane, measurement of ζ -potential have been used for evaluation of colloid stability (Zhang, 1997) where suspensions with high values of ζ are expected to be more stable than similar suspensions with low values of ζ . Roy and Dzombak (1996) used measurements of ζ -potential to provide qualitative predictions of colloid mobility in natural porous media.

The ζ -potential is determined from measurements of electrophoretic mobility of colloids. Electrophoresis refers to the movement of charged colloids relative to a stationary solution in an applied potential gradient. The charged colloids will move with a speed and direction that depends on the size and type of the charge. The electrophoretic mobility (μ) is defined as the particle velocity (v) per unit of electric field (E):

$$\mu = \frac{v}{E} \quad [8]$$

The velocity for a spherical particle is given by: $v = zeE/6\pi\eta r$, where r is the radius of the particle (Hiemenz, 1986). Typical values of electrophoretic mobility of natural soil colloids are in the range 10^{-8} to 10^{-7} $m^2 V^{-1} s^{-1}$ (Sposito, 1992). When a particle is moving in an electrical field both the charged colloid and the diffuse double layer are contributing to the electrophoretic mobility and Henry derived the following expression for electrophoretic mobility (Hiemenz, 1986):

$$\mu = \frac{2\varepsilon\zeta}{3\eta} \left(1 + \frac{1}{16}(\kappa r)^2 - \frac{5}{48}(\kappa r)^3 - \frac{1}{96}(\kappa r)^5 - \left[\frac{1}{8}(\kappa r)^4 - \frac{1}{96}(\kappa r)^6 \right] \exp(\kappa r) \int_{\infty}^{\kappa r} \frac{e^{-t}}{t} dt \right) \quad [9]$$

Two approximations exist for Henry's equation. When κr approaches 0, Eq. [9] reduces to Hückel's approximation:

$$\mu = \frac{2\varepsilon\zeta}{3\eta} \quad [10]$$

Hückel's approximation is applicable for spherical particles when $\kappa r < 0.1$. In cases where κr approaches ∞ Eq. [9] is reduced to Helmholtz-Smoluchowski's equation:

$$\mu = \frac{\varepsilon\zeta}{\eta} \quad [11]$$

Helmholtz-Smoluchowski's equation is applicable to particles of arbitrary shape provided that the particle radius is much greater than the double-layer thickness, that is for $\kappa r \gg 1$. In **Paper IV** Eq. [11] was used to estimate ζ from measurements of the electrophoretic mobility.

3.3 Stability properties of water-dispersible soil colloids

As revealed in the previous chapter the stability properties for natural soil colloids depend on (i) the surface potential of the colloids which is related to the mineralogy or composition of the colloid surface, and (ii) the solution ionic strength affecting the double layer extension and/or specific adsorption and pH affecting the ionization of pH-dependent charge sites. The following sections will focus on the stability properties of the natural WDC isolated from the Flakkebjerg profile (**Paper IV**) compared to the stability behavior of two reference colloids; a Ca-montmorillonite (sWy-1) which is a smectite belonging to the group of 2:1-layer silicates and a Ca-kaolinite (KGa-2) a 1:1-layer silicate.

3.3.1 Physico-chemical characteristics of natural water-dispersible colloids

Several investigations have been concerned with the physicochemical characteristics of WDC or eluted soil colloids and a diversity of dispersible or mobilized colloids has been found differing among soil types (Grolmund *et al.*, 1996; Kaplan *et al.*, 1996, 1997; Seta and Karathanasis, 1997a). According to Kretzschmar *et al.* (1999) is the composition of *in situ* mobilized colloids generally similar to that of the clay fraction, although the quantitative proportions of different mineral or organic phases may vary. Colloids with high negative surface charge density like smectite and vermiculite has traditionally been assumed to be highly dispersible and mobile, however, several observations have documented that surface adsorbed organic matter increases the stability of low charge density minerals like kaolinite (Frenkel *et al.*, 1992; Kretzschmar *et al.*, 1997, 1998) and heterogeneous charged minerals like sesquioxides (Tipping and Higgins, 1982).

The physico-chemical characteristics and mineralogy of the WDC from the Flakkebjerg profile revealed that the WDC were composed of a mixture of minerals generally dominated by smectite. This mineralogy also corresponded to that of the total clay fraction of this soil (Rasmussen *et al.*, 2001), indicating that there was no preferential dispersion of any clay mineral phase. The WDC fractions were generally enriched in organic carbon and sesquioxides. WDC from the Ap-horizon and from macropore deposits differed markedly from the remaining WDC fractions due to a significantly higher content of OC, Al_{CBD} and a much smaller N₂-adsorption surface area, indicating that the surfaces of these colloids were at least partly coated with OC known to have extremely low N₂-adsorption surface area (Chiou *et al.*, 1990). This hypothesis was supported by a large increase in the N₂-adsorption surface area after oxidative removal of OC. The results suggested that NOM was sorbed to the layer-silicates through complexation with sesquioxides, thereby controlling the surface properties of these colloids.

3.3.2 Effect of solution pH

The stability of pure reference clay mineral suspensions is generally demonstrated to decrease as pH decreases (e.g. Dixit, 1982; Goldberg and Glaubig, 1987; Goldberg and Forster, 1990; Hesterberg and Page, 1990b). The effect of pH on the stability behavior can be explained by the pH-dependent charge on sesquioxides, colloid associated humic substances and on the edge of layer silicates. With decreasing pH, the pH dependent surface sites become positively charged, resulting in electrostatic attraction with negatively charged sorption sites. The pH-dependence on the colloid stability behavior depends on the relative significance of pH-dependent surface charge sites on mineral edges compared to the permanent surface charge on the basal surface. This was illustrated by the ζ -potential versus pH behavior for the reference minerals representing the charge characteristics for a permanent charged (Ca-montmorillonite) and a pH-dependent charged (Ca-kaolinite) mineral (Figure 9a). The ζ -potential for the montmorillonite displayed no pH variation, while the ζ -potential for the kaolinite reflected the increased protonization of surface hydroxyls as pH decreased. The PZC for the kaolinite was estimated to pH 4, which agrees with results from earlier studies (Sposito, 1992; Anderson and Bertsch, 1993). The stability properties of the reference minerals were reflected by the changes in the hydrodynamic particle diameter as a function of pH, demonstrating rapid flocculation as pH decreased (Figure 9b).

The effect of pH on the stability properties of suspensions of natural soil colloids has also been found to decrease as pH decreases (Gupta *et al.*, 1984; Suarez *et al.*, 1984; Goldberg and Forster, 1990; Miller *et al.*, 1990), but, observations have indicated that natural soil colloids often exhibit a higher suspension stability compared with the corresponding reference minerals (e.g. Rengasamy, 1983; Frenkel *et al.*, 1992; Heil and Sposito, 1993a). In the case of the natural WDC isolated from the Flakkebjerg profile (**Paper IV**), the ζ -potential versus pH behavior generally displayed a pH independence resembling the behavior of the montmorillonite (Figure 9c). All the natural WDC fractions, however, exhibited more negative ζ -potentials than the reference montmorillonite, with the most negative potentials observed for

the OC-enriched WDC from Ap and the least negative potential for the Btg₂ (<0.2 μm). In contrast to the reference colloids, the natural WDC showed stable colloid suspension with no flocculation taking place at pH 5-7 (Figure 9d). A relative increase in d_H was observed at pH <5 and at pH <4 the destabilization of the colloid suspensions was marked for all WDCs. At pH >7 there was a slight decrease in d_H for some of the WDCs indicating dispersion at higher pH. These results agree with the general conclusions, that natural soil colloids exhibit greater stability compared to pure reference colloids. The resistance against flocculation was most pronounced for the OC-enriched Ap-WDC, while the Btg₂ displayed the lowest stability. The existence of colloid associated NOM is generally suggested to be responsible for the larger stability of natural soil colloids compared to pure reference colloids (e.g. Ryan and Gschwend, 1990; Heil and Sposito, 1993b, 1995; Kretzschmar *et al.*, 1993). From the evaluation of the pH–stability relationship of the natural WDC it was demonstrated that the average ζ-potential could not be used to predict the stability behavior. This was probably a consequence of a low contribution of pH-dependent charge sites to the total surface charge. This also agrees with results of Elimelech *et al.* (2000) demonstrating that the use of the average measured ζ-potentials lead to erroneous results when predicting colloid deposition in chemically heterogeneous sand.

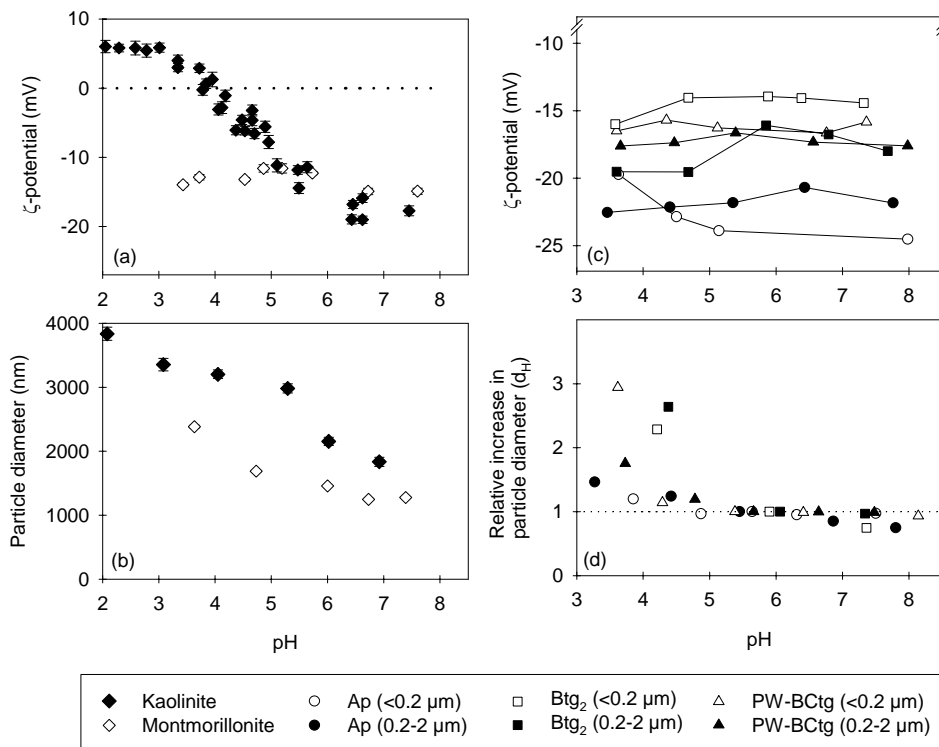


Figure 9. Influence of pH on (a) ζ-potential and (b) mean hydrodynamic particle diameter (d_H) of Ca-kaolinite and Ca-montmorillonite reference colloids (unpublished results), and influence of pH on (c) ζ-potential and (d) relative increase in mean hydrodynamic particle diameter of water-dispersible colloids (WDC) from different soil horizons and colloidal size fractions (Modified figure from **Paper IV**).

3.3.3 Effect of ionic strength

Several investigations have documented that increasing ionic strength reduces colloid stability (e.g. Chorom and Rengasamy, 1995) in agreement with the predictions from the DLVO theory of colloid stability. The effect of increasing ionic strength on the stability behavior can be explained by the compression of the diffuse double layer around charged surfaces and a subsequent reduction in the electrical potential at the plane of shear (Hunter, 1981). In addition, increasing Ca^{2+} concentration in solution may result in increased Ca^{2+} binding to functional groups of colloid bound humic substances and a subsequent charge reduction (Amirbahman and Olson, 1995). The results from the present study (**Paper IV**) confirmed this, demonstrating a decrease in the negative ζ -potential for both the reference minerals (Figure 10a) and the natural WDC (Figure 10c). The ζ -potential for the Ap-WDC was significantly more negative than the other colloid fractions over the entire EC range, except for the highest concentration. WDC from the macropore coatings (MP-BCtg) had slightly more negative ζ -potentials than the Btg₂-WDC. Both reference minerals exhibited ζ -potentials similar to or less negative than the ζ -potentials of the Btg₂-WDC, with the montmorillonite having slightly more negative ζ -potentials compared to the kaolinite over most of the EC range.

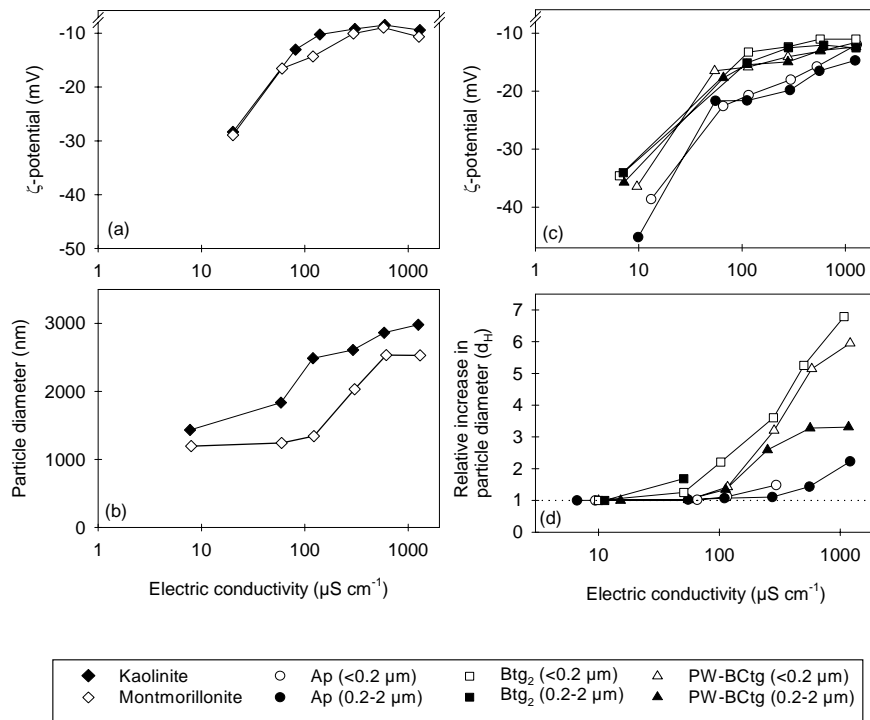


Figure 10. Influence of electric conductivity of CaCl_2 -suspensions on (a) ζ -potential and (b) mean hydrodynamic particle diameter (d_H) of Ca-kaolinite and Ca-montmorillonite reference colloids (unpublished results), and influence of pH on (c) ζ -potential and (d) relative increase in mean hydrodynamic particle diameter of water-dispersible colloids (WDC) from different soil horizons and colloidal size fractions (Modified figure from **Paper IV**).

The reduction in ζ -potential indicates reduction in the repulsive forces, which is confirmed by the relative increase in the average hydrodynamic particle diameter for both reference minerals (Figure 10b) and natural WDC (Figure 10d). The relative increase in d_H differed among the natural WDC. At low EC the suspensions were stable and no flocculation occurred, but at a certain critical concentration flocculation was initiated with the onset of flocculation differing among the WDC, and a two fold increase of the initial particle diameter occurred at an EC of $91 \mu\text{S cm}^{-1}$ for the least stable Btg₂ colloids, $171\text{-}185 \mu\text{S cm}^{-1}$ for MP-BCTg, and $1023 \mu\text{S cm}^{-1}$ for the most stable Ap-WDC. The Btg₂ (0.2-2 mm) fraction was very unstable and allowed only measurements at low concentration before flocculation reaches a level where further increase in particle size could not be measured due to sedimentation.

The stability behavior of the WDC could, at least partly, be explained by their respective ζ -potentials, the colloids having the most negative ζ -potentials also exhibited the largest resistance against flocculation. However, at higher EC when the ζ -potential was reduced to a minimum level for all WDC fractions, large differences occurred in the resultant relative increase in d_H , reflecting large differences in the colloidal stability properties. These differences can be attributed to steric stabilization forces from surface adsorbed organic matter. Organic coatings have been found to promote colloid dispersion by steric hindrance and may induce colloid stability at high ionic strength conditions (Hunter, 1987). Tiller and O'Melia (1993) investigated the relative importance of steric and electrostatic stabilization of hematite colloids by adsorbed polyelectrolytes and natural organic matter. They found, based on computer simulations, that at low to moderate ionic strength ($<0.1 \text{ M}$) the adsorbed polyelectrolyte layer thickness was small compared to the diffuse double layer thickness, while at high ionic strength ($>0.1 \text{ M}$) the predicted adsorbed layer thickness was at the same order of magnitude as the diffuse double layer thickness. This led to the conclusion that adsorbed polyelectrolytes or natural organic matter may provide additional steric repulsion at high ionic strength conditions. Kretzschmar *et al.* (1998) concluded that the stabilizing effect of adsorbed humic acid to kaolinite colloids at low ionic strength (0.01 M) was purely electrostatic, while stabilization at 1 M ionic strength may have been partly due to steric stabilization. These interpretations are in agreement with the results from this study indicating steric stabilization at high ionic strength conditions.

3.3.4 The role of colloid associated organic carbon and sesquioxides

The ζ -potential and stability behavior of the intact WDC fractions suggested that organic matter contributed to the stabilization of the most stable colloids. The lowest specific surface areas were observed for the Ap and MP-BCTg fractions, also having the largest content of OC, indicating that organic matter dominated the surfaces of these WDC-fractions. A hypothetical model for the structure of colloids stabilized by organic matter could be that OC is associated with the layer-silicate phase through complexation with sesquioxides (Figure 11).

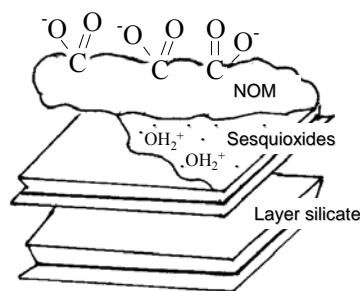


Figure 11. Conceptual model of a natural water-dispersible colloid stabilized by surface adsorbed organic matter through complexation with sesquioxides to the layer-silicate phase.

If such a model represent a typical WDC stabilized by organic matter, selective removal of each of the components should reflect the surface properties of the underlying component. Oxidative removal of organic carbon from the OC-enriched WDC resulted in an increase in the specific surface area by 171-225% (Paper IV), supporting the hypothesis that the surfaces of these WDC are at least partly coated by OC, known to have extremely low ($<1 \text{ m}^2 \text{ g}^{-1}$) N_2 -gas adsorbing surface areas (Chiou *et al.*, 1990). Additional treatment with CBD for removal of Fe- and Al-oxides decreased the specific surface area of the Ap-WDC, but had less effect on the surface area of MP-BCtg fractions. Generally, oxides have larger specific surface area than layer silicates and removal of oxides would therefore be expected to contribute to a reduction in the specific surface area. In the present case removal of oxides resulted in reduction of the resulting particle size and the effect of oxide removal on specific surface area may be masked by the increase in specific surface area resulting from particle size reduction.

The oxidative removal of NOM from Ap and MP-BCtg fractions had two significant effects on the ζ -potential (Figure 12). Removal of NOM (i) reduced the negative ζ -potential, and (ii) caused the ζ -potential to become affected by pH. The reduction in ζ -potential was more pronounced for the WDC fractions from MP-BCtg compared to the Ap, but the resulting pH-dependence of the ζ -potential showed similar patterns. As pH increased the reduction in ζ -potential due to removal of NOM became less marked. An explanation for this change in ζ -potential versus pH characteristics is that removal of NOM exposes a surface of sesquioxides with pH-dependent charge behavior. At low pH the oxides will be dominantly positively charged and therefore contribute to a marked decrease in negative ζ -potential when removing surface adsorbed NOM. As pH increases the positive charge of the oxides is reduced, and hence the contribution of the sesquioxides to change in ζ -potential decreases. These considerations was supported by the increase in the negative ζ -potential for the OX+CBD treated fractions compared to the OX treated fractions (Figure 12). Oxidative removal of NOM from Ap fractions reduced the ζ -potential less than removal of NOM from the MP-BCtg fractions despite the larger content of OC and the more negative ζ -potential of the Ap fractions. The reason for this cannot be deduced from this study, but it is likely to be related to the type and morphology of the underlying layer silicate and sesquioxide fraction.

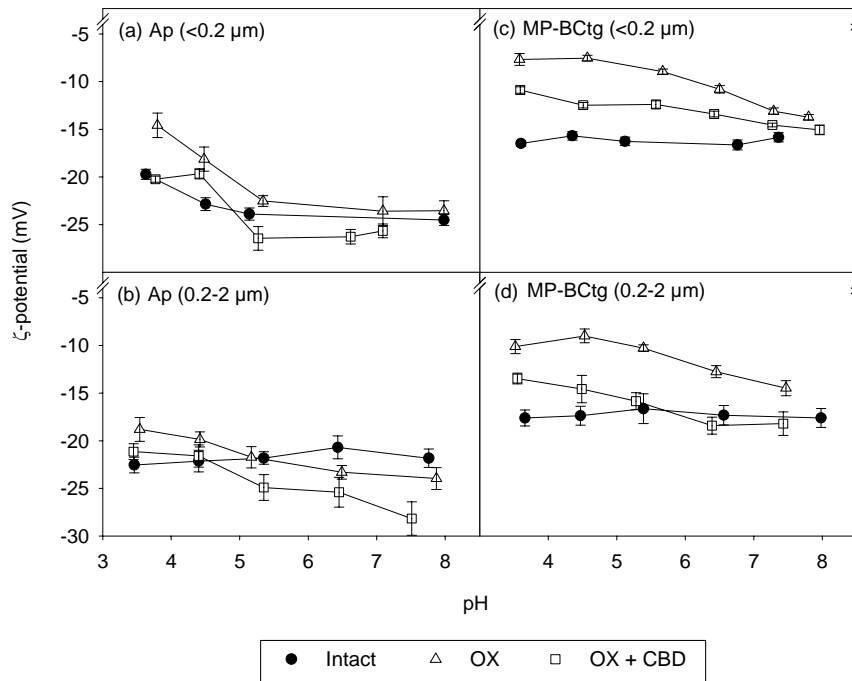


Figure 12. Effect of removal of organic matter (OX) and organic matter plus sesquioxides (OX+CBD) on the ζ -potential of water-dispersible colloids (WDC) from different soil horizons and colloidal size fractions as a function of pH. Error bars: \pm SE. (Figure from **Paper IV**).

The destabilizing effect of NOM removal on the WDC fractions was reflected in the flocculation behavior (**Paper IV**). The OX-treated colloids rapidly flocculated even at high pH, whereas the suspensions of Intact colloids remained stable at pH above 4-5. Furthermore removal of sesquioxides from the OX treated fractions resulted in a reduction in the average particle diameter. Smaller particle size of OX+CBD fractions results from loss of sesquioxides as “cement” gluing particles together, and the reduction in particle flocculation when surface coatings of positively charged sesquioxides are removed. The larger stability of the NOM coated colloids suggests that NOM plays a significant role in stabilization of suspended colloids in this soil type dominated by 2:1-layer silicates. This is in agreement with results reported earlier for suspensions of natural variable charged soil colloids (Kretzschmar et al., 1993), and for artificial mixtures between variable charged minerals and humic acids (Jekel, 1986; Kretzschmar et al., 1998). This study demonstrated that for WDC with rather similar mineralogical composition, large variations were observed in the flocculation behavior. These findings clearly demonstrate that model predictions of colloid deposition based on colloid mineralogy may lead to erroneous conclusions. Also for colloid fractions where the stability behavior is controlled by surface adsorbed organic matter large variation may occur in colloidal stability. This suggests that model predictions of colloid deposition should be based on direct examinations of colloid stability behavior.

3.4 Concluding remarks

The results from the present study documented that:

- Colloid associated organic matter increased the suspension stability of natural water-dispersible colloids in a Typic Agrudalf dominated by 2:1-layer silicates. The contribution of OC to the colloidal stability was inferred from:
 - More negative ζ -potential and larger suspension stability from WDC with larger content of OC
 - Reduced negative ζ -potential as well as reduced suspension stability after OC removal.

- The ζ -potential and stability behavior of natural WDC were strongly dependent on solution EC (CaCl_2 concentration), while solution pH had less effect on the stability behavior of the WDC:
 - A two-fold increase of the initial particle diameter occurred at an EC of $91 \mu\text{S cm}^{-1}$ for the least stable colloids, and at $1023 \mu\text{S cm}^{-1}$ for the most stable and OC-enriched colloids. The stability behavior of the WDC was related to ζ -potential measurements in the lower concentration range, while at higher CaCl_2 concentrations when ζ -potential was reduced to a minimum level for all WDC fractions, steric stabilization forces from surface adsorbed organic matter probably controlled suspension stability
 - Flocculation was only significant at pH below 4.5, and this was not reflected in the average ζ -potential.

- Practical and environmental implications:
 - The results from this study suggested in agreement with other studies, that the average ζ -potential alone cannot be used for predicting colloid stability of natural colloids due to the effect of heterogeneously charged surface sites and steric repulsion forces.
 - The presence of surface adsorbed organic matter presumably masked the underlying silicate and sesquioxide components, and consequently controlled the stability behavior of the WDC. Thus, model predictions of colloid deposition based on colloid mineralogy may lead to erroneous conclusions.
 - The results implies that under ionic strength conditions observed in the effluent from the Lerbjerg columns ($200\text{-}700 \mu\text{S cm}^{-1}$) only the most stable OC-enriched colloids will remain suspended, while the least stable colloids will flocculate. This also suggests that the least stable WDC isolated by the high-energy dispersion procedure used in the present study may not resemble the actual mobile and leachable colloids under field conditions.

4. SOIL STRUCTURE AND PREFERENTIAL FLOW

As highlighted in Figure 2 both the *in situ* mobilization and the subsequent transportability of mobilized colloids depend on the pore size and geometry of the actively conducting pore network. Investigations have shown that macropores may provide preferential pathways for water flow and suspended colloids (Smith *et al.*, 1985; Camobreco *et al.*, 1996). The flow velocities within these preferential flow paths can be orders of magnitude higher than the surrounding matrix, and they thereby constitute a risk for rapid transport of contaminants to drain and groundwater. The volume fraction of macropores and the continuity of these pores have a major influence on water flow and transport of suspended colloids (White, 1985). Smith *et al.* (1985) found that when the continuity of macropores was destroyed by disturbing part or all of the column, the recovery of *E. coli* was much reduced. Less is, however, known about the actual role of soil structure and preferential flow on *in situ* colloid mobilization and transport in unsaturated structured soils. In this thesis a study was carried out (**Paper II**) in order to provide an analysis of the soil structure characteristics and the flow behavior of the soils from the Lerbjerg clay gradient. These results were used to evaluate the role of preferential flow on *in situ* colloid mobilization (**Paper III**).

4.1 Soil structure

Extensive literature dealing with the subject of soil structure and structure stability is available (Tisdall & Oades, 1982; Dexter, 1988; Oades & Waters, 1991; Oades, 1993; Horn *et al.*, 1994; Kay and Angers, 2002). In general, soil structure is defined as the arrangement of solids and pores in soils. As stated by the various reviews, the definition of soil structure should also include the stability of the structure because structure is not static, but changes with water content and other types of internal or external stress which may be applied to the system. The dynamic properties of soils and the changes in soil structure may be very important with respect to *in situ* mobilization of colloids, since changes in structure stability changes the cohesive forces between colloids, expose new surfaces and change the flow pathways. Information about soil structure and the active flow pathways and the changes in structure upon soil exposure to internal stresses such as drying and rewetting is therefore a relevant issue when dealing with *in situ* colloid mobilization. In addition, the structural boundaries such as shrinkage cracks may provide possible pathways for water movement, which highlights the importance in structure stability to drying and rewetting. From the reviews available several soil properties have been found to exert dominant influence on soil structure. Among these are texture and clay mineralogy, soil moisture conditions, organic matter, oxides, exchangeable ions, plant and soil organisms, and tillage. In this thesis focus will be mainly on the influence of soil clay content and soil-water on soil structure and structure stability.

4.1.1 Evaluation of pore structure characteristics

Pores of different size are arbitrarily grouped into different size classes. According to the Soil Science Society of America (1997) glossary pore size classification, soil pores are divided into five groups: Cryptopores (<0.1 μm), ultramicropores (0.1-5 μm), micropores (5-30 μm),

mesopores (30-75 μm), and macropores ($>75 \mu\text{m}$). The water held in pores $<0.1 \mu\text{m}$ is often referred to as “adsorbed”, “bound”, or “residual” water, which does not participate actively in water flow. Pores with equivalent diameters of 0.1 to 30 μm are often termed storage pores, since they include the water that is potentially available to plants, and these pores also provide habitat for microorganisms. Meso- and macropores, in this thesis collectively referred to as macropores, have been found to exert a dominant influence of water flow and solute transport (White, 1985). Macropores includes biopores, shrinkage cracks and other interaggregate pores (Beven and German, 1982; White, 1985).

The most commonly used conceptual models for describing the size-distribution and structure of pores rely on a simplified picture of soil pore space as a bundle of parallel capillaries. The pore size-distribution can be estimated from the water-retention characteristics using the Capillary theory giving the equivalent pore diameter d (μm) at a given pressure potential ψ (hPa):

$$d = -\frac{2919}{\psi} \quad [12]$$

Problems associated with this method are the non-uniqueness of the estimated pore diameter, since the pore-size distribution is affected by hysteresis in the wetting or drying process (e.g. Nielsen *et al.*, 1986). In addition, shrinkage and swelling phenomena result in a different total porosity and a different pore-size distribution at each level of soil-water content (Dexter, 1988). Derivation of the pore-size distribution from water-retention characteristics is, however, a widely used and accepted characteristic describing soil structure. Though estimates of the pore size-distribution or the soil macroporosity are not necessarily related to the efficacy of pores in conducting water (Beven and German, 1982; White, 1985).

Approaches to identify the functional porosity have involved dye tracer studies (e.g. Bouma and Wösten, 1979; Seyfried and Rao, 1987). Bouma *et al.* (1977, 1979) developed a method for the quantitative interpretation of the number, size, shape, volume and connectivity of macropores based on thin sections of undisturbed soil. Dye tracer studies have been used to visually investigate active flow pathways in soils and illustrate the effect of flow rate and initial water content (Ghodrati and Jury, 1990; Flury *et al.*, 1994) and the role of soil structural elements such as macropores (Booltink and Bouma, 1991; Wildenschild *et al.*, 1994) and the size of soil aggregates (Vervoort *et al.*, 1999). These studies have also highlighted the importance of pore continuity on the functionality of the pore network (Bouma *et al.*, 1977). More recent studies related to the quantification of the soil macropore system and visualizing of preferential flow involve x-ray computer-assisted tomography (CAT) scanning (Perret *et al.*, 1999; Vanderborght *et al.*, 2002) or single photon emission computed tomography (SPECT) scanning (Perret *et al.*, 2000). These techniques allow the determination of the 3-D density structure in a non-destructive way (Vanderborght *et al.*, 2002).

Measurement of soil air-permeability has also been identified as a valuable tool for characterizing soil structure (Groenevelt *et al.*, 1984; Ball, 1988; Schjønning, 1989; Blackwell *et al.*, 1990; Granovsky and McCoy, 1997; Moldrup *et al.*, 2001). The air-permeability expresses the soils capacity to conduct air by convection, and measuring air-flow at pressure potentials where the water has drained from the macropores allow examination of the macropore network. From the parallel tube model, where the soil pores are presented by tortuous tubes of uniform radius, Ball (1981) derived expressions that allowed calculation of equivalent pore radius, tortuosity and number of pores per unit area from measurements of air-permeability (k_a), relative diffusivity (D/D_0) and air-filled porosity (ϵ_a). As revealed from the following presentation, the permeability of air in soil can be derived from the laws of Darcy and Poiseuille and the relative diffusivity from Ficks law of diffusion (Ball, 1981). The volumetric convective one-dimensional flow of air (q_a) through a sample cross-section (A) can be calculated from Darcy's law:

$$q_a A = -A \frac{k_a}{\eta} \frac{dP}{dL_s} \quad [13]$$

where k_a is the permeability of the air-filled pore space, η the viscosity of soil air, and dP/dL_s the gradient of soil air pressure and L_s the length of the sample.

At the microscopic scale of individual pores, approximated as a cylinder of given radius (r), the volumetric flow of air in n pores is described by Poiseuilles equation:

$$q_a n \pi r^2 = -\frac{n \pi r^4}{8 \eta} \frac{dP}{dL} \quad [14]$$

where L is the length of the individual pore.

Equating Eq. [13] and [14] yields an expression of soil air-permeability as a function of pore number, radius and tortuosity (L/L_s):

$$k_a = \frac{n \pi r^4}{8 A} \frac{L_s}{L} \quad [15]$$

Similarly, the one-dimensional diffusive transfer of air through a soil sample can be calculated from Ficks law:

$$J_a A = -D_a A \frac{dC}{dL_s} \quad [16]$$

where J_a is the rate of diffusive transfer per unit area of cross-section, D_a is the sample diffusion coefficient, and C the concentration. The rate of transfer of air in n cylindrical pores in the sample is:

$$J_a A = -D_0 n \pi r^2 \frac{dC}{dL} \quad [17]$$

where D_0 is the diffusion coefficient in free air. Equating Eq. [16] and [17] yields the relative diffusivity (D_a/D_0):

$$\frac{D_a}{D_0} = \frac{n \pi r^2 L_s}{AL} \quad [18]$$

The air-filled porosity of the sample is given by:

$$\varepsilon_a = \frac{n \pi r^2 L}{AL_s} \quad [19]$$

From measurements of k_a , D_a/D_0 and ε_a the equivalent pore diameter can be found by dividing Eq. [15] by [18]:

$$d = 2 \sqrt{\frac{8k_a}{D_a/D_0}} \quad [20]$$

the tortuosity L/L_s by dividing Eq. [19] by [18]:

$$\frac{L}{L_s} = \sqrt{\frac{\varepsilon_a}{D_a/D_0}} \quad [21]$$

and the number of pores (n) in a sample by substituting Eq. [20] and [21] in Eq. [15]:

$$n = \frac{\varepsilon_a^{0.5} (D_a/D_0)^{1.5}}{8\pi k_a} \quad [22]$$

An empirical expression of the pore organization (PO) representing the continuity and tortuosity of pores may also be inferred from relationships among air-permeability and air-filled porosity as suggested by Groenevelt *et al.* (1984):

$$PO = \frac{k_a}{\varepsilon_a} \quad [23]$$

since k_a/ε_a represent the air-permeability normalized with respect to the actual air-filled porosity, thus, related to the size and shape of the air-filled pores rather than the total pore volume.

Equations [20], [21], [22], [23] represent soil structure characterizing parameters. Different combinations of these parameters have been widely used for characterizing the structure of macropore space (Blackwell *et al.*, 1990; Granovsky and McCoy, 1997; Iversen *et al.*, 2001; Moldrup *et al.*, 2001) and assessing changes in soil pore characteristics brought about by soil management, tillage and traffic (e.g. Ball *et al.*, 1988; Schjønning, 1989; Roseberg and McCoy, 1992; Schjønning *et al.*, 2002). Based on data from 144 undisturbed soils, Moldrup *et al.* (2000) found a highly significant relationship ($r^2=0.98$) for D_a/D_0 as a function of ε_a at -100 hPa soil matric potential:

$$\frac{D_{a,100}}{D_0} = 2\varepsilon_{a,100}^3 + 0.04\varepsilon_{a,100} \quad [24]$$

where $D_{a,100}$ is the diffusion coefficient at -100 hPa and $\varepsilon_{a,100}$ is the air-filled porosity at -100 hPa. This implies that estimations of the above-mentioned soil structure characterizing parameters can be derived from measurements of only air-permeability and air-filled porosity. In **Paper II** measurement of air-permeability and air-filled porosity were used to estimate pore organization (Eq. [23]), equivalent pore diameter (Eq. [20]), and number of macropores (Eq. [22]) in order to examine the influence of clay content and initial matric potential (predrying) on the soil (macropore) structure.

4.1.2 Texture effect on soil structure

Soil structure and the physical properties of soil strongly depend on the texture (Rengasamy *et al.*, 1984). According to Oades (1993) the influence of biotic or abiotic processes on soil structure formation depends on soil clay content. Soils with $<15\%$ is not affected by shrink-swell phenomena and biology plays a major role in structure formation. As the clay content increases the importance of shrink-swell phenomena increases, while the influence of biology decreases. The present study (**Paper II**) investigated the soil (macropore) structure of soils from the Lerbjerg clay gradient ranging in clay contents from 12 to 43%. The size distribution of pores, calculated from the water retention characteristics (Eq. [12]) demonstrated that the fraction of pores $<0.2 \mu\text{m}$ (textural pores) increased with clay content, while the fraction of pores between 0.2 to $30 \mu\text{m}$ seemed independent of clay content and the volume fraction of macropores $>30 \mu\text{m}$ decreased with increasing clay content. Evaluation of the dependency of clay content on the macropore space characterizing parameters revealed that while the volume and number of macropores decreased with increasing clay content up to 24% clay, the soils exhibited pronounced structural similarity with respect to pore organization index and the equivalent macropore diameter (Figure 13). Large variability in the structure characterizing parameters occurred among the replicates, reflecting the structural variability between soils with identical clay contents. The large values of PO_{100} ($200\text{-}600 \mu\text{m}^2$) indicated a macropore network with a high continuity for all clay soils. Compared to the PO_{100} values obtained in the present study Iversen *et al.* (2001) obtained PO_{100} -values ranging from $1\text{-}200 \mu\text{m}^2$ in sandy and

sandy loam soils with weak structure and from 1-500 μm^2 in a moderate to strongly structured sandy clay loam. Similar high values were obtained for equivalent macropore diameter (200-700 μm^2). For the similar soils Moldrup *et al.* (2001) observed d_{100} values around 50 μm , when the soils were sieved and repacked, and these values increased to 100-250 μm after 17 month of regeneration. The high values of both PO_{100} and d_{100} indicate a highly developed macropore structure that was independent of clay content, in the undisturbed soils columns of this clay gradient.

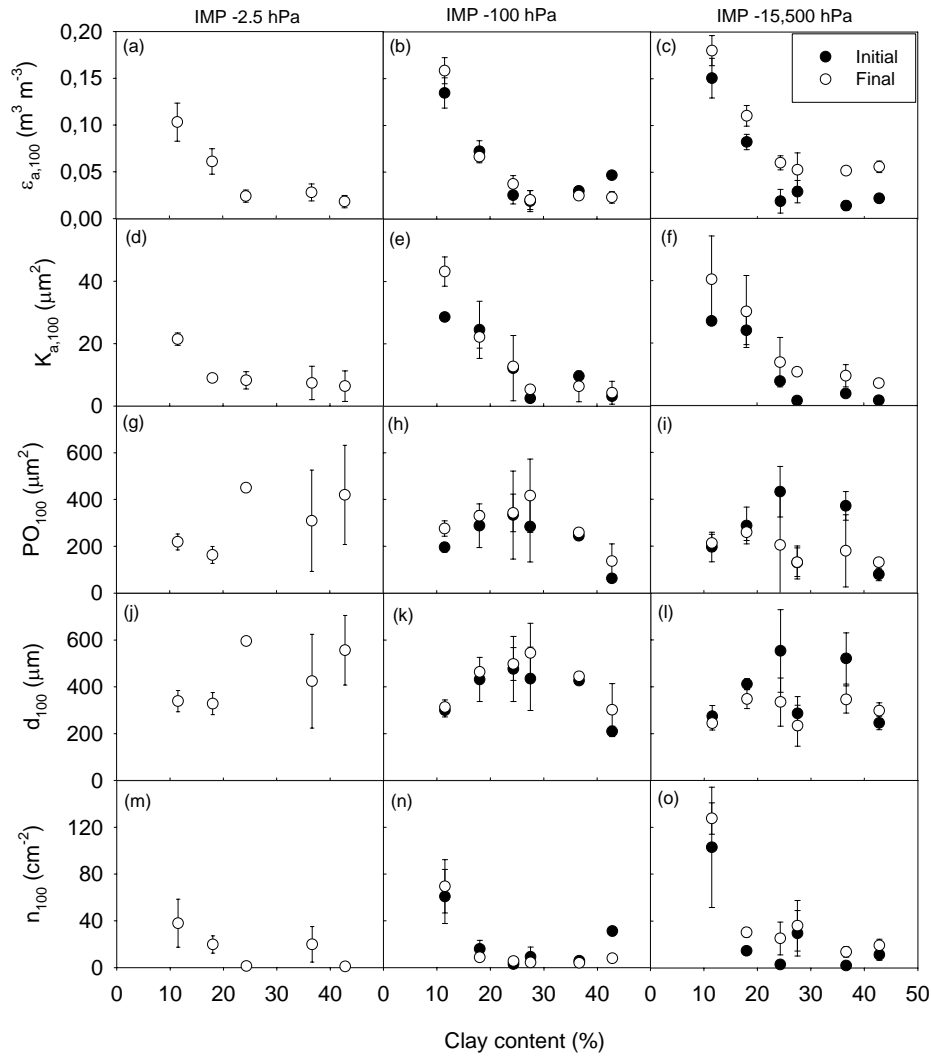


Figure 13. Soil structure characteristics determined at -100 hPa as a function of clay content and initial matric potential (IMP) before (initial) and after (final) the tracer experiment: (a-c) measured air-filled porosity, $\epsilon_{a,100}$, (d-f) measured air-permeability, $k_{a,100}$, (g-i) calculated index of macropore organization, PO_{100} , (j-l) calculated index of equivalent macropore diameter, d_{100} , and (m-o) calculated number of macropores ≥ 30 μm , n_{100} . Error bars: $\pm\text{SE}$. (Figure from **Paper II**).

4.1.3 Structure stability – effect of drying and rewetting

Structure stability refers to the ability of soils to retain its arrangement of solids and pore space, when exposed to internal stresses such as freeze-thaw or drying-rewetting cycles or external stresses such as tillage and traffic (Kay and Angers, 2002). The pore space may experience stress during drying and rewetting. On drying, the particles are forced into closer contact and the soil shrink and generate cracks at the plane of weaknesses. Dexter (1988) describes the development of desiccation cracks in a drying soil. The process of drying results in a successive development from vertical cracks to tertiary vertical and horizontal cracks. As the soil is re-wetted air-entrapment and differential swelling generate stresses, which may cause the aggregates to disintegrate (see discussion in chapter 2) with subsequent changes in the pore structure. Hussein and Adey (1998) demonstrated that drying and wetting cycles resulted in development of structural features (crumb structures) in an initial dense massive soil. Several studies have documented that drying and re-wetting cycles are associated with decreasing aggregate size (e.g. Shiel *et al.*, 1988; Hussein and Adey, 1995) and increasing porosity (e.g. Pardini *et al.*, 1996; Hussein and Adey, 1998; Czarnes *et al.*, 2000). Bouma and Wösten (1979) concluded that the increased porosity resulting from shrinkage and swelling was composed of a larger volume of finer pores, while the larger pores were closed upon swelling. The closing of larger pores upon swelling was also reported by Dexter (1988) and Collis-George (1991). Brewer (1964) reported that while planar voids or cracks may close upon swelling, tubular worm and root channels may remain open.

In the present study (**Paper II**) visual observations and measurements of volume changes upon drying and rewetting revealed that soils with $\geq 24\%$ clay reacted to drying by shrinkage and conversely to rewetting by swelling. The dependency of clay content on shrinkage agree with the results of Reeve *et al.* (1980) showing a close correlation between total clay content and shrinkage. The analysis of the dependence of initial matric potential on the soil structure characterizing parameters revealed that drying to $\psi = -15,500$ hPa and rewetting increased the number and volume of macropores and decreased the equivalent macropore diameter and the pore organization index, indicating closing of the largest pores and reduced continuity (Figure 13). This agrees well with the previous mentioned results on drying and rewetting.

4.2 Water flow and solute transport in structured soils

The flow of water and transport of solutes in the vadose zone have been under investigation for many decades (e.g. review by Nielsen *et al.*, 1986). A major focus in the recent research within this area has been directed towards understanding the link between soil structure, water flow and solute transport.

4.2.1 Equilibrium transport

Classical theory of water flow (Richards equation based on Darcys law) and solute transport is based on equilibrium assumptions. The steady-state (time invariant), one-dimensional solute transport through homogeneous soil is quantitatively described by the convective-dispersive equation (CDE):

$$\frac{\partial C}{\partial t} = \frac{D}{R} \frac{\partial^2 C}{\partial x^2} - \frac{v}{R} \frac{\partial C}{\partial x} \quad [25]$$

where C is the solute concentration, t is the time, D is the hydrodynamic dispersion coefficient, R is the retardation factor (dimensionless), x is the depth, and v is the average pore water velocity, defined as q/θ , where q is the Darcy flux velocity, and θ is the volumetric water content. The CDE assumes: (i) uniform convective transport, (ii) equilibrium lateral solute mixing, (iii) equilibrium adsorption, and (iv) a uniform distribution of sorption sites. Solute breakthrough curves for non-reactive solutes described by the CDE are sigmoidal in shape and symmetrical about the front of the advancing solution, with the inflection representing 50% displacement at a cumulative out-flow of one pore volume (PV). Conceptually, the dispersion coefficient reflects the lateral mixing of solute due to diffusion and mechanical dispersion:

$$D = D_{mec} + D_e \quad [26]$$

where D_{mec} is the mechanical dispersion and D_e is the effective diffusion coefficient. In homogenous porous media the mechanical dispersion accounts for (i) the microscale spreading caused by the parabolic velocity distribution within single pores, (ii) the variability in flow velocities between different pores, and (iii) the tortuosity of the flow path. The mechanical dispersion is often expressed as a linear function of the pore-water velocity:

$$D_{mec} = \tau v \quad [27]$$

where τ is the dispersivity. The effective diffusion is a function of the molecular diffusion coefficient of the solute in water (D_0) and the tortuosity of the medium (λ):

$$D_e = \lambda D_0 \quad [28]$$

In practice D is used as an empirical parameter that includes all of the solute spreading mechanisms that are not directly included in the CDE (Nielsen *et al.*, 1986). Application of the CDE to solute transport through repacked homogeneous soil columns involving nonreactive or only weakly reactive solutes has been fairly successful (Nielsen *et al.*, 1986).

4.2.2 Non-equilibrium transport

Solute breakthrough experiments in undisturbed, structured soils are often characterized by non-equilibrium flow phenomena, where breakthrough curves exhibit asymmetrical distributions or non-sigmoidal concentration fronts with very early appearance of tracer, pronounced tailing and high values of the dispersion coefficient (e.g. Elrick and French, 1966; Kissel *et al.*, 1973; Cassel *et al.*, 1974; Anderson and Bouma, 1977; Bouma *et al.*, 1977; Seyfried and Rao, 1987). Such asymmetric BTCs indicate that solutes are conducted relatively rapid through the soil columns by a small fraction of the soil water, accompanied by diffusive

mass transfer of solute between the mobile and immobile regions (e.g. Seyfried and Rao, 1987; Langner *et al.*, 1999). The rapidly conducting flow paths have been related to interaggregate regions (Anderson and Bouma, 1977; Seyfried and Rao, 1987) and macropores (White, 1985). Several studies report that preferential flow of water is not restricted to structured soils that contain large macropores or cracks, but also occur in structureless sandy soils (e.g. Ghodrati and Jury, 1990). Preferential flow is used as a general term to describe non-equilibrium flow and includes flow through macropores, fingering and funnel flow (see review by Gish and Shirmohammadi, 1991). Finger flow occurs in unstructured sandy soils and refers to non-equilibrium wetting fronts caused by horizon interfaces or by water repellency, while funnel flow refers to preferential flow caused by scale heterogeneity due to lenses or layers of various particle size fractions. Macropore flow refers to the flow of water in structural macropores. Macropore flow is often reflected in large increases in unsaturated hydraulic conductivity with small increases in soil-water potential close to saturation. At the pore scale, macropore flow is initiated when the soil-water potential increases to near saturation, such that the water-entry pressure of the macropore is exceeded. The following discussion will focus on preferential flow in structured soils.

4.3 Modeling water flow and transport in structured soils

An increasing number of models have been developed which can account for physical non-equilibrium processes (e.g. see review by Brusseau and Rao, 1990; Feyen *et al.*, 1998). Which transport model is the most appropriate to describe transport depends on the soil type and the scale on which transport is described (Feyen *et al.*, 1998).

4.3.1 Mobile-immobile model approach

A widely used approach to account for the non-equilibrium flow behavior has been to modify the CDE to account for partition of the water phase into mobile and immobile regions, where convective-dispersive transport is restricted to the mobile region, and a diffusive exchange of solute exists between the mobile and immobile region (Figure 14a). The mobile-immobile conceptualization for soils dates back 50 years, when it was used by Gardner and Brooks (1956). Mathematical models employing this conceptualization were presented by Coats and Smith (1964), Skopp and Warrick (1974), van Genuchten *et al.* (1974) and by van Genuchten and Wierenga, (1976):

$$\frac{\partial C_m}{\partial t} = \frac{D}{R} \frac{\partial^2 C_m}{\partial x^2} - \frac{v}{R} \frac{\partial C_m}{\partial x} - \frac{\alpha}{R} (C_m - C_{im}) \quad [29a]$$

$$\frac{\partial C_{im}}{\partial t} = \frac{\alpha}{R} (C_m - C_{im}) \quad [29b]$$

where C_m and C_{im} refers to the solute concentration in the mobile and immobile region, respectively, and α is a diffusional mass transfer coefficient, interpreted as a diffusion

coefficient divided by some average diffusion pathlength, accounting for solute exchange between mobile and immobile regions.

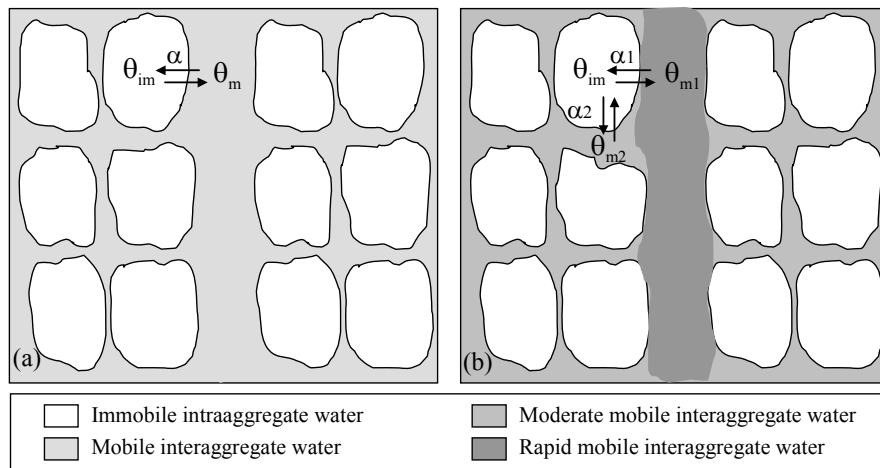


Figure 14. Conceptualization of (a) the mobile-immobile model (MIM) approach, and (b) the two mobile – one immobile model (2MIM) approach. θ_{im} represents the immobile intraaggregate water, θ_m represents all mobile water in the MIM model, θ_{m1} is the region of rapid mobile water (e.g. larger continuous interaggregate pores) and θ_{m2} is the moderate mobile water (e.g. smaller more tortuous interaggregate pores). α is the mass transfer coefficient that accounts for diffusive exchange of solute between mobile and immobile regions, α_1 accounts for diffusive transfer between the rapid mobile water and the immobile water, and α_2 accounts for diffusive transfer between the moderate mobile and the immobile water.

As reviewed by Brusseau and Rao (1990) solute transfer between the mobile and immobile regions can be accounted for in three ways: (i) using Fick's law to describe the physical mechanism of diffusive transfer, (ii) using an empirical first-order mass-transfer coefficient to approximate solute transfer (Eq. [29]) or (iii) using an effective or lumped dispersion coefficient that includes the effect of sink/source diffusion, as well as hydrodynamic dispersion and thereby replaces D in the CDE. In the physical diffusion model, solute transfer from mobile to immobile regions is described by two steps: diffusion through a boundary layer surrounding the particle, followed by diffusion within the aggregate. To develop the diffusion equation a geometric description of the porous medium is required. Generally, a spherical uniformly-sized aggregate structure has been assumed. Natural porous media however, differ considerable from this idealization. Several physical diffusion models have been proposed (see review by Brusseau and Rao, 1990).

By applying the mass transfer approach (Eq. [29]) an actual description of the aggregate geometry is not required. As reviewed by van Genuchten and Wierenga (1976) the mass transfer coefficient (α) depends both on the solute and on the medium, since this parameter involves the diffusion coefficient of the solute, the length over which the average concentration difference is considered, and the cross-sectional area through which the lateral diffusion process takes place. When evaluating the influence of the mass transfer coefficient on the shape of the BTCs van Genuchten and Wierenga (1976) found that when $\alpha=0$ (no diffusion of

solutes into the immobile water) the BTC was more or less symmetrical. When α was small (slow exchange of solute between mobile and immobile domains) a significant decrease in peak concentration and considerable tailing was observed. With increasing values of α (the rate of exchange increases) a new equilibrium may be established where the concentration of solute in the mobile and immobile water is identical. Rao *et al.* (1980) demonstrated that the time-averaged mass transfer coefficient decreased with increasing time of diffusion. They concluded that during solute breakthrough experiments, the time available for diffusion into and out of immobile water regions is inversely related to pore-water velocity. The time-averaged mass transfer coefficient is therefore expected to increase with increasing pore-water velocity, which is consistent with the experimental observations reported by van Genuchten and Wierenga (1977). The mass transfer coefficient was also found to decrease with the radius of spheres (Rao *et al.*, 1980), in agreement with an increase in the length over which the average concentration difference is considered, and an increase in the cross-sectional area through which the lateral diffusion process takes place.

The application of the mobile-immobile region approach (MIM model) to laboratory scale transport processes has been demonstrated by several studies e.g. van Genuchten and Wierenga (1977, aggregated clay loam), Gaudet *et al.*, (1977; unsaturated sand), Gaber *et al.* (1995; unsaturated, undisturbed silt loam), and Langner *et al.* (1999; saturated and unsaturated, undisturbed silt loam).

4.3.2 Multi-compartment models

As reviewed by Brusseau and Rao (1990) the mobile-immobile model approach has been incapable of describing the extensive tailing exhibited by some BTCs, and Brusseau and Rao (1989) proposed a three-region model. They hypothesized the extensive tailing to result from an additional intraaggregate diffusion mechanism, where the aggregate was conceptualized as consisting of two discrete porosity regions (meso- and micropore) with diffusive transfer between the two intraaggregate (immobile) regions, and between the interaggregate (mobile) regions. Morisawa *et al.* (1986) evaluated a three-region model where the mobile region was divided into two regions with convective-dispersive transport in both the “rapidly” mobile and the “moderately” mobile region, and mass-transfer was assumed to occur between the rapid and the moderate mobile region, and between the moderate mobile and the immobile region (c.f. Brusseau and Rao, 1990).

In this study (**Paper II**), several $^3\text{H}_2\text{O}$ -BTCs exhibited distinct double-peaks (Figure 15). Even though the MIM-model can be used to describe the existence of double-peaks (e.g. Mortensen, 2001), the second peak being a consequence of diffusive exchange between the mobile and immobile region, we suggested that a multi-compartment model may give a more accurate representation of the transport conditions in these soils. Consequently, in order to describe the transport of tritium in these soils we assumed that the water phase conceptually consisted of three separate physical pore regions: (i) a region with rapid water flow (e.g. in the larger interaggregate pores) occupying a pore volume of θ_{m1} , (ii) a region with moderate water flow

(in the smaller interaggregate pores) occupying a pore volume of θ_{m2} , and (iii) a region with immobile water (in the intraaggregate pores) occupying a pore volume of θ_{im} (Figure 14b). The model employing this conceptualization is described as an extended mobile-immobile approach, with two mobile and one immobile region (2MIM-model):

$$\frac{\partial C_{m1}}{\partial t} = \frac{D_{m1}}{R} \frac{\partial^2 C_{m1}}{\partial x^2} - \frac{v_{m1}}{R} \frac{\partial C_{m1}}{\partial x} - \frac{\alpha_{m1}}{R} (C_{m1} - C_{im}) \quad [30a]$$

$$\frac{\partial C_{m2}}{\partial t} = \frac{D_{m2}}{R} \frac{\partial^2 C_{m2}}{\partial x^2} - \frac{v_{m2}}{R} \frac{\partial C_{m2}}{\partial x} - \frac{\alpha_{m2}}{R} (C_{m2} - C_{im}) \quad [30b]$$

$$\frac{\partial C_{im}}{\partial t} = -\frac{\theta_{m1}}{\theta_{im}} \frac{\alpha_{m1}}{R} (C_{im} - C_{m1}) - \frac{\theta_{m2}}{\theta_{im}} \frac{\alpha_{m2}}{R} (C_{im} - C_{m2}) \quad [30c]$$

Since tritium exhibited retardation in these soils (see discussion **Paper II**) a retardation factor (R) assuming linear equilibrium sorption ($R = 1 + \rho_b K_d / \theta$) of tritium was added to the model.

The two mobile regions are assumed to have independent pore water velocities (v_1, v_2) and dispersion coefficients (D_1, D_2). The dispersion coefficients are calculated using:

$$D_{m1} = v_{m1} \tau_{m1} \quad [31a]$$

$$D_{m2} = v_{m2} \tau_{m2} \quad [31b]$$

where τ_{m1} and τ_{m2} are the independent dispersivity coefficients in the mobile regions. If the input flux of water per cross sectional area of column (the Darcy velocity (q)) is known:

$$q = v_{m1} \theta_{m1} + v_{m2} \theta_{m2} \quad [32]$$

and the value of θ_{m2} is given as:

$$\theta_{m2} = \frac{q - v_{m1} \theta_{m1}}{v_{m2}} \quad [33]$$

First order diffusional mass transfer of tritium is assumed between each mobile region and the immobile region. Direct transfer between the two mobile regions is not included in the model as mass transfer will occur indirectly via the immobile region. The mass transfer coefficients for each mobile region (α_{m1}, α_{m2}) were also assumed independent and functions of the pore water velocity (De Smedt and Wierenga, 1979; Wierenga and van Genuchten, 1989). The α values were calculated as:

$$\alpha_{m1} = v_{m1} \kappa \quad [34a]$$

$$\alpha_{m2} = v_{m2} \kappa \quad [34b]$$

where κ is a constant assumed identical for both mobile regions.

4.4 Experimental and modeling results

In this thesis an analysis of the unsaturated flow behavior in undisturbed soil columns from the Lerbjerg clay gradient were carried out in order to evaluate the influence of soil structure as determined by (i) the clay content, and (ii) the initial matric potential (predrying), on unsaturated tritium transport (**Paper II**).

4.4.1 Results from the Lerbjerg clay gradient

The important features to be highlighted from these experiments were (Figure 15): (i) BTCs obtained at 12% clay exhibited symmetrical behavior, while non-equilibrium behavior, as indicated by asymmetrical BTCs with early breakthrough of tritium and tailing, were characteristic at higher clay contents ($\geq 18\%$ clay), (ii) as the clay content increased the tendency for double peaks increased, (iii) predrying generally resulted in a right-hand displacement of the BTCs at $\geq 18\%$ clay. This was most pronounced after drying to $-15,500$ hPa, and resulted in symmetrical BTCs at 18 and 24% clay.

The BTCs from the 12% clay were fitted to the MIM-model (Eq. [29]) showing negligible amounts of immobile water, indicating matrix-dominated flow behavior or very rapid exchange of tracer between the mobile and immobile region. The existence of double peaks at the higher clay soils was interpreted as the existence of two mobile flow regions; a region (e.g. continuous interaggregate pores, biopores or root channels) with very rapid water flow yielding the first peak and a region (e.g. more tortuous interaggregate pores) with moderate water flow yielding the second peak. Tailing indicated diffusive mass transfer between the mobile and immobile regions. The second peak could also be interpreted as a result of rapid diffusive mass transfer between mobile and immobile regions, however, rapid mass transfer is not expected to occur within these high clay soils, and we find that application of the 2MIM-model may give a more accurate representation of the transport conditions compared to the MIM-model. As discussed in Paper II the different shapes of the double-peaked BTCs may be interpreted as a result of different pore structures differing in the quantitative influence of the different water regions. Wildenschild *et al.* (1994) also observed multiple peaks in saturated chloride transport from a large undisturbed soil monolith and attributed this behavior to differences in pore-size distribution, tortuosity and connectivity of the macropore system as well as redistribution of entrapped air. The problem associated with the application of the 2MIM-model with six fitting parameters is the interpretation of the parameter estimates. As discussed by Jensen *et al.* (1996) when evaluating different forms of the CDE, more complex models may possess more flexibility to provide better fits of the BTC, however, the more complex models are also associated with larger uncertainties in the parameter estimates.

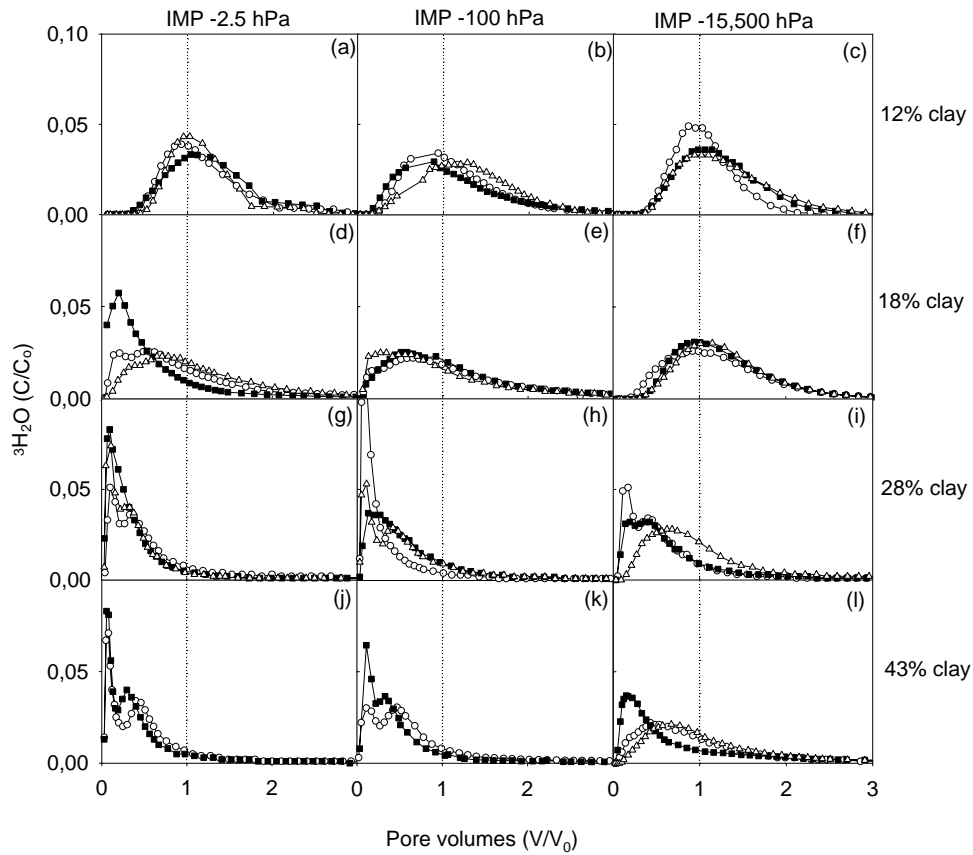


Figure 15. Tritium ($^3\text{H}_2\text{O}$) breakthrough curves plotted as relative concentration (C/C_0) against number of eluted pore volumes (V/V_0) as a function of clay content and initial matric potential (IMP) of -2.5 , -100 and $-15,500$ hPa. Dotted line marks one pore volume. Replicates represented by different symbols. (Figure from **Paper II**).

From the evaluation of the estimates of immobile water predicted by the 2MIM-model it appeared that the model provided a physically realistic description of the BTCs. Generally, the estimates of θ_{im} agreed with the interpretations based on the shapes of the BTCs, with the lowest values of θ_{im} obtained for the soil columns showing the highest degree of symmetry in the BTCs, in accordance with the conclusions of van Genuchten and Wierenga (1976), that when no immobile water is present, no intraaggregate diffusion takes place, and the BTCs become more or less symmetrical. In general, the degree of non-equilibrium flow behavior or preferential transport, as indicated by early tracer breakthrough (12.5% $^3\text{H}_2\text{O}$ -displacement) and the existence of immobile water regions, increased with increasing clay content up to 24% clay, and decreased with decreasing initial matric potential as a consequence of closing of the largest pores following drying and re-wetting (see discussion **Paper II**) (Figure 16).

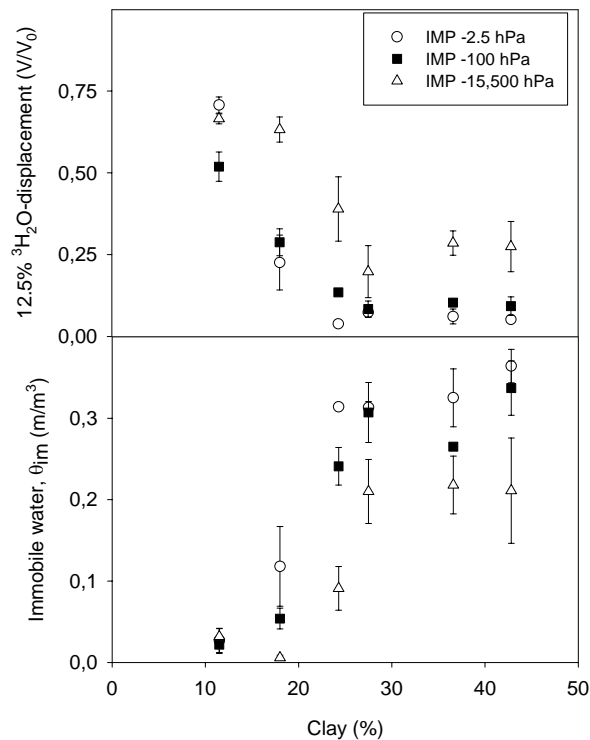


Figure 16. Effect of clay content and initial matric potential (IMP) on the degree of preferential transport as indicated by (a) early tracer breakthrough (12.5% ³H₂O-displacement), and (b) the existence of immobile water regions (θ_{im}). (Data from **Paper II**).

The matrix-dominated flow behavior of the 12% clay soils was conspicuous, as these soil cores actually contained a very large macroporosity and also a rather high pore continuity as evidenced from the analysis of the macropore structure characteristics. The functionality of the macropore is, however, determined both by the effective pore continuity and the soil-water content. In order to interpret the flow behavior in the soils from the Lerbjerg clay gradient, we must first consider the effect of soil-water content on the flow behavior.

4.4.2 Effect of matric potential on flow behavior

Several studies have investigated the effect of soil structure on water flow and solute transport in saturated systems of packed and undisturbed soil columns. These studies generally conclude that during saturated conditions water flow is dominantly influenced by soil structure, with continuous macropores, cracks or large interaggregate pores facilitating preferential flow. Nkedi-Kizza (1979) documented that in a saturated system increasing aggregate size (larger interaggregate pores) lead to earlier breakthrough of tritium (c.f. Nielsen *et al.*, 1986). Anderson and Bouma (1977) concluded that while large vertical continuous pores will conduct very high quantities of water in all types of soil under saturated conditions, this was not the case at steady and unsteady, unsaturated flow. Flury *et al.* (1994) also reported that saturated

ponding infiltration facilitated transport in cracks and earthworms channels, which was not the case for irrigation under unsaturated conditions. When the soil is saturated, vertical flow of water will be dominated by the flow in macropores. However, these pores drain at low suctions, which is often illustrated by a rapid decline in hydraulic conductivity with only small increases in suction near saturation. In unsaturated soils the actively conducting pore system depends on the soil matric potential, but only few studies have systematically investigated the effect of soil matric potential on solute transport in unsaturated, structured soils (Seyfried and Rao, 1987; Langner *et al.*, 1999). These studies have reported increasing symmetrical shapes of breakthrough curves when increasing the soil-water tension. Seyfried and Rao (1987) observed that BTCs obtained under saturated conditions were asymmetric, characterized by a very early appearance of tracer in the effluent and tailing. When increasing soil-water tension successively from 0 to -2 kPa the BTCs became more symmetric with later arrival of the tracer and less tailing. They obtained very good agreement between unsaturated BTCs ($h < -0.1$ kPa) and the CDE, while the use of the MIM-models was not justified for the unsaturated BTCs. The saturated BTCs ($h > -0.1$ kPa) were, however, poorly described by the CDE and agreed much better with the MIM-model. Their results using the MIM-model, however, indicated an extremely broad range in pore-water velocities in the mobile region, which suggested that the compartmentalization of soil-water into only two regions was insufficient to account for the range of pore-water velocities. Based on dye experiments (Seyfried and Rao, 1987) concluded that the highly asymmetric BTCs obtained under saturated conditions were due to rapid transport in restricted regions of conducting pore sequences rather than discrete macropores, and the application of tension disconnected the largest effective pore sequences, resulting in the more symmetric BTCs. Additionally, Langner *et al.* (1999) reported increasing equilibrium behavior of the BTCs when soil-water tension was increased and suggested that the transition from equilibrium to nonequilibrium transport occurred between $h = -5$ cm to -11 cm. Bejat *et al.* (2000) obtained BTCs from an unsaturated (-2 kPa) undisturbed silt loam soil that was well described by the CDE. In a field experiment, Flury *et al.* (1994) found no clear effect of initial soil-water content (wet and dry) on the flow pattern and the maximum penetration depth of a dye tracer at 14 sites. The maximum penetration depth of tracer was in general deeper in the wet soil, but the authors concluded that the differences were too small to draw general conclusions. A possible explanation for these findings could be that differences in water content between the “wet” and the “dry” soils were too low to induce any differences in flow behavior, since the “wet” soils were not at saturation, some of the rapidly conducting flow pathways were probably already deactivated.

In contrast to the studies on undisturbed soil columns, studies performed on packed sand columns have demonstrated that tailing in BTC increases with increasing soil-water tension (Nielsen and Biggar, 1961; Gaudet *et al.*, 1977; DeSmedt and Wierenga, 1984). This observation has been attributed to elimination of the larger pores and a consequent increase in the proportion of immobile or stagnant water, which does not readily move. Brusseau and Rao (1990) discussed the influence of unsaturated conditions on solute transport and suggested that the influence of soil matric potential depends on the pore-size distribution of the porous

medium. They described two general cases: (i) For porous media with a relatively narrow and uniform pore-size distribution, nonequilibrium will generally increase as soil-water content is reduced from saturation. The BTCs obtained under saturated conditions will exhibit a relatively small dispersion because of the uniform pore-size distribution. Upon drainage a fraction of the pores will no longer transmit water and become immobile domains that act as sink/source for the solute, hereby increasing the solute dispersion, (ii) For porous media with a nonuniform pore-size distribution, solute transport under saturated conditions is characterized by a wide pore-size distribution (e.g. the presence of macropores) resulting in nonequilibrium flow behavior. When the larger pores empty upon drainage, the effective pore-size distribution is narrowed and nonequilibrium flow behavior is reduced as the soil-water content is reduced from saturation.

Based on this knowledge the interpretation of the flow behavior of the soils from the Lerbjerg clay gradient can be explained by the effect of soil-matric potential on the actively conducting flow pathways. The combination of a lower relative saturation and a higher volume of large pores may have resulted in a disconnection of the rapidly conducting pore network in the 12% clay soils, thereby narrowing the pore-water velocity distribution, consequently resulting in negligible amounts of immobile water and matrix dominated flow behavior. This condition was less pronounced at 18% clay, while the higher clay soils were at saturation at the applied suction, allowing the macropore structures to be fully functional. This is probably the key factor explaining the observed flow behavior, however, when fully functional the larger macroporosity in the 12% clay soils may facilitate a greater lateral solute mixing compared to soils with lower macroporosity. Vanderborght *et al.* (2002) observed that the existence of a large dense pore network in the upper soil layers facilitated lateral mixing of two dye tracers and resulted in homogeneous transport, which was well predicted by the CDE. In the deeper layer the density of the large pore network was much smaller and the tracers were transported preferentially through a few larger pores without lateral mixing.

4.5 Linking soil structure to preferential flow

Feyen *et al.* (1998) suggested that the choice of an appropriate transport model that conceptualizes transport in soils should be linked to soil structure. They suggested that model parameters should be inferred directly from the soil structure characteristics, or from empirical relationships between model parameters and soil structural properties. Using analytical solutions for flow through porous media composed of immobile regions of known geometry, van Genuchten (1985) was able to express the mass transfer coefficient (α) in terms of an average sphere (c.f. Brusseau and Rao, 1990). This approach was used by Seyfried and Rao (1987) to estimate the radii of spherical immobile regions. Expressions for the mass-transfer coefficient in terms of physical diffusion model parameters have also been presented by Rao *et al.* (1980a,b). This allows the possibility of independent determination of values of this parameter, eliminating a fitting parameter in the mobile-immobile domain models. Several studies have used dye stained areas to estimate the fraction of pore volume in which rapid leaching occurred (e.g. Villholth *et al.*, 1998; Villholth and Jensen, 1998; Vanderborght *et al.*,

2002). Addiscott *et al.* (1978) suggested that independent estimates of mobile/immobile water can be obtained by assuming that water held at field capacity ($\psi \approx -100$ hPa) is immobile. This approach, however, underestimated the fraction of mobile water found by Seyfried and Rao (1987) and likewise found in the present study. A combined analysis of tracer BTCs and visualization of the flow pathways, e.g. by CAT scanning, would also markedly improve the interpretation of the BTCs and verify the choice of conceptual transport models.

Several studies have referred to macropore continuity as an important parameter with respect to predicting soil susceptibility to preferential flow. The validity of this perception during saturated flow should not be contested from this study. The present study, however, documented that for soils having rather similar values of macropore continuity and equivalent macropore diameter, the functionality of the macropore network was controlled by the relative saturation as determined by the pore size-distribution. This implies that predicting the susceptibility to preferential flow during unsaturated conditions requires an understanding of the changes in the actively conducting flow pathways when successively increasing suctions is applied to the system.

4.6 Concluding remarks

Evaluating the effect of soil structure and preferential flow of water on *in situ* mobilization and transport of colloids requires a thorough analysis of the prevailing flow conditions under the given experimental conditions.

- The analysis of the flow behavior of the Lerbjerg clay gradient revealed that the degree of preferential transport, as indicated by early tracer breakthrough (12.5% $^3\text{H}_2\text{O}$ -displacement) and immobile water regions:
 - Increased with increasing clay content up to 24% clay
 - Decreased with decreasing initial matric potential as a consequence of closing of the largest pores upon drying and rewetting.
- The analysis of the influence of soil structure on the susceptibility of preferential flow revealed that:
 - The matrix dominated flow behavior observed in the 12% clay soils, having the largest macroporosity, was interpreted as a result of a combination of a lower relative saturation at the applied pressure potential and a higher volume of large pores, which may have resulted in disconnection of a part of the rapidly conducting pore system.
 - Predrying to IMP $-15,500$ hPa also resulted in matrix dominated flow behavior at 18 and 24% clay soils, probably as a consequence of closing of the largest pores resulting from the shrinkage and swelling following drying and rewetting.
 - The susceptibility for preferential flow in the higher clay soils was not related to the soil macroporosity, but rather to the existence of few large macropores with high continuity.

- Practical and environmental implications:
 - The flow behavior in the Lerbjerg soils implies that the contact area between the infiltrating water and colloids associated in aggregates decreases with increasing clay content, which may affect the potential for *in situ* colloid mobilization.
 - Filtering of colloids may increase when matrix dominated flow behavior prevail, reducing the actual leaching of mobilized colloids.

5. Colloid mobilization and transport in structured soils

A comprehensive amount of literature exists on the topic of colloid mobilization and transport in model systems of packed sand (e.g. Tan *et al.*, 1992; Ryan and Gschwend, 1994; Roy and Dzombak, 1996) or packed soil columns (e.g. Grolimund *et al.*, 1998; Kretzschmar and Sticher, 1997; Grolimund and Borkovec, 1999; Noack *et al.*, 2000). Several reviews also address this topic (McDowell-Boyer *et al.*, 1986; McCarthy and Zachara, 1989; Swanton, 1995; Ryan and Elimelech, 1996; Kretzschmar *et al.*, 1999). These studies have demonstrated the importance of physical and chemical perturbations on the mobilization and transport of colloids. In structured soils, however, the processes of colloid mobilization and transport may be further complicated by the profound effect of pore structure on the active flow pathways of water, affecting both *in situ* colloid mobilization and subsequent transport. At present, few studies have investigated colloid mobilization and transport in natural structured soils (e.g. Kaplan *et al.*, 1993; Jacobsen *et al.*, 1997; Seta and Karathanasis, 1997a,b; de Jonge *et al.*, 1998, 2000; Ryan *et al.*, 1998; Karathanasis, 1999; Lægdsmand *et al.*, 1999; El-Farhan *et al.*, 2000; Villholth *et al.*, 2000; Schelde *et al.*, 2002; Petersen *et al.*, 2003) and no studies have systematically investigated the role of preferential flow on *in situ* colloid mobilization. This study aims to elucidate the processes controlling colloid mobilization and transport in natural structured soils.

5.1 Principles of *in situ* colloid mobilization and transport

In chapter one the principles of *in situ* colloid mobilization and transport in structured soils were presented introducing the main issues in the overall process of colloid mobilization and transport. In the previous chapters the processes and properties involved in colloid dispersion and colloid stability were elucidated and an analysis of the flow behavior of the Lerbjerg clay gradient was presented. In **Paper III** the overall process of *in situ* colloid mobilization and transport was investigated in order to evaluate the role of colloid dispersibility and preferential flow on colloid mobilization from the Lerbjerg clay gradient.

From the knowledge in the previous sections the principal diagram of *in situ* colloid mobilization can be extended to include all processes influencing colloid mobilization and transport illustrating the complexity of *in situ* colloid mobilization in structured soils (Figure 17). Colloids may be mobilized, or mobilization may be initiated by the processes of aggregate breakdown, involving slaking, differential swelling, raindrop impact and physicochemical dispersion. In addition, colloids may also be released as a result of dissolution of cementing agents, e.g. the reductive dissolution of iron oxides or cheluviations of iron or aluminum oxides are key soil forming processes resulting in translocation of clay colloids (Fanning and Fanning, 1989). Ryan and Gschwend (1990) observed higher colloid concentrations in anoxic groundwater zones compared to oxic zones, suggesting colloid mobilization by reductive dissolution of iron oxides. However, this could not be confirmed in laboratory studies (Ryan and Gschwend, 1994), the results of which suggested that electrostatic interaction was the dominating binding mechanisms of colloids to grain surfaces. Finally, mobilization of colloids

by hydraulic shear following rapid infiltration of water has also been reported as a possible process of colloid release (Kaplan *et al.*, 1993). Ryan and Gschwend (1994) did not observe any shear stress effect on mobilization of hematite colloids from packed sand columns and reported that hydrodynamic shear forces are generally negligible compared to electrostatic cohesive forces. From investigations of effluent from macroporous soil lysimeters Ryan *et al.* (1998) did not find any correlation between infiltration velocity and particle concentration, and Petersen *et al.* (2003) observed a negative relationship between out-flow turbidity and drain flow rates, indicating that the *in situ* mobilization was not governed by shear stresses. In the laboratory Schelde *et al.* (2002) demonstrated that *in situ* colloid mobilization in natural undisturbed sandy loam soil columns was not affected by hydrodynamic shear.

The various processes involved in colloid mobilization result in a number of interacting inherent and dynamic soil properties affecting colloid mobilization. The inherent soil properties, controlling the maximum colloid dispersibility include (i) clay mineralogy (Frenkel *et al.*, 1978; Seta and Karathanasis, 1996), and (ii) total clay content (Pojasok and Kay, 1990; Rasiah *et al.*, 1992; Brubaker *et al.*, 1992; Levy *et al.*, 1993; Curtin *et al.*, 1994). The dynamic properties determining the prevailing conditions for colloid mobilization and transport include (i) electrolyte concentration, composition and pH in the infiltrating water phase (Rengasamy, 1983), (ii) organic matter content (Pojasok and Kay, 1990; Rasiah *et al.*, 1992), (iii) initial soil-water content (Pojasok and Kay, 1990; Rasiah *et al.*, 1992), wetting rate/irrigation intensity, and as will be discussed in this chapter (iv) the prevailing flow conditions, such as degree of preferential flow.

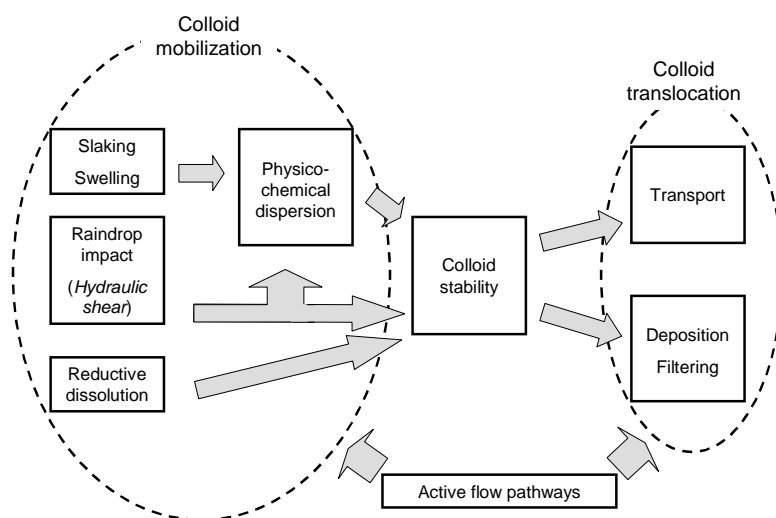


Figure 17. Principal diagram of the processes involved in *in situ* colloid mobilization in structured soils.

The transport of colloids through the vadose zone may be impeded by filtering of colloids. Filtering is used as a general term covering several processes such as sedimentation or flocculation of colloids, which is controlled by the size and stability of the suspended colloids, and physical straining in small pores, which depends on the pore size and geometry of the actively conducting flow-pathways. Complex theories have been developed to predict filtering for homogeneous porous media (e.g. see review by McDowell-Boyer *et al.*, 1986; Ryan and Elimelech, 1996; Kretzschmar *et al.*, 1999). These theories, however, are not applicable to natural soils due to the presence of both structural heterogeneities such as macropores, cracks or fractures, or chemical heterogeneities such as macroscopic charge heterogeneities, surface coatings of organic matter or oxides (Kretzschmar *et al.*, 1999). Only few studies have investigated colloid transport in physically heterogeneous media (Smith *et al.*, 1985; Toran and Palumbo, 1992; Saiers *et al.*, 1994; Silliman, 1995; Jacobsen *et al.*, 1997; Seta and Karathanasis, 1997a,b; Karathanasis, 1999). These results generally demonstrate that the presence of macropores, cracks or fractures increases colloid recovery, as a consequence of reduced filtering due to the larger pore size and smaller contact surface area per volume of soil. Several studies have observed that colloids travel faster than conservative tracers (e.g. Smith *et al.*, 1985; Toran and Palumbo, 1992; Kretzschmar *et al.*, 1995). This is explained as a size exclusion effect, where colloids are transported in larger pores and excluded from diffusion into the matrix in contrast to solute tracers. In the present study the quantitative importance of filtering or deposition of *in situ* mobilized colloids was not investigated, as we examined the net result of colloid mobilization and transport.

5.1.1 Mechanisms of colloid mobilization

Theories describing the mechanisms of colloid mobilization where colloids are considered attached to a collector surface of larger grains, have been presented by Ryan and Gschwend (1994), Swanton (1995), Roy and Dzombak (1996), Ryan and Elimelech (1996), and Kretzschmar *et al.* (1999). Ryan and Gschwend (1994) suggested that the release of hematite colloids from quartz surfaces in a packed bed column was controlled by either (i) detachment from a collector surface, or (ii) diffusion from the surface to the convective water phase:



where $C_{surface}$ is the colloid concentration at the grain surface, C_{det} the concentration of detached colloids, C_{bulk} the concentration of colloids in the bulk convective water phase, k_{det} is the first-order rate coefficient of detachment, k_{att} the first-order rate coefficient of attachment and k_{dif} the first-order rate coefficient of diffusion. Equation [35] assumes that convective flow maintains C_{bulk} at low levels, so that diffusion-driven transport from the bulk water to the surface can be neglected. The rate of colloid detachment (or attachment) is proportional to an exponential function of the size of the intersurface potential energy barrier as described by the DLVO-theory (see section 2.1.3):

$$k_{\text{det}} \propto \exp\left(-\frac{|\Phi_{\text{max}} - \Phi_{\text{min}}|}{k_B T}\right) \quad [36a]$$

$$k_{\text{att}} \propto \exp\left(-\frac{|\Phi_{\text{max}}|}{k_B T}\right) \quad [36b]$$

where Φ_{max} is the maximum of potential energy and Φ_{min} the primary minimum. When repulsive forces dominate, the rate of colloid detachment may be limited by diffusion. By assuming that the distance traveled by a diffusing colloid (corresponding to thickness of the boundary layer, δ_{bl}) can be calculated as $(2D_{\text{Col}} t_{\text{dif}})^{1/2}$, where t_{dif} is the characteristic time of diffusion and D_{Col} the colloid diffusion coefficient, Ryan and Gschwend (1994) estimated the rate coefficient of colloid diffusion as:

$$k_{\text{diff}} = t_{\text{dif}}^{-1} = \frac{D_{\text{Col}}}{\delta_{\text{bl}}^2} \quad [37]$$

The results from Ryan and Gschwend (1994) suggested that the rate-limiting step in release of hematite colloids from quartz surfaces in a packed bed column was diffusion across the boundary layer. This was evidenced by a decrease in the detachment rate coefficients normalized to accumulated out-flow, when the flow rate increased.

5.1.2 Experimental state of the art

In contrast to the large number of studies conducted to describe the mobilization and transport of colloids in model systems of packed soil columns, few studies have investigated *in situ* colloid mobilization in undisturbed laboratory soil columns (Kaplan *et al.*, 1993; Jacobsen *et al.*, 1997; de Jonge *et al.*, 1998, 2000; Lægdsmand *et al.*, 1999; Schelde *et al.*, 2002) or in field studies (Ryan *et al.*, 1998; El-Farhan *et al.*, 2000; Petersen *et al.*, 2003).

In soil cores of undisturbed sandy loam soils Jacobsen *et al.* (1997) investigated the impact of flow rate on both *in situ* mobilization of natural colloids and transport of suspended illite colloids. They irrigated undisturbed soil columns with tap water ($\text{EC } 300 \mu\text{S cm}^{-1}$) at relatively high intensities (11 and 30 mm h^{-1} , corresponding to storm flow events under Danish conditions) having free drainage of the soil columns, thereby promoting macropore transport. The mobilization and transport of *in situ* colloids were initially high, followed by a gradual decrease, and a final constant low concentration. No effect of irrigation intensity was observed on *in situ* mobilization of colloids, while irrigation intensity affected the mass recovery of suspended illite colloids, with higher mass recovery at high irrigation intensity. Smith *et al.* (1985) also found higher mass recovery of *E. coli* with increasing flow rate. Increasing flow rate has been found to increase the degree of preferential flow (decrease the lateral mixing) in

structured soils (Gaber *et al.*, 1995) and this may reduce the filtering of colloids, explaining the higher mass recovery. On two undisturbed soil monoliths originating from the same location as the soil columns used by Jacobsen *et al.* (1997), Lægdsmand *et al.* (1999) examined *in situ* colloid mobilization following irrigation (6.5 mm h^{-1}) with electrolyte solution resembling natural rainwater ($30 \mu\text{S cm}^{-1}$). The results of Lægdsmand *et al.* (1999) showed, in contrast to the findings of Jacobsen *et al.* (1997), that the concentration of leached colloids increased during the experiment. During the late experiment the colloid concentration was generally higher from the soil column having the largest macroporosity and the most pronounced tailing in the BTC. This suggested a higher diffusive exchange of water between mobile and immobile water regions, probably contributing to a higher leaching of colloids. Using the same soil as Jacobsen *et al.* (1997) and Lægdsmand *et al.* (1999), Schelde *et al.* (2002) examined the time dynamics of colloid mobilization from undisturbed soil columns following irrigation (11 mm h^{-1}) with artificial rainwater ($22.4 \mu\text{S cm}^{-1}$) with flow interruptions for 30 min, 1 day or 7 days followed by resumed infiltration. These results were consistent with the findings of Jacobsen *et al.* (1997) showing an initially high colloid concentration followed by a decline to a constant low value. The application of flow interruptions clearly demonstrated that colloid mobilization was not controlled by hydrodynamic shear, but was a time-dependent process and possibly a diffusion-limited process. This was suggested based on a linear relation between the cumulative mass of colloids and the square root of time indicating, but not proving, diffusion-limited kinetics (e.g. Kookana *et al.*, 1992).

In a field study on an unsaturated macroporous loamy soil Ryan *et al.* (1998) investigated the effect of tap water ($30 \mu\text{S cm}^{-1}$) irrigation intensity (4.2 , 8.3 and 16.7 cm h^{-1}) on colloid mobilization and transport to zero-tension samplers. They observed high initial concentrations followed by low concentrations in the later samples. No effect of irrigation intensity on particle concentration or size was evident from this study. In a highly structured silt loam field site El-Farhan *et al.* (2000) investigated the importance of transient ponding flow events on particle mobilization and transport to zero-tension samplers. In agreement with most of the above-mentioned studies they observed the largest particle concentrations during the initial infiltration followed by a lower but continuous supply of particles. All peak particle concentrations occurred near either the rising limb or the falling limb of the water flux hydrograph and they attributed this to the movement of air-water interfaces during imbibition and drainage.

In general, some similarities in the leaching pattern of colloids can be observed from the above-mentioned studies, all applying sampling at zero tension facilitating macropore pore flow. Except for Lægdsmand *et al.* (1999) all studies have reported high initial colloid concentrations followed by declining concentrations to a constant low concentration, indicating a continuous rate of particle supply. Lægdsmand *et al.* (1999) also found a continuous supply of colloids to be leached but in their experiment colloid concentrations increased throughout the leaching experiment. Typically reported peak concentrations varies from $300\text{-}1700 \text{ mg L}^{-1}$ (Kaplan *et al.*, 1993), $300\text{-}550 \text{ mg L}^{-1}$ (Jacobsen *et al.*, 1997); 1200 mg L^{-1} (Ryan *et al.*, 1998), $40\text{-}190 \text{ mg L}^{-1}$ (El-Farhan *et al.*, 2000), $200\text{-}800 \text{ mg L}^{-1}$ (Schelde *et al.*, 2002), and typical low

constant concentrations between 10-200 mg L⁻¹ have been reported. From these studies it has been demonstrated that *in situ* colloid mobilization is a dynamic and time-dependent process. Some of these studies have attributed the macropores as the source of *in situ* mobilized colloids, but the actual lack of knowledge concerning the diffusive exchange of water between mobile and immobile water regions, does not elucidate the actual role of preferential flow on *in situ* colloid mobilization.

5.2 Concept of *in situ* colloid mobilization in unsaturated structured soils

In the present experimental study (**Paper III**) it was hypothesized that the key properties controlling *in situ* colloid mobilization in natural structured soils are (i) the ability of colloids to disperse in response to infiltration of low-ionic strength rainwater, and (ii) the degree of preferential flow. Inter- and intraaggregate porosity affects the accessibility of the colloids to the infiltrating water and ion diffusion. Several studies (e.g. see review by White, 1985) have suggested that when nitrate is held within soil aggregates it will be protected from leaching when preferential flow occurs. The same concept may be applied to *in situ* mobilization of colloids located within aggregates. Colloid dispersion depends on the exchange of high-ionic strength resident water with low-ionic strength infiltration water. Horn and Taubner (1989) investigated the release rates of potassium from single aggregates of structured and homogenized soil under saturated conditions and found the release rates per unit mass were highest for homogenized material. In aggregates, however, K release from internal sites was retarded. The larger the aggregates, the smaller were the release rates. Based on this knowledge and the previous discussion we may therefore anticipate that preferential flow may accelerate the transport of externally applied colloid-contaminant complexes or colloid-contaminant complexes located close to the preferential pathways, but decrease the *in situ* mobilization and leaching of colloids located within aggregates.

5.3 Investigating colloid mobilization in unsaturated, structured soils

The investigation carried out in the present study focused on the influence of soil clay content and initial soil matric potential as two key soil properties controlling colloid mobilization and transport. Soil clay content and initial soil matric potential both affected the amount of water-dispersible colloids (**Paper I**) and the actively conducting flow-pathways (**Paper II**) of the soils from the Lerbjerg clay gradient. The experimental details concerning the setup and procedures is described in **Paper II** (see Figure 2, Paper II) and **Paper III**. Unsaturated flow was facilitated by applying a suction of 5 hPa to the lower boundary of the soil.

5.3.1 Mobilization and leaching of colloids and organic carbon

Generally, two types of leaching behavior were observed with increasing effluent concentration from the low clay (12 and 18%) and initially wet and moderate wet (IMP -2.5 hPa and -100 hPa) soils, while declining effluent concentrations to a constant low level (10 mg L⁻¹) were observed for all soils with IMP -15,500 hPa and ≥18% clay (Figure 18). Generally the highest effluent concentrations (180 mg L⁻¹) were observed from the initially moderate wet soils, and colloid effluent concentrations declined with increasing clay content up to 24% clay.

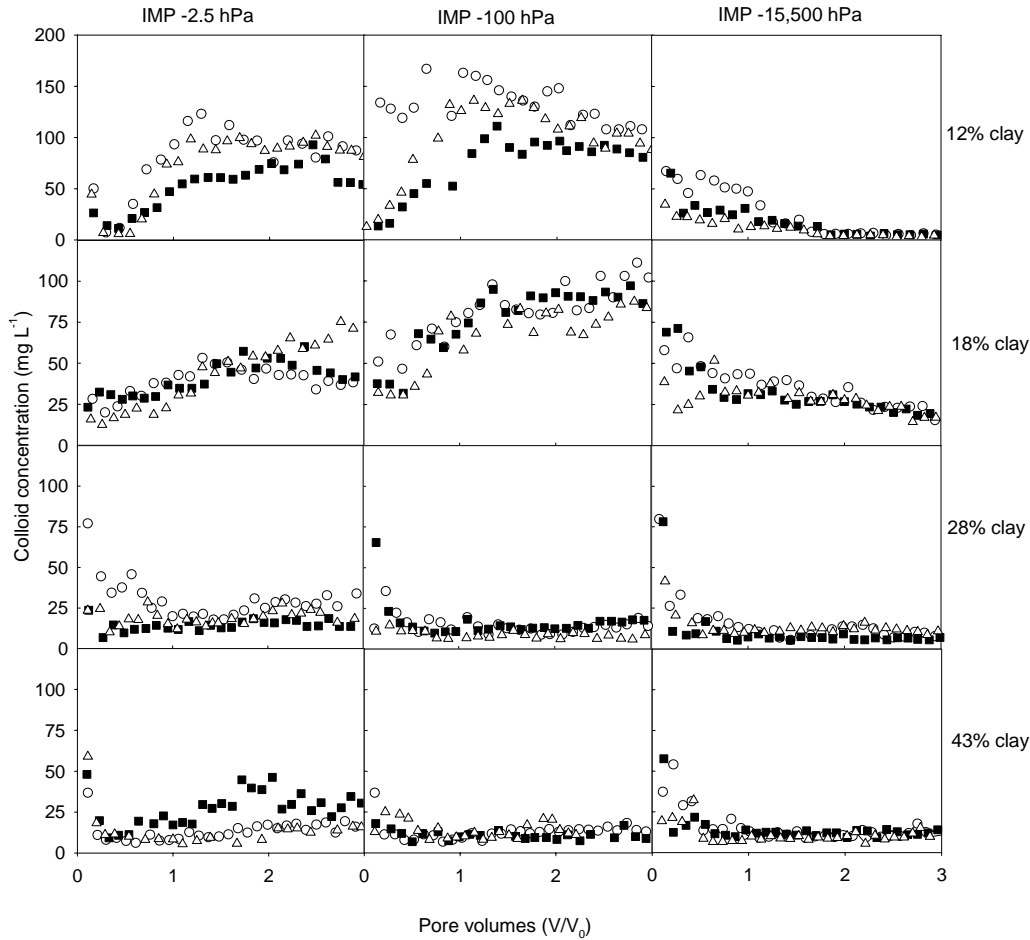


Figure 18. Effluent colloid concentration against number of eluted pore volumes (V/V_0) as a function of clay content and initial matric potential (IMP). Replicates represented by different symbols. Note that two different y-axis are used (120 and 200 mg L^{-1}). (Modified figure from **Paper III**).

As a result of this leaching pattern the following conclusion could be drawn from the accumulated leaching of colloids after three pore volumes (~ 120 - 140 mm) (Figure 19a): (i) For initially wet (IMP -2.5 hPa) and moderate wet (IMP -100 hPa) soils the accumulated mass of colloid leached after three pore volumes decreased with increasing clay content from 49 mg (IMP -2.5 hPa) and 74 mg (IMP -100 hPa) at 12% clay to a minimum of 7 - 19 mg at more than 24% clay. (ii) Leaching of colloids from initially dry soils (IMP $-15,500$ hPa) was low (11 - 24 mg) and independent of clay content. (iii) Initial matric potential affected colloid leaching only at lower clay content (12 and 18% clay) and the highest amount of colloids were leached from initially moderate wet (IMP -100 hPa) soils followed by the wet (IMP -2.5 hPa) soils, and the lowest amount of colloids were leached from the initially dry (IMP $-15,500$ hPa) soils.

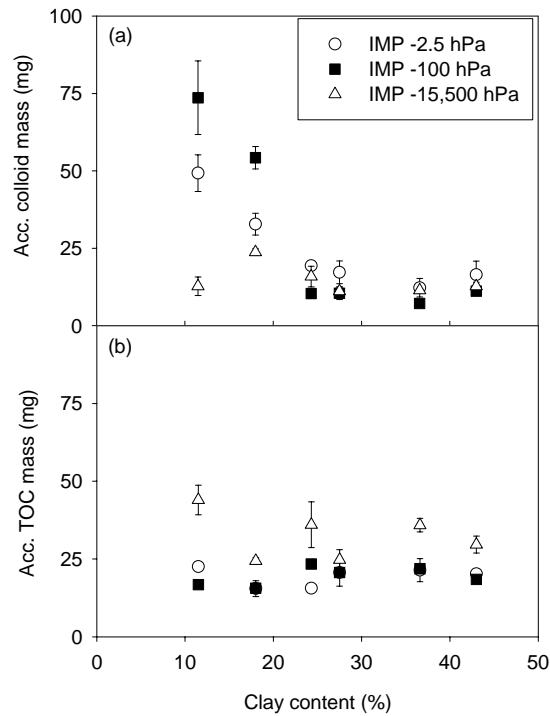


Figure 19. Effect of clay content and initial matric potential (IMP) on (a) accumulated colloid mass leached after three pore volumes, and (b) accumulated total organic carbon (TOC) leached after three pore volumes. Error bars: \pm SE. (Figure from **Paper III**).

From the accumulated leaching of carbon (mainly DOC) two important features should be highlighted (Figure 19b): (i) For initially wet (IMP -2.5 hPa) and moderate wet (IMP -100 hPa) soils the accumulated leaching of carbon after three pore volumes (16-23 mg) was independent of clay content and initial matric potential, and (ii) carbon leaching from the initially dry soil (IMP -15,500 hPa) generally increased (25-49 mg), and this increase was more pronounced at lower clay contents ($\leq 24\%$ clay).

In order to evaluate the processes controlling colloid mobilization the cumulative mass of colloids (Figure 20) and TOC (Figure 21) were plotted against the square root of time for the different initial matric potentials at 12, 18 and 28% clay, since these soils represent the main issues to be discussed. In addition, the time-dependent change in the electric conductivity of the effluent water is illustrated in the same plots. Leaching of one pore volume of water is indicated with vertical dotted lines, representing the upper and lower value of one pore volume for the three replicates.

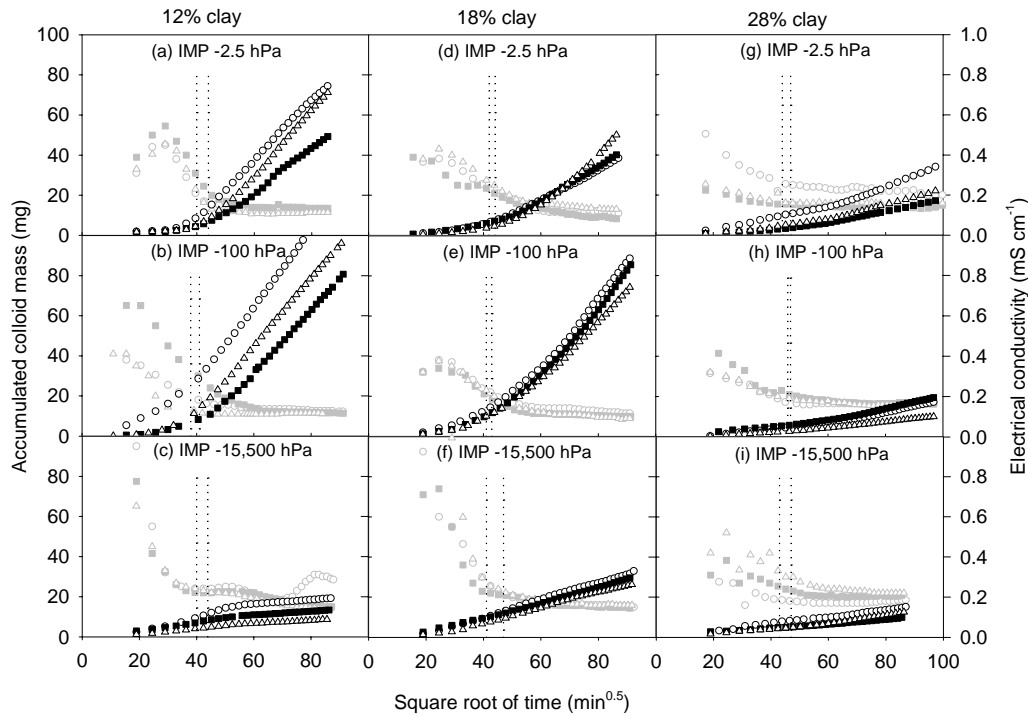


Figure 20. Plot of accumulated colloid mass (black symbols) and electrical conductivity EC (gray symbols) against square root of time for 12, 18 and 28% clay and initial matric potential (IMP) of -2.5, -100 and -15,500 hPa. Dotted lines mark leaching of one pore volume. Replicates represented by different symbols. (Figure from **Paper III**).

Several important characteristics were observed from these curves: (i) Generally the curves were non-linear within the first part, except for some curves at IMP -15,500 hPa, but became linear after some time, (ii) curve shapes and slopes for the TOC vs. square root of time relationship revealed only small differences among clay content and IMP -2.5 and -100 hPa, while slopes were steeper at IMP -15,500 hPa, (iii) curve shapes and slopes for the colloid vs. square root of time relationship revealed large differences among both clay content and initial matric potential, and (iv) there seemed to be some relationship between the electrical conductivity and the colloid vs. square root of time relationship. In order to understand these relations we need to address the soil inherent dispersibility and the role of preferential flow on colloid mobilization.

5.3.2 The role of colloid dispersion

From the investigations of colloid dispersibility (**Paper I**) we would expect dispersion-limited mobilization of colloids to become increasingly important with increasing clay content and decreasing initial matric potential (Figure 6b). These predictions agreed reasonable well with the actual leaching of colloids (Figure 19), but the accumulated leaching of colloids deviated from the predictions based on the LE-WDC measurements at two points. First, higher colloid leaching was observed from moderate wet soils (IMP -100 hPa). Second, no effect of initial matric potential was observed at higher clay content ($\geq 24\%$). The likely explanation for the

higher accumulated colloid leaching at IMP -100 hPa, in contrast to what was predicted from the LE-WDC measurements, is different ionic strength conditions. The pretreatment procedure for the packed aggregates used for measuring LE-WDC involved: (i) saturation with low-ionic strength water and drainage of the soil to the respective potentials, (ii) incubation for 14 days, and (iii) re-saturation with low-ionic strength water prior to measurement. As part of the re-saturation, samples incubated at -2.5 hPa were shortly drained to -100 hPa and subsequently saturated with low-ionic strength water in order to have identical treatments with respect to changes in electrolyte composition for all samples. The pretreatment procedure for the intact columns involved step one and two as described for the LE-WDC measurement. However, after the incubation the column leaching experiment was started with the different initial matric potentials as the initial conditions. This implied that soils with IMP -2.5 hPa had a higher initial ionic strength in the soil solution resulting in reduced repulsive forces between colloids and subsequently in reduced leaching from these soils compared to soils with IMP -100 hPa, indicating the important role of ionic strength in controlling colloid mobilization. The ionic strength effect did not affect colloid leaching at higher clay contents ($\geq 24\%$), where leaching generally was low and independent of both clay content and initial soil matric potential. This was not expected based on the predictions from the LE-WDC measurements and indicated the possible role of diffusion-limited mobilization. The agreement between the LE-WDC estimates and the actual leaching of colloids illustrate the importance in the choice of dispersion procedure in the WDC measurement. Predictions based on classical WDC estimates (Figure 6a) would have predicted increased colloid leaching with increasing clay content, which would certainly have lead to wrong conclusions under these experimental conditions.

The accumulated leaching of carbon, mainly DOC, was independent of clay content, and initial matric potential at -2.5 and -100 hPa. DOC is continuously produced by microbial activity, however, Christ and David (1996a) documented that DOC produced by microbial activity is stored in soils as an adsorbed reservoir rather than a pool of readily soluble material. This agreed with Reemtsma *et al.* (1999) concluding that release of carbon under long-term irrigation seemed to represent release of organic compounds held by the soil matrix. Reemtsma *et al.* (1999) and later Münch *et al.* (2002) suggested that the release of carbon in mineral soils is governed by two processes; a large initial mobilization of readily soluble material followed by a steady-state diffusion-controlled phase of detachment. Studies have shown that decreased ionic strength favors the detachment of organic molecules sorbed to the soil particles (Reemtsma *et al.*, 1999; Münch *et al.*, 2002). The ionic strength effect on carbon release may result from expansion of the electrical double layer, and/or the uncoiling of the molecular configuration (Ghosh and Schnitzer, 1980), which renders it more hydrophilic (Swift, 1989). No indication of increased DOC mobilization due to increased electrostatic repulsion from the infiltration of low-ionic strength solution were observed from the Lerbjerg soils, based on the lack of differences between the IMP -2.5 and -100 hPa treatments.

Several studies have focused on the influence of drying and rewetting on microbial activity and carbon dynamics (e.g. Bloem *et al.*, 1992; Magid *et al.*, 1999; Deneff *et al.*, 2001), and

increased release of DOC when remoistening dry soils is frequently reported (e.g. Münch *et al.*, 2002). This effect has been attributed to microbial death and lysis of microbial cells (Christ and David, 1994, 1996a,b) and release of protected organic matter as a result of aggregate breakdown upon drying and rewetting (Elliot, 1986). Bartlett and James (1980) and Kaiser and Zech (1998) showed that DOC release, as a consequence of microbial death, represented a pool of readily soluble organic matter, which rapidly dissolves upon rewetting. Results from this study documented that drying and rewetting resulted in a marked increase in carbon leaching and this was most pronounced at the lower clay contents ($\leq 24\%$). The reason for the minor effect of drying on carbon release at the higher clay contents is not clear, but it could be attributed to the presence of a larger fraction of water-filled intraaggregate pores in these soils, which may reduce microbial death.

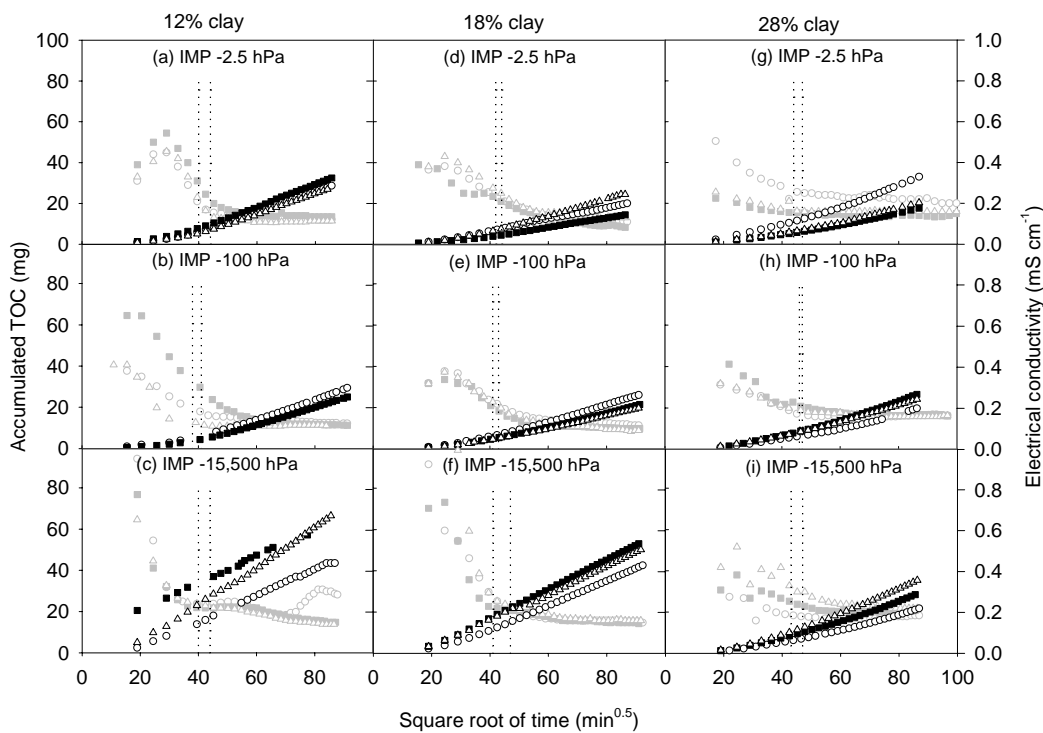


Figure 21. Plot of accumulated total organic carbon TOC (black symbols) and electrical conductivity EC (gray symbols) against square root of time for 12, 18 and 28% clay and initial matric potential (IMP) of -2.5, -100 and -15,500 hPa. Dotted lines mark leaching of one pore volume. Replicates represented by different symbols. (Figure from **Paper III**).

5.3.3 The role of preferential flow

Preferential flow conditions may affect colloid mobilization with respect to both colloid dispersion and colloid diffusion. When low-ionic strength rainwater is infiltrated through the soil, the mixing of infiltration water with the resident water depends on the degree of preferential flow and the diffusive exchange of water between the mobile and immobile water regions. With an increasing degree of preferential flow a decreasing fraction of the soil water

will actively participate in water movement. When the amount of immobile water increases the diffusion distances also increase, and the rate of diffusive exchange will consequently decrease (van Genuchten and Wierenga, 1976). This means that the displacement of low-ionic strength rainwater with high-ionic strength intraaggregate soil-water will be reduced or delayed, and this may impede dispersion of colloids. Indications of this phenomenon can be deduced from the curves of electric conductivity in Figure 20 and 21. At 12% clay the effluent EC is initially very high and declines rapidly to a constant low value after leaching of a little more than one pore volume of water. This observation and the matrix dominated flow behavior obtained from the 12% clays (Figure 15) indicate that after leaching of about one pore volume all resident high-ionic strength water has been displaced with the low-ionic strength rainwater. This condition also applies to the 18% clay soil at IMP -15,500 hPa. At higher initial matric potentials (IMP -2.5 and -100 hPa) preferential flow was abundant in the 18% clay soils, and consequently resulted in lower initial EC in the effluent water, and a slower decline in EC that continued after leaching of one pore volume of water. In the higher clay soils the EC curves became flatter indicating decreasing diffusive exchange of water between the mobile and immobile water regions. Thus, the reduced or delayed displacement of resident water with low-ionic strength rainwater may add to the inherent lower dispersibility of the higher clay soils, and increase the importance of colloid dispersion as the limiting process in colloid mobilization.

When the repulsive forces dominate, colloid mobilization may be limited by colloid diffusion. Whereas colloid transport in the mobile region takes place by convection and dispersion it is limited to diffusion within the immobile region. This is evidenced from the initial flush of colloids in the beginning of leaching experiments (Figure 18) and after non-flow periods (Jacobsen *et al.*, 1997; Schelde *et al.*, 2002). During non-flow periods, diffusion of colloids from immobile intraaggregate water to mobile interaggregate water builds up colloid concentrations in the mobile region, leading to an initial flush when irrigation is started. However, during prolonged infiltration colloid leaching may be limited by diffusion. As discussed above we would expect diffusion-limited mobilization of colloids to become increasingly important with increasing degree of preferential flow.

5.3.4 Interpretation of the processes controlling colloid mobilization

The discussion above and the variations in the cumulative mass of leached colloids vs. square root of time relationship (Figure 20) revealed that several interacting properties affected colloid mobilization. The results presented in this study lead to the following interpretation of the processes controlling colloid mobilization: (i) At 12% clay (IMP -2.5 and -100 hPa), displacement of high-ionic strength resident water with low-ionic strength rainwater gradually increases the repulsive forces among colloids as leaching approaches one pore volume. After about one pore volume of leaching all resident water has been displaced and colloid mobilization is clearly time-dependent, probably controlled by dispersion, as continued leaching of low-ionic strength water gradually increases colloid dispersion and the leaching of colloids (Figure 18). The steeper slopes of the IMP -100 hPa curves (Figure 20) indicates that

these soils were initially more dispersed compared to the IMP -2.5 hPa curves, as discussed earlier. At IMP -15,500 hPa the flat curves indicate that colloid dispersion is impeded by the strong cohesive forces resulting from the drying, (ii) at 18% clay (IMP -2.5 and -100 hPa) the curves of electric conductivity and accumulated colloid mass indicate that the rate of colloid mobilization is limited by diffusive exchange of low-ionic strength irrigation water with the high ionic-strength intraaggregate water. As irrigation continues diffusive exchange of high-ionic strength intraaggregate water with low ionic-strength rainwater leads to a gradual increase in colloid leaching. The steeper slope of the IMP -100 hPa curves, having lower initial ionic strength conditions, supports these considerations. As with 12% clay the flat curves at IMP -15,500 hPa indicate that colloid dispersion is impeded by the strong cohesive forces resulting from the drying. At higher clay content, illustrated by the 28% clay soil, colloid mobilization may be limited by dispersion partly as a consequence of the low diffusive exchange of low-ionic strength irrigation water with the high ionic-strength intraaggregate water, and partly by the reduced dispersibility due to a very high volume of clay particles increasing the cohesive bonding of colloids in the aggregate (IMP -2.5 and -100 hPa) and stronger colloid associations upon drying (-15,500 hPa).

In contrast to colloid mobilization, the accumulated leaching of DOC was independent of both clay content and initial matric potential at IMP -2.5 hPa and -100 hPa (Figure 21). The reason for this could not be deduced from this study, but it may be attributed to the localization of the microbial community close to the mobile water regions which would eliminate the differences in diffusion pathways among the soils.

The interpretation of the role of preferential flow in this study may also explain the generally observed colloid leaching behavior from structured soils with high initial concentrations declining to constant low levels (e.g. Jacobsen *et al.*, 1997; Ryan *et al.*, 1998; Schelde *et al.*, 2002). In these studies preferential flow was promoted by zero-tension lower boundaries and high irrigation intensities increasing the degree of preferential flow and reducing the lateral mixing of infiltrating water. This may consequently result in the macropores as the primary source of mobile colloids and lead to a rapid depletion in effluent colloid concentration followed by a slow but continuous release of intraaggregate colloids as the intraaggregate water is slowly displaced with infiltrating water, and the colloids diffuse to the convective flow pathways. Additionally, it is important to realize that the effect of flow rate cannot be directly related to the interpretation of the mechanisms of colloid mobilization, as changing the flow rate in structured soils may also change the actively conducting flow pathways and thereby the contact source area of colloids. This also implies that knowledge of processes controlling colloid mobilization in systems with packed aggregates cannot be directly applied when interpreting processes controlling colloid mobilization in natural structured soils.

5.4 Concluding remarks

The results from this experimental study have revealed the complexity in the process of colloid mobilization in unsaturated structured soils.

- Accumulated colloid leaching:
 - Decreased with increasing clay content to a minimum leaching at $\geq 24\%$ clay from the initially wet (IMP -2.5 hPa) and moderate wet (IMP -100 hPa) soils as a consequence of increased colloid cohesion resulting from the higher volume of clay.
 - Was larger from the initially moderate wet compared to the wet soils due to the initially lower ionic strength following the extra drainage.
 - Was low and independent of clay content from the initially dry soils (IMP $-15,500$ hPa) as a consequence of stronger particle associations upon drying.
 - Initial matric potential affected only colloid leaching from the lower clay soils (12 and 18% clay). This may be a consequence of low fraction of pores >30 μm minimizing the effect of drainage, or the possible role of diffusion-limited transfer of colloids.
- Accumulated carbon leaching:
 - Consisted mainly of DOC and was independent of clay content.
 - Increased after pre-drying to $-15,500$ hPa, probably due to microbial death and lysis of microbial cells.
- Colloid mobilization seemed to be limited by colloid dispersion due to either:
 - The time-dependent increase in repulsive forces due to continued infiltration of low-ionic strength rainwater (IMP -2.5 and -100 hPa at 12 and 18% clay).
 - Low diffusive exchange of high-ionic strength resident water with low-ionic strength rainwater
 - A combination of low diffusive exchange of high-ionic strength resident water with low-ionic strength rainwater and increasing colloid cohesive forces induced by either a high volume of clay ($\geq 24\%$ clay) or stronger particle associations upon drying (IMP $-15,500$ hPa for all soils).
- Diffusion limited transport of colloids:
 - At higher clay contents it was not possible to single out the importance of diffusion-limited exchange of resident water with rainwater, nor the eventually diffusion-limited transfer of colloids from the immobile to the mobile water regions, since the stronger cohesive forces already impeded the dispersion of colloids.
 - Based on the results from this study, preferential flow may be expected to impede *in situ* colloid mobilization from aggregates due to either dispersion-limited diffusive exchange of high ionic strength resident water with low-ionic strength rainwater, or diffusion-limited transfer of colloids from immobile intraaggregate water to mobile interaggregate water.

- Practical and environmental implications:
 - Colloid dispersibility should be considered a key parameter when developing predictive models for *in situ* colloid mobilization in the vadose zone.
 - The largest accumulated leaching of colloids observed in the 12% clay soil exhibiting matrix dominated flow behavior, documented that even though filtering of colloids may increase during matrix flow, quantitative significant colloid leaching is certainly not restricted to preferential transport in macropores.

6. CONCLUSIONS

The occurrence of strongly sorbing environmental contaminants in groundwater and the ability of mobile soil colloids to facilitate the transport of strongly sorbing contaminants have created a demand to understand the processes involved in controlling colloid mobilization and transport in the vadose zone, and predict the quantitative importance of this phenomenon. Most of our basic understanding of colloid science arises from simplified model systems of packed sediment or soil columns neglecting the paramount influence of soil structure and structure dynamics on colloid association, mobilization and transport. This study was intended to improve our knowledge concerning the processes controlling colloid mobilization and transport in natural structured soils.

From the study of a natural clay gradient having similar mineralogy and management history, total clay content and initial soil matric potential were key properties in controlling colloid mobilization and transport in structured soils. Soil clay content determined the inherent soil dispersibility, with a decrease in the amount of WDC as the clay content increased as a consequence of increased colloid cohesion in aggregates. In addition soil clay content affected the dynamics of the actively conducting flow system, as a result of the influence of clay on the pore-size distribution and the shrinkage-swelling properties. Initial matric potential affected the initial state of colloid cohesion, with a decrease in the amount of WDC as the water content was reduced in the period prior to infiltration as a consequence of increased colloid cohesion upon drainage and drying. The main part of the decrease in dispersibility occurred during or immediately after adjustment of the moisture status, but dispersibility slowly continued to decrease with time, and the effect of decreasing initial matric potential persisted at least a week after complete rewetting. Additionally, initial matric potential also affected the actively conducting flow system as a result of shrinkage and swelling following drying and rewetting, resulting in closing of the largest pores and decreased degree of preferential flow.

The actual leaching of colloids decreased with increasing clay content and was consequently well predicted from the estimates of low-energy dispersible colloids. In addition estimates of LE-WDC also predicted reduced colloid leaching that was independent of clay content after drying to $-15,500$ hPa. The larger colloid leaching at moderate wet (-100 hPa) compared to wet (-2.5 hPa) initial conditions was caused by the lower initial ionic strength conditions resulting from the extra drainage at -100 hPa. This highlights the major influence of ionic strength conditions in controlling colloid dispersibility. Based on the results from this study colloid dispersibility should be considered as a key parameter, when developing predictive models for *in situ* colloid mobilization in the vadose zone. This also highlights the importance in choosing estimates of WDC that resembles the relevant conditions. Based on the results from this study it is concluded that a low-energy input in the dispersion procedure more accurately predict the pool of potentially mobile colloids following low or average intensity precipitation events, while the use of classical WDC estimates would have lead to wrong conclusions.

It was hypothesized that two properties controlling colloid mobilization in natural structured soils were the ability of colloids to disperse in response to infiltration of low-ionic strength rainwater and the degree of preferential flow. These properties turned out to be key properties with respect to interpreting the complex processes of colloid mobilization and transport. Colloid mobilization seemed to be limited by colloid dispersion due to either: (i) the time-dependent increase in repulsive forces due to continued infiltration of low-ionic strength rainwater (IMP -2.5 and -100 hPa at 12 and 18% clay), (ii) low diffusive exchange of high-ionic strength resident water with low-ionic strength rainwater (IMP -2.5 and -100 hPa at 18% clay), and (iii) a combination of low diffusive exchange of high-ionic strength resident water with low-ionic strength rainwater, and increasing colloid cohesive forces induced by either a high volume of clay ($\geq 24\%$ clay) or stronger particle associations upon drying (IMP $-15,500$ hPa). At higher clay content it was not possible to single out the importance of diffusion-limited exchange of high-ionic strength resident water with low-ionic strength rainwater, nor the eventually diffusion-limited transfer of colloids from the immobile to the mobile water regions, since the stronger cohesive forces already impeded the dispersion of colloids. Based on the results from this study, preferential flow may be expected to impede *in situ* colloid mobilization from aggregates due to either dispersion-limited diffusive exchange of resident water with rainwater, or diffusion-limited transfer of colloids from immobile intraaggregate water to mobile interaggregate water.

Investigating the stability properties of natural high-energy dispersible colloids separated from bulk horizons and macropore deposits of a typical Danish clayey soil documented that colloid associated organic matter increased the suspension stability of natural WDC. The contribution of OC to the colloidal stability was inferred from: (i) a higher negative ζ -potential and larger suspension stability from WDC with larger content of OC, and (ii) increased N_2 -adsorption surface area, reduced negative ζ -potential as well as reduced suspension stability after OC removal. The ζ -potential and stability behavior of natural WDC were strongly dependent on solution EC ($CaCl_2$ concentration), while solution pH had less effect with significant flocculation only below pH 4.5. A two-fold increase of the initial particle diameter occurred at an EC of $91 \mu S cm^{-1}$ for the least stable colloids, and $1023 \mu S cm^{-1}$ for the most stable and OC-enriched colloids, suggesting that only the most stable OC-enriched colloids will remain stable under the ionic strength conditions observed in the out-flow water of the Lerbjerg columns. This additionally calls attention to the high-energy dispersion procedure in separating some colloidal fractions that may not resemble the actual mobile and leachable colloids under field conditions.

7. PERSPECTIVES

The awareness of the impact of industrial activity and agricultural production on the ground- and drinking water quality has increased the focus on contaminant behavior in the vadose zone. The majority of the contaminant sources are located at or within the topsoil, requiring transport through the vadose zone in order for the contaminants to cause ground- or drinking water pollution. Special attention has been directed towards quantifying the impact of preferential flow phenomena on contaminant transport. In addition the possible risk of leaching of strongly sorbing contaminants by colloid-facilitated transport has gained increasing attention. The ability of mobile colloids to facilitate the transport of strongly sorbing contaminants is widely documented, however, we still face some important questions: “*Is colloid-facilitated transport of contaminants environmentally significant?*”, “*Should the process of colloid-facilitated transport be implemented in risk assessment, concerning ground- and drinking water pollution?*”, “*Where and when do we expect this phenomenon to occur?*”, “*What key properties and processes should be used in predictive modeling of colloid-facilitated transport in natural structured soils?*”

In order to answer these questions improved understanding of the processes controlling *in situ* colloid mobilization and transport in natural structured soils is required. To date surprisingly little attention has been directed towards understanding the influence of soil structure and structure stability on *in situ* mobilization and transport of colloids. This concerns the associations of colloids in aggregates, colloid dispersion from aggregates, and the profound effect of pore structure and pore structure dynamics on the active flow pathways of water affecting both *in situ* colloid mobilization and transport. This thesis has contributed to an improved understanding on these aspects, however, further process understanding within this area should be considered as primary aims in future research.

This study suggests that measurements of low-energy water-dispersible colloids can be used as an easily accessible index defining the pool of potentially and easily mobile colloids in predictive field models. From this study, using a natural clay gradient having similar mineralogy and management history, soil clay content turned out as a key parameter controlling the amount of low-energy dispersible and mobile colloids. However, further research is needed in order to differentiate the relative effects of clay content and other important inherent and dynamic soil properties such as clay mineralogy, soil chemistry, soil management and tillage on low-energy dispersible colloids. Initial soil water content was shown to strongly affect colloid mobilization. Even though this was not surprising it appears that the influence of soil-water on colloid dispersibility has not drawn the deserved attention in the research field of colloid mobilization and transport. This study clearly suggests that the effect of initial matric potential should be implemented in predictive field models, while the time dynamics and reversibility in colloid dispersion should be explored further. In this study wetting rate turned out to be of minor importance. The effect of wetting rate on colloid release, however, may be more important in other mineralogical systems. The effect of raindrop kinetic

impact has gained much attention in erosive modeling, since the splash effect of raindrop impact has resulted in movement of relatively large amounts of soil. The quantitative effect of raindrop impact on the release of stable elementary colloids that are capable of being transported through the vadose zone, however, remains to be elucidated.

The source and composition of stable colloids have implications for the role of colloids in facilitating contaminant transport. When predicting colloid deposition rates it is important to consider the surface properties of the natural soil colloids, since prediction of colloid deposition based on colloid mineralogy alone may lead to under-estimation of the actual amount of colloid transport. In addition the surface properties of the potentially mobile colloids determine the sorption affinity for contaminants and future investigation should consider the type of environmental contaminants that could be relevant depending on the surface properties of natural soil colloids. The present study suggests that future characterizations of potentially mobile colloidal fractions should be done on fractions of low-energy dispersible colloids.

Colloid dispersion and preferential flow are key properties when interpreting the complex processes of *in situ* colloid mobilization and transport. From this study it was, however, difficult to single out the importance of preferential flow on colloid mobilization. Continuation of this study should focus on clarifying the role of preferential flow. By focusing on one soil type colloid leaching should be investigated with increasing degree of preferential flow. This can be accomplished by decreasing the suction towards saturation or by steadily increasing the irrigation intensities. Understanding colloid mobilization and transport in structured soils requires an understanding of the link between soil structure and water flow including the diffusional transfer of both water and colloids across the interface between intraaggregate immobile water and mobile water. There is consequently a need for more data on contact areas and exchange rates between mobile and immobile water during preferential flow in structured soils.

The modeling of colloid mobilization was beyond the scope of this investigation, and the results obtained in the present study indicate that modeling *in situ* colloid mobilization and transport in structured soils is very complex. Further investigations improving our understanding of colloid mobilization and transport should also lead towards estimation of relevant parameters with respect to predicting release rates and filtering coefficients etc. This study has strongly indicated that measurements of WDC made under the relevant experimental conditions may be a good approximation for the fraction of potentially mobile colloids. However, we strongly need more basic understanding of water flow and *in situ* mobilization and transport of colloids in unsaturated structured soils to improve predictions of field scale colloid leaching.

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Supporting papers

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**Water-dispersible colloids: Effects of measurement method, clay content, initial soil
matric potential and wetting rate**

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Water-dispersible colloids: Effects of measurement method, clay content, initial soil matric potential and wetting rate

ABSTRACT

The fraction of clay that disperses in water (water-dispersible clay - WDC) is recognized as an important property with respect to predicting soil erosion and colloid leaching. This study determined the influence of soil clay content (using six mineralogically similar soils with 12, 18, 24, 28, 37 and 43% clay), initial matric potential (IMP) $\psi = -2.5, -100$ and $-15,500$ hPa, and wetting rate on WDC released in response to infiltration of low-ionic strength rainwater, using a low-energy input measurement of WDC (LE-WDC). These results were referenced by WDC obtained by a conventional, high-energy input measurement based on air-dried soil (HE-WDC). The energy input in the dispersion procedure significantly affected the release of WDC. The amount of HE-WDC increased with clay content, while the amount of LE-WDC decreased with increasing clay content. The decrease in LE-WDC was explained by an increase in cohesive strength, reflected by the increase in water-stable aggregates (≥ 4 mm). A strong dependency of IMP on LE-WDC was observed, with maximum release of LE-WDC from soils that were at -2.5 hPa prior to measurement. Decreasing soil matric potential in the period prior to measurement reduced LE-WDC and also reduced the dependency of soil clay content, with soils incubated at $-15,500$ hPa releasing a low amount of LE-WDC independent of clay content. The content of particulate organic carbon (POC) in the LE-WDC decreased with increasing clay content, and increased after drying to $-15,500$ hPa. Colloid dispersibility changed as a function of time and moisture status with the main changes occurring during or immediately after adjustment of the moisture content. Increasing the wetting rate resulted in a doubling in the amount of LE-WDC released from the initially dry soil ($-15,500$ hPa), while no effect of wetting rate was observed at higher initial matric potentials.

List of abbreviations:

CEC: Cation exchange capacity; DOC: Dissolved organic carbon; EC: Electrical conductivity; HE-WDC: High-energy water-dispersible colloids; IMP: Initial matric potential; LE-WDC: Low-energy water-dispersible colloids; POC: Particulate organic carbon; SAR: Sodium adsorption ratio; TOC: Total organic carbon; WDC: Water-dispersible colloids; WSA: Water-stable aggregates.

INTRODUCTION

The ability of mobile soil colloids to facilitate the transport of strongly sorbing contaminants in structured soils has been widely documented (e.g. Seta and Karathanasis, 1997; de Jonge et al., 1998, 2000; Laubel et al., 1999; Karathanasis, 1999; Sprague et al., 2000; Villholth et al., 2000; Petersen et al., 2003). Despite the potential importance of this phenomenon, the available information about the intrinsic and dynamic soil properties that control colloid mobilization in structured soils is at present insufficient to predict the risk of colloid leaching. When investigating colloid mobilization in structured soils, two important issues should be considered: (i) the inherent ability of colloids to disperse from aggregates in response to infiltration of low-ionic strength rainwater, and (ii) the profound effect of pore structure on the active flow volume of the infiltrating water, affecting both *in situ* colloid mobilization and the subsequent transport of mobilized colloids.

In general, the main fraction of soil colloids is associated in aggregates as a result of the cohesive nature of colloids (Oades and Waters, 1991; Oades, 1993), and released following disintegration of aggregates. Le Bissonnais (1996) summarized four main mechanisms for disintegration of aggregates: (i) slaking, which is disintegration caused by the compression of entrapped air during wetting, (ii) differential swelling, (iii) mechanical breakdown by raindrop impact and (iv) physicochemical dispersion. These processes differ in the intensity of disintegration and the size of the resulting fragments. Disintegration of aggregates by slaking and swelling results in breakdown of larger aggregates into minor units, which consequently increases the surface area and exposes new surfaces, which may ultimately increase colloid dispersion. Dispersion is the ultimate state of breakdown that results in release of clay particles as a consequence of expanding electrical double layers and dominating repulsive forces as described by the DLVO theory (Derjaguin and Landau, 1948; Verwey and Overbeek, 1948). It

is generally recognized that the fraction of clay that disperses in water (water-dispersible colloids, WDC) has been found to have statistically significant relationships with soil erodibility (Miller and Baharuddin, 1986; Shainberg et al., 1992). The soil WDC fraction has been used as input parameter for predicting soil erosion (Brubaker et al., 1992), colloid leaching and colloid-facilitated transport through the vadose zone (Jarvis et al., 1999; Villholth et al., 2000).

The predominant effect of clay mineralogy (e.g. Frenkel et al., 1978; Goldberg et al., 1988; Seta and Karathanasis, 1996), solution ionic strength and pH (e.g. Rengasamy, 1983, Rengasamy et al., 1984; Grolimund and Borkovec, 1999; Flury et al., 2002) on colloid dispersion has been documented from several studies. In natural field soils, the effect of mineralogy and solution ionic strength may, however, be influenced by the presence of surface adsorbed organic carbon which may mask the direct importance of clay mineralogy, or promote increased aggregate stability by increasing the bonding strength of aggregates or reducing the wettability and consequently the slaking potential of aggregates. From regression analysis comparing a range of soil factors, several studies have identified total clay content as one of the most important properties in determining the amount of WDC (Pojasok and Kay, 1990; Brubaker et al., 1992; Rasiah et al., 1992; Levy et al., 1993; Curtin et al., 1994). In addition, the matric potential of aggregates prior to measurement (e.g. Pojasok and Kay, 1990; Rasiah et al., 1992; Brubaker et al., 1992), and management in terms of crop sequence, application of organic manures, soil tillage, and field traffic (e.g. Watts et al., 1996ab; Watts and Dexter, 1997, Schjønning et al., 2002) have been shown to significantly affect dispersibility of clay in soil structural elements.

Different properties may influence WDC in different soil types, but comparison among data is complicated by the numerous methods that have been used to determine WDC. Studies have shown that values of aggregate stability and WDC depend on sample pretreatment, initial moisture content, length of time aggregates were allowed to wet up and equilibrate, and the length of the shaking period (e.g. Pojasok and Kay, 1990; Kay and Dexter, 1990). Generally, most studies have used air-dry soil for measurements of WDC. Air-drying is meant to standardize initial conditions. However, air-drying may introduce changes in chemical or physical characteristics that can alter stability (Alderfer, 1946; Reid and Goss, 1981). These changes are further augmented due to swelling or slaking when re-wetting the samples (Panabokke and Quirk, 1957). Based on these observations, Pojasok and Kay (1990) recommended that soil stability and dispersible clay should be measured using field-moist soils.

WDC can be measured for different purposes, one of which is to yield an estimate of the fraction of potentially mobile colloids released during the infiltration of low-ionic strength rainwater through the soil. Clay may become mechanically dispersed at the soil surface layer by erosive raindrop impact. However, determinations of WDC with low energy inputs are probably more indicative of *in situ* colloid mobilization from the upper soil horizon, especially when the soil surface is protected from raindrop kinetic energy by vegetation cover. Although the most frequently applied dispersion methods involve sieved, air-dried soil and application of mechanical energy, we see a need for modified methodologies that better simulate the potential amount of WDC released from soil aggregates with different initial moisture conditions prior to a rain event. This paper is concerned with the process of colloid dispersion with the objective of (i) evaluating the results from a low-energy input measurement of WDC against a conventional, high-energy input measurement based on air-dry soil, and (ii) using the low-

energy input WDC measurement to determine the influence of soil clay content, initial soil matric potential and wetting rate on colloid dispersion following infiltration of low-ionic strength rainwater. The soils used in these studies were collected from six locations along a naturally occurring clay gradient from an arable field (Lerbjerg, Denmark) with clay contents ranging from 12 to 43%. The use of soil with similar mineralogy and management history allows examination of the interacting effects of soil clay content and initial soil matric potential on colloid dispersion.

MATERIALS AND METHODS

Field site and soil characteristics

Soil samples were collected in the early spring 2000 from 1 m² areas and 10-18 cm depth, at six sites along a naturally occurring clay gradient (Fig. 1) of an arable field, Lerbjerg, Denmark (56°22'N, 9°59'E). The soil is developed on push morainic deposits from the Weichselian Glacial Age, and the site has been under conventionally tilled winter wheat for several years. The mineralogy of the site was found typical for intermediately weathered, well-drained soils under cold climate conditions (Schjønning et al., 1999). Primary minerals quartz, micas and feldspars dominated the sand and silt fractions, while the clay fraction was dominated by secondary minerals illite (20-30%), smectite - predominantly montmorillonite (10-30%), and vermiculite (10-20%).

To avoid disturbing the soil structure, samples were carefully excavated as intact cubes (650 cm³) and placed in plastic boxes with pieces of polystyrene placed above and below to support the soil (see Fig. 1 of Schjønning et al., 2002). The intact soil cubes were stored at 2°C field-moist conditions (water content close to field-capacity ~ -100 hPa). A part of the soil samples was air-dried, sieved at 2-mm and used for analysis of soil properties (Table 1). Soil texture

was determined using a combination of wet-sieving and the hydrometer method. Total C was determined on a LECO Carbon Analyzer coupled to an infrared CO₂ detector. Soil pH was determined in 0.01 M CaCl₂ with a 1:2.5 (w:w) soil:electrolyte suspension. The content of calcite was measured gas-volumetrically. Exchangeable cations and cation exchange capacity (CEC) on these soils was determined by Schjønning et al. (1999) as the NH₄⁺-equivalents found in the leachate following saturation with NH₄⁺ (NH₄OAc, pH 7) (Kalra and Maynard, 1991). Sodium-adsorption ratio (SAR) were calculated from the concentrations of Ca²⁺, Mg²⁺ and Na⁺ in the leachate.

Water-dispersible colloids

Water-dispersible colloids (WDC) were measured by applying either a high- or a low-energy input in the dispersion procedure. The high-energy input WDC (HE-WDC) measurement resembled the conventionally used procedures for estimating dispersible colloids based on air-dry soil and mechanical shaking of the soil:water suspension. Pretreatment of the six soil types prior to measurement involved air-drying and sieving bulk soil samples at 2 mm. The dispersion procedure involved direct immersion of the soil samples in an electrolyte solution, having a chemical composition identical to natural rain-water (electrical conductivity (EC) 0.025 mS cm⁻¹ and sodium adsorption ratio (SAR) 0.736), and mechanical shaking at a 1:8 (w/w) soil:water ratio for 16 hours on a reciprocal shaker at 29 rpm and 0.5 m diameter rotation. After mechanical dispersion the ≤2-μm fraction was separated by siphoning off the upper suspension in one-step gravity sedimentation. The amount of HE-WDC in the retrieved suspension was measured as mass dry weight. Measurements of HE-WDC were carried out in triplicate.

The pretreatment procedures of the six soil types subjected to low-energy input dispersion measurements are illustrated in Figure 2. The pretreatment included: (a) saturation by capillary wetting and drainage to three initial soil matric potentials $\psi = -2.5, -100$ and $-15,500$ hPa, which covered the moisture conditions from near saturation to the crop wilting point, and (b) re-saturation with either slow wetting with controlled tension over seven days or fast wetting within four hours. The experiments were carried out using three replicates of each combination, giving a total of 108 samples. The pretreatment involved the following procedure: (i) Field-moist soil, with known soil-water content, was passed through an 8-mm sieve and packed in 100-cm^3 steel cylinders at a bulk density of 1.1 Mg m^{-3} . Care was taken not to press the soil through the sieve. Aggregates were separated by hand at the planes of weakness until they obtained a size that allowed them to pass the sieve. The packed samples were sealed at the bottom with a $0.45\text{-}\mu\text{m}$ nylon disc filter. (ii) Initially the packed soils were saturated with electrolyte solution by slow capillary wetting on tension tables with a slowly increasing potential from -100 to 0 hPa during six days, and finally allowed to equilibrate for 48 hours. (iii) After initial saturation, one third of the samples were drained to -2.5 hPa and two third were drained to -100 hPa on tension tables, and allowed to equilibrate for one week. Half of the samples drained to -100 hPa were subsequently dried by passing through dry air until the samples reached a gravimetric water content corresponding to a soil matric potential at $-15,500$ hPa. The water content of $-15,500$ hPa was estimated using water retention data from Schjønning et al. (1999). (iv) After drainage all samples were weighed, sealed and allowed to equilibrate for 14 days at 10°C . Water loss at -2.5 hPa was prevented by incubating the samples in containers with a water saturated atmosphere, and water gain at $-15,500$ hPa was prevented by incubating the samples in containers with silica gel. (v) After the 14 days incubation period the samples were re-weighed. Water loss or gain was found to be insignificant. The packed soil samples were then placed on tension tables and re-saturated with

electrolyte solution. Samples incubated at -2.5 hPa were initially drained to -100 hPa and subsequently saturated. This procedure was done in order to have identical treatments with respect to changes in electrolyte composition for all samples. Half of the treatments were saturated by slow capillary wetting from an initial soil matric potential at -100 hPa with slowly increasing potential over seven days, and the other half by fast capillary wetting within four hours. The volume change after slow and fast wetting was measured with a specially constructed caliper. (vi) Immediately after the re-saturation, the samples were transferred quantitatively to 1-L polyethylene sedimentation bottles with electrolyte solution and further electrolyte solution was added to reach a final soil:water ratio of 1:8. The dispersion procedure for the low-energy input WDC (LE-WDC) measurement involved turning the soil suspension upside down manually ten times. Also in this case, the colloid fraction ($\leq 2\text{-}\mu\text{m}$) was separated by one-step gravity sedimentation. The amount of LE-WDC after one-step gravity sedimentation was measured as mass dry weight. Stock suspensions from each soil were used for making turbidity calibration curves for determination of colloid concentration in later experiments. Fractions of LE-WDC released after slow re-wetting (Fig. 2) were used for the following experimental investigations: (i) comparison of HE-WDC with LE-WDC, (ii) evaluating the effect of initial matric potential, (iii) investigating the time dependency of colloid dispersion, and finally (iv) for investigating the effect of wetting rate by comparing with fractions of LE-WDC released after fast re-wetting.

Characterization of colloid suspensions

LE-WDC suspensions were characterized for total organic carbon (TOC), particulate organic carbon (POC), and dissolved organic carbon (DOC). TOC was measured by carbon combustion using a Total Organic Carbon Analyzer (TOC-5000A, Shimadzu) equipped with a suspended particle kit and coupled to an auto sampler with magnetic stirring. DOC was

determined on colloid suspensions after centrifuging for one hour at 4180 g, yielding a size separation at ~50 nm assuming spherical particles with 2.63 g cm⁻³ density. This separates the fraction of organic matter bound to the mineral fraction (mineral bound POC) from the DOC. POC is given as POC = TOC – DOC. The results were used for calculating the POC:LE-WDC ratio.

Dispersion kinetics

The time dependency of colloid dispersion was investigated using the same experimental setup as described for the low-energy input dispersion measurement. LE-WDC was measured at 11.5% clay with three initial soil matric potentials $\psi = -2.5, -100$ and $-15,500$ hPa and five time periods 0, 12, 26, 72 and 145 hours. Initially all samples were saturated with electrolyte solution by slow capillary infiltration on tension tables and allowed to equilibrate for 48 hours. After initial saturation, one third of the samples were drained to -2.5 hPa and two thirds were drained during 24 hours to -100 hPa on tension tables. Half of the samples drained to -100 hPa were subsequently dried by passing through dry air for six hours until the samples reached a gravimetric water content corresponding to a soil matric potential of -15,500 hPa. Immediately after reaching the desired soil matric potentials LE-WDC was measured at time 0. The rest of the samples were capped and stored at 2°C, and samples were taken for LE-WDC measurements after 12, 26, 72 and 145 hours.

Wet aggregate stability

Approximately 50 g of field-moist soil was taken from three intact soil cubes for determination of water-stable aggregates (WSA) by methods as described by Pojasok and Kay (1990). The soil was gently passed through an 8 mm sieve. A subsample of 10 g was used for determining water-content, and 30 g were taken to a 4 mm sieve installed in a wet-sieving apparatus

(Yoder, 1936). Thirty seconds of initial capillary wetting were followed by 2 min of vertical movement of the sieve (stroke length 32 mm, 38 strokes min^{-1}). The water used for the wet-sieving procedure was identical to the electrolyte solution used for the HE-WDC and LE-WDC measurements. Stable aggregates remaining on the sieves (≥ 0.250 mm and ≥ 4 mm) were transferred quantitatively to a beaker, water was evaporated at 80°C and the soil further dried at 105°C followed by weighing. Finally the soil was dispersed by end-over-end shaking for 24 hours with a 0.002 M $\text{Na}_4\text{P}_2\text{O}_7$ solution, and poured through the 0.250 mm and 4 mm sieves. Primary particles ≥ 0.250 mm and ≥ 4 mm were weighed following drying at 105°C. Results are given as percentage of water-stable aggregates.

RESULTS AND DISCUSSION

Caveats in interpreting water-dispersible colloids

The quantification of dispersible clay in this study was based on suspensions derived from one-step gravity sedimentation. This inevitably will underestimate the clay dispersed from the sample. A total recovery of dispersed clay would require repeated sedimentations. This would, however, induce extra dispersion of clay. Christensen (1985) examined the relative amount of dispersed clay retrieved by repeated sedimentations for a sandy loam soil. For that soil, it appeared that approximately 86% of total clay in suspension was retrieved in the first sedimentation. This deviation from full recovery will depend on soil type due to differences among soils in the particle size distribution of clay particles. Hence, in the present study we obviously did not recover all dispersed clay and we also anticipate some difference in the degree of recovery among the six soils. However, we consider this error not to compromise the issues addressed.

The fact that all six soil types were sampled along a texture gradient within one single field is important in ruling out management-induced differences in clay dispersibility. Several investigations have shown that management may affect clay dispersibility (e.g. Watts et al., 1996ab, Watts and Dexter, 1997). As the six soils used for this study have experienced the same management in all respects, we consider them similar for the study. We cannot exclude some difference in the energy the soils have received during tillage, the soils holding more clay being cloddier and less friable than the less clayey soils. This would be expected also to influence clay dispersibility (Watts et al., 1996a, Schjønning et al. 2002). However, such effects would still be minor compared to soils sampled at different locations.

High- versus low-energy input dispersible colloids

Mechanically dispersible colloids obtained by the classical, HE-WDC procedure increased with increasing clay content from 1458 mg kg⁻¹ at 11.5% clay to 5989 mg kg⁻¹ at 28% clay, followed by an in-significant increase to 6283 mg kg⁻¹ at 43% clay (Fig. 3a). The positive correlation between HE-WDC and total clay agrees with observations from other studies having different pretreatments, but all applying mechanical shaking in the measuring procedure (Table 2). The application of mechanical energy breaks down the aggregates and thereby increases the surface area. As a consequence, more clay is dispersed as the soil content of clay increases. The maximum HE-WDC at 28% clay could be explained by (i) the samples with 37 and 43% clay also containing small amounts of calcite (1 to 1.7%), which may reduce the dispersibility of the soil, (ii) more energy is probably required to break down aggregates when the clay content increases, and (iii) even though aggregates do break down at first, the volume of clay is so large that shaking without any dispersion agent probably results in the production of new flocs. Other studies have found both linear correlations (Brubaker et al., 1992) and logarithmic relations (Levy et al., 1993) between WDC and total clay, and these

inconsistencies may be a possible consequence of differences in the input of mechanical energy in the dispersion procedure (Table 2).

The employment of a low-energy input in the dispersion procedure displayed an opposite trend of a decreasing amount of LE-WDC with increasing clay content (Fig. 3b). These results also revealed a strong dependency of initial soil matric potential, and an interactive effect between clay content and initial soil matric potential on LE-WDC. For soils incubated at high water content (-2.5 hPa), LE-WDC decreased from 3174 mg kg⁻¹ at 11.5% clay to 1247 mg kg⁻¹ at 43% clay. The same pattern was observed for soils incubated at intermediate water content (-100 hPa), but the amount of LE-WDC was reduced with LE-WDC decreasing from 1974 mg kg⁻¹ at 11.5% clay to 1025 mg kg⁻¹ at 43% clay. The L4 soil (28% clay) in both cases showed a considerably lower dispersibility compared to the other clay-rich soils. The reason for this lower dispersibility is not clear, but it could be due to differences among soils in the content of strongly bonding agents such as sesquioxides. Soils incubated at very low water content (-15,500 hPa) released a small amount of LE-WDC, about 450 to 500 mg kg⁻¹, which was independent of clay content.

The decrease in LE-WDC with increasing clay content can be explained by a combination of two interrelated properties: (i) increasing cohesive strength between clay particles due to the larger number of clay particles increasing the area of contact, and (ii) a higher ionic strength in the pore-water of aggregates from the higher clay soils, as indicated by the increase in CEC with increasing clay content (Table 1). In addition, it is also evidenced from the ratio of POC to LE-WDC (Table 3) that the composition of the colloid fraction differs, with a decrease in the content of POC as the clay content increases. This is probably a consequence of the lower TOC:clay ratio with increasing clay content (Table 1) and may indicate that organic carbon

associated with mineral colloids may increase the dispersibility of colloids. The influence of organic matter on aggregate stability and clay dispersion has been the subject of much discussion, since it has been found that organic matter may promote both aggregation and dispersion (e.g. Shanmuganathan and Oades, 1983; Durgin and Chaney, 1984; Barzegar et al., 1997). The stabilizing effect of soil organic matter has been attributed to the role that roots and hyphae have in stabilizing macroaggregates, thereby preventing clay dispersion. When these bonds are broken by aggregate disruption, the dispersive effects of organic matter may predominate (e.g. Goldberg et al., 1990; Nelson et al., 1998).

The increase in the amount of water-stable aggregates (WSA) with increasing clay content clearly indicates that the decrease in LE-WDC is related to an increase in aggregate stability (Fig. 4). Two size fractions of WSA (≥ 0.250 mm and ≥ 4 mm) are correlated with the clay content. The fraction ≥ 0.250 mm represents the traditionally used size discrimination between micro- and macro-aggregates (Tisdall and Oades, 1982), and the fraction ≥ 4 mm was chosen based on experiences from preliminary investigations. The fraction of WSA ≥ 0.250 mm showed a significant positive correlation ($R^2=0.827^*$) between the percentage of WSA and clay content, with the soil mass increasing from 51% at 11.5% clay to 74% at 43% clay. Using the fraction of WSA ≥ 4 mm significantly improved the correlation ($R^2=0.989^{***}$) between the percentage of WSA and clay content, with a soil mass ranging from 26% at 11.5% clay to 61% at 43% clay. This demonstrated that the increase in clay content from 11.5 to 43% resulted in a minor increase in the total percentage of stable macro-aggregates ≥ 0.250 mm, while the increase in aggregate stability with increasing clay content is mainly explained by the fraction of very large water-stable aggregates (≥ 4 mm). The positive correlation between clay content and WSA has been reported in several studies (e.g. Kemper et al., 1987; Pojasok and Kay, 1990). It may be speculated that estimates of WSA could be used to predict WDC. However,

the results from this study showed that a poor correlation existed between LE-WDC and WSA (Fig. 5). At lower clay content (<25%), the amount of LE-WDC increased as WSA decreased, while at higher clay content ($\geq 28\%$), no correlation existed between LE-WDC and WSA. WSA continued to increase with increasing clay content, while LE-WDC maintained a constant minimum value. Generally, attempts to use aggregate stability to predict soil susceptibility to erosion has had limited success due to conflicting results (Amezqueta et al., 1996). The differences in HE-WDC and LE-WDC displayed from this study agrees with the conclusions from Kay and Dexter (1990), documenting that the amount of mechanically dispersed clay increased with increasing aggregate size, while the amount of spontaneously dispersed clay increased with increasing surface area, which required initial aggregate breakdown. This highlights the importance in the choice of dispersion procedure, especially the input of energy. When using estimates of WDC as input parameter for modeling colloid mobilization and transport, one should be aware of the coherence between energy input and the result of the WDC measurement. The application of mechanical energy by the shaking procedure may resemble “worst case” scenarios, where storm flow events or soil tillage increases dispersion by breaking down aggregates, while the use of low-energy input dispersion measurements may resemble the *in situ* release of colloids from the upper horizons during average precipitation events.

Effect of initial soil matric potential on LE-WDC

Two properties should be considered when interpreting the decrease in the amount of LE-WDC resulting from the decrease in soil-water content following drainage and drying: (i) the dependency between soil-water content and separation distance of colloids, and (ii) the role of ionic strength. Drainage and drying may increase interparticle bonding or cementation of colloids due to a closer distance approach of colloids following a decrease in soil-water

content. In addition, drying may increase the ionic strength of the resident soil-water, thereby increasing the interparticle bonding. In this experiment, the soils incubated at -2.5 hPa were actually drained on tension tables to -100 hPa before re-saturation (Figure 2). This means that soils incubated at -2.5 and -100 hPa have received the same treatment with respect to changes in ionic strength. This indicates that the effect of initial matric potential reflects the soil-water content, where a greater resistance against dispersion would be expected when a decreasing soil-water content increases the surface contacts of colloids. This was clearly reflected in the reduction in LE-WDC from soils at -100 hPa, which was still observable even after one week of complete rewetting. Regarding the soils incubated at -15,500 hPa, these soils were also initially drained to -100 hPa on tension tables, and then additionally dried by passing through dry air. Since the drying procedure does not result in leaching of ions, the ionic strength of the resident soil-water will increase as the soil-water content decreases and this will add to the stronger interparticle bonding or cementation of colloids following drying. When drying is severe, as in the -15,500 hPa treatment, the colloids seemed to be able to maintain this strong bonding even after one week of complete rewetting. An investigation of the colloid fractions showed that a much higher POC to LE-WDC ratio was observed in colloid fractions released after drying to -15,500 hPa (Table 3). This may be a consequence of microbial death and lysis of microbial cells (Christ and David, 1994, 1996a,b), increasing the fraction of mineral bound OC, and/or it may indicate that mineral colloids with surface coatings of OC are more easily dispersed as a result of lower bonding strength among these colloids.

It is interesting that no effect of clay content on LE-WDC was evident after drying to -15,500 hPa. Kemper and Rosenau (1984) found greater cohesion in 40% clay compared to 15% clay after air-drying. The reason that no effect of clay content is evident from this study might be that the cohesive forces created during the drying of low-clay soils was sufficient to withstand

dispersion under the mild stresses applied by the low-energy input. It is important to note that the effect of initial soil matric potential declines with increasing clay content. This is probably a consequence of pores $<30 \mu\text{m}$ constituting an increasing fraction of the pore volume with increasing clay content as documented for this clay gradient by Kjaergaard et al. (2004). These pores will retain water after drainage to -100 hPa , while only pores $\geq 30 \mu\text{m}$ will drain, and this consequently minimizes the effect of soil matric potential on colloid dispersion at higher clay contents.

Time dependency of colloid dispersion

In the field, the soil is subjected to drying and wetting events that continuously change the moisture status of the soil, and thus the dispersibility as illustrated previously. This raises the important question of the time-dependency of the dispersion process. This was investigated as a function of soil matric potential at 11.5% clay, since the effect of soil matric potential was most pronounced at this clay content. The results revealed that colloid dispersion changed as a function of time and that the rate of change depended on the moisture status of the soil (Fig. 6). When the moisture content was near saturation (-2.5 hPa), LE-WDC increased with time from 1636 mg kg^{-1} at time 0 to 3046 mg kg^{-1} after 26 hours, when the rate of change leveled off with only a minor increase to 3091 mg kg^{-1} after 145 hours. Additionally, 24 hours drainage of soils to -100 hPa immediately reduced LE-WDC to 1455 mg kg^{-1} , followed by a continuing small decrease in LE-WDC during the incubation period to 1333 mg kg^{-1} after 166 hours, with a rate of decreasing dispersibility of $0.859 \text{ mg kg}^{-1} \text{ h}^{-1}$. Additional six hours air-drying to $-15,500 \text{ hPa}$ resulted in an immediate reduction in LE-WDC to 409 mg kg^{-1} , followed by a continuing small decrease in LE-WDC during the incubation to 303 mg kg^{-1} after 172 hours, with a rate of decreasing dispersibility of $0.747 \text{ mg kg}^{-1} \text{ h}^{-1}$. At this clay content, the main change in dispersibility appeared to occur during or immediately after adjustment of the moisture status.

The increase in dispersibility at -2.5 hPa occurred within the first 26 hours, and the decrease in dispersibility at -100 and -15,500 hPa occurred primarily during the change in moisture status. However, the dispersibility at -100 and -15,500 hPa continued to decrease with time. This is consistent with the results of Kemper and Rosenau (1984) who found an increase in cohesive strength with duration of storage, and suggested that the increase in cohesion under air-dry conditions indicate that migration of bonding components continue even when there is as little as one molecular layer of water on the mineral surfaces.

Effect of wetting rate on LE-WDC

Drying and successive wetting can also cause a decrease in strength. When dry aggregates are wetted, their breakdown can result from the effect of entrapped air and differential swelling (Grant and Dexter, 1989). In this study, the sensitivity of LE-WDC released due to slaking and swelling was examined by comparing LE-WDC released after slow and fast re-wetting. The volume change after fast wetting showed that soils incubated at -2.5 or -100 hPa experienced no or only very small volume changes after fast wetting, while for soils incubated at -15,500 hPa the volume increased from $10 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$ at 11.5% clay to $90 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$ at 43% clay (Fig. 7a). The application of water during wetting of the -15,500 hPa soils ranged from $33 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$ to $41 \times 10^{-6} \text{ m}^3 \text{ m}^{-3}$, which indicated that a considerable part of the volume change at >24% clay was a consequence of swelling and/or slaking. An examination of the resultant release of LE-WDC as a consequence of fast wetting showed no significant effect of wetting rate on LE-WDC released from soils incubated at -2.5 and -100 hPa (results not shown). In contrast, for soils incubated at -15,500 hPa the amount of LE-WDC released after fast wetting almost doubled compared to the amount of LE-WDC released after slow wetting. At both wetting rates no effect of clay content was observed (Fig. 7b). The reason for fast wetting only affecting colloid dispersion for the initially dry soils is probably because slaking decreases as

the initial water content increases until saturation is reached (Panabokke and Quirk, 1957). This is a consequence of the reduction of the volume of air that is entrapped during wetting and also the reduction of soil matric potential gradients. In addition, the capillary wetting probably resulted in some escape of air, which would minimize the effect of wetting rate compared to a situation with downward infiltration. The lack of a clay effect on colloid dispersion after fast wetting may be a consequence of the counteracting effect of swelling and slaking with increasing clay content. According to Le Bissonnais (1996), aggregate breakdown by slaking decreases when clay content increases in the range of 10 to 30%. In contrast to slaking, aggregate breakdown by differential swelling increases with increasing clay content, which indicates that the increase in volume with increasing clay content (Fig. 7a) may partly be a consequence of swelling. The results obtained from these soils indicate that the quantitative effect of wetting rate on colloid release, as a consequence of slaking and swelling, is of minor importance, since it only increases LE-WDC from dry soils with initially low dispersibility. It is however, important to be aware that the effect of slaking depends on the pore system of the soil aggregates, which in turn depends on the associations of particles. Results have shown that the air-filled porosity in aggregates varies according to the type of clay, with aggregates dominated by kaolinite and illite having a higher air-filled porosity than aggregates dominated by smectite (Tessier et al., 1990). Tessier et al. (1990) investigated the influence of wetting on micro-structural changes of kaolinite, illite and smectite. In aggregates dominated by smectite the pores were mainly isolated due to the parallel association of the flexible sheets, the hydraulic conductivity was consequently low and the aggregates were able to maintain their cohesion even after complete rehydration. In contrast, the wetting rate was very rapid for kaolinite and illite, and entrapment of air resulted in aggregate breakdown by slaking. In general, aggregate breakdown by slaking is most important in aggregations with large blocky particles because of the larger pore size. The importance of slaking in the process of colloid

dispersion therefore depends on the mineralogy of the soil, with the soils used in this study probably being more resistant to slaking compared to soils with a higher content of kaolinite and illite.

CONCLUSIONS

The results from the present study revealed that measurements of WDC were extremely sensitive to pretreatment (moisture status) and energy input in the dispersion procedure, which highlights the importance of identifying the methods for measurements of WDC that resemble the relevant conditions when predicting the affinity of soils to colloid dispersion. In contrast to most previous studies observing positive correlations between clay content and mechanically dispersible colloids, we found that applying a low-energy input, better resembling a situation of water infiltration through the soil, less colloids were released with increasing clay content as a consequence of increased aggregate stability.

This study also documented that there is no unique relation between WDC and clay content, as WDC significantly depended not only on the energy input but also on the initial conditions of the soils. This was reflected both by the pronounced effect of initial matric potential, and by the interacting effect of initial matric potential and wetting rate on LE-WDC. Based on the sensitivity of the LE-WDC towards initial matric potential as well as wetting rate, we also anticipate that the use of the low-energy dispersion procedure would result in measurements of WDC that would be much more sensitive towards other important soil factors such as mineralogy, chemistry, management conditions and the interactions between these properties, compared to the classical estimates of WDC. We therefore recommend that estimates of WDC to be used in predictive models should not be based on empirical relationships, but need to be measured using methods that resemble the conditions of interest.

Future studies intended to investigate the potential of colloid dispersion from aggregates should consider the importance of these different mechanisms of aggregate breakdown and colloid release. The results from this study additionally highlight the general problems of using air-dry or dried soils when investigating colloid mobilization and transport. Clearly the effect of initial matric potential should be taken into consideration when studying colloid mobilization. In addition, the time dynamics and reversibility of changing moisture conditions on colloid dispersibility should be explored further.

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Table 1. Basic characteristics of Lerbjerg soils.

Location	Texture class (μm)			Organic-C g kg ⁻¹	CEC [†] mmol _c kg ⁻¹	SAR [‡] %	pH _{CaCl2}	CaCO ₃ g kg ⁻¹
	<2 g kg ⁻¹	2 - 20 g kg ⁻¹	20 - 2000 g kg ⁻¹					
L1	115	65	820	10.9	114	0.044	6.6	0
L2	180	85	735	16.7	150	0.036	6.7	0
L3	243	113	644	15.5	181	0.035	7.2	0
L4	275	125	600	17.1	229	0.030	7.4	0
L5	366	99	535	15.5	264	0.036	7.5	9.8
L6	428	108	464	17.4	325	0.035	7.5	16.9

[†] CEC: Cation exchange capacity (data from Schjøning et al., 1999).

[‡] SAR: Sodium activity ratio [SAR = Na/(Ca+Mg)^{0.5}, concentrations in mmol L⁻¹]

1 Table 2. Methods used for measuring water-dispersible colloids (WDC) as a function of total clay content.

Form of sample	Wetting conditions	Suspension type	Soil:water ratio	Type of dispersion	Dispersion time	WDC-determination	Relation between WDC and clay	Total clay content (%)	Reference
Field-moist aggregates	Slow wetting	DI-water	†	Mechanical shaking end-over-end: 0.8 m diam. rotation, 25 rpm	†	Light transmission	Positive correlation	4 - 58	Pojasok & Kay, 1990
Air-dry soil	‡	‡	‡	Mechanical shaking	Overnight	‡	Positive linear correlation	5 - 50	Brubaker et al., 1992
Air-dry soil <2 mm	Directly immersed	DI-water	1:15	Mechanical shaking horizontal shaker: 125 rpm	5 min, 15 min or 60 min	Gravimetrically after sedimentation	Positive logarithmic correlation	5 - 45	Levy et al., 1993
Field-moist aggregates	Slow wetting	DI-water	†	Mechanical shaking end-over-end: 0.8 m diam. Rotation, 25 rpm	3 min	Light transmission	Positive correlation	6 - 71	Rasiah et al., 1992
Air-dry soil <0.38 mm	Directly immersed	DI-water	1:10	Mechanical shaking end-over-end	4 hours	Optical density at 641 nm	Positive correlation	20 and 63	Curtin et al., 1994
Air-dry soil <1 mm	Directly immersed	DI-water	1:5	Undisturbed for 12 h + stirring (0.16 rev s ⁻¹) Mechanical shaking end-over-end (0.5 rev s ⁻¹)	30 sec. 1 hour	Turbidity after sedimentation	Positive correlation	9 - 55	Barzegar et al., 1994
Moist soil	Directly immersed	DI-water	1:20	Mechanical shaking	Overnight	Gravimetrically after centrifugation	No correlation	21 - 75	Seta & Karathanasis, 1996
Air-dry soil <2 mm	Directly immersed	Electrolyte solution§	1:8	Mechanical shaking Reciprocal shaker: 0.5 diam. rotation, 29 rpm	16 hours	Gravimetrically after sedimentation	Positive correlation	12 - 43	<i>Kjaergaard et al.</i> , (Present paper)
Field-moist (field capacity)	Slow wetting on tension tables	Electrolyte solution§	1:8	Manually turning up side down: 10 times	1 min	Gravimetrically after sedimentation	Negative correlation	12 - 43	<i>Kjaergaard et al.</i> , (Present paper)

2 † Information not available from paper.

3 ‡ NSSL, Lincoln, NE using a modified version of the standard procedure for particle-size analysis (Soil Survey Staff, 1984)

4 § Electrolyte solution corresponding to natural rainwater with electrical conductivity 0.025 mS cm⁻¹ and SAR 0.736

Table 3. Ratio of particulate organic carbon (POC) to low-energy water-dispersible colloids (LE-WDC) from LE-WDC having different initial matric potential (IMP).

	POC:LE-WDC-ratio		
	IMP -2.5 hPa	IMP -100 hPa	IMP -15,500 hPa
L1	0.050 (0.005) †	0.046 (0.005)	0.086 (0.017)
L2	0.047 (0.007)	0.043 (0.001)	0.082 (0.008)
L3	0.036 (0.006)	0.040 (0.004)	0.074 (0.003)
L4	0.030 (0.003)	0.025 (0.005)	0.045 (0.004)
L5	0.018 (0.0004)	0.020 (0.007)	0.013 (0.002)
L6	0.014 (0.0003)	0.016 (0.002)	0.011 (0.0001)

† Values in parentheses indicate standard errors of estimates (n=3).

FIGURE CAPTIONS

Fig. 1. Map of the sampling area at Lerbjerg with contours of soil clay content. The designations of L1 to L6 refer to sampling locations.

Fig. 2. Pretreatment procedures for measurement of low-energy water-dispersible colloids (LE-WDC) as a function of initial matric potential (IMP) and wetting rate.

Fig. 3. Amount of (a) high-energy water-dispersible colloids (HE-WDC) as a function of clay content, and (b) low-energy water-dispersible colloids (LE-WDC) as a function of clay content and initial matric potential (IMP). Error bars: \pm SE.

Fig. 4. Percentage of water-stable aggregates (WSA) in fractions >0.25 mm and >4 mm as a function of clay content. Error bars: \pm SE.

Fig. 5. Regression plot between water-stable aggregates (WSA) and low-energy water-dispersible colloids (LE-WDC) at IMP -2.5 hPa. Error bars: \pm SE.

Fig. 6. Amount of low-energy water-dispersible colloids (LE-WDC) as a function of time and initial matric potential (IMP) at 11.5% clay. Error bars: \pm SE.

Fig. 7. Effect of wetting rate on (a) volume change after fast infiltration as a function of clay content and initial matric potential (IMP), and (b) amount of low-energy water-dispersible colloids (LE-WDC) at $-15,500$ hPa as a function of clay content.

Figure 1.

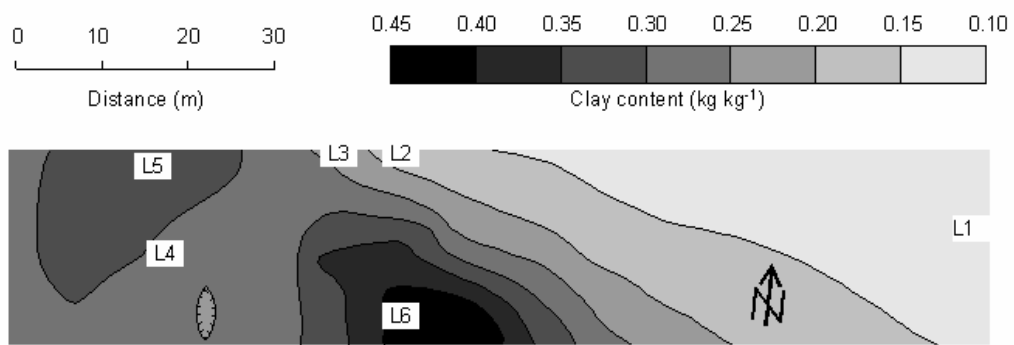


Figure 2.

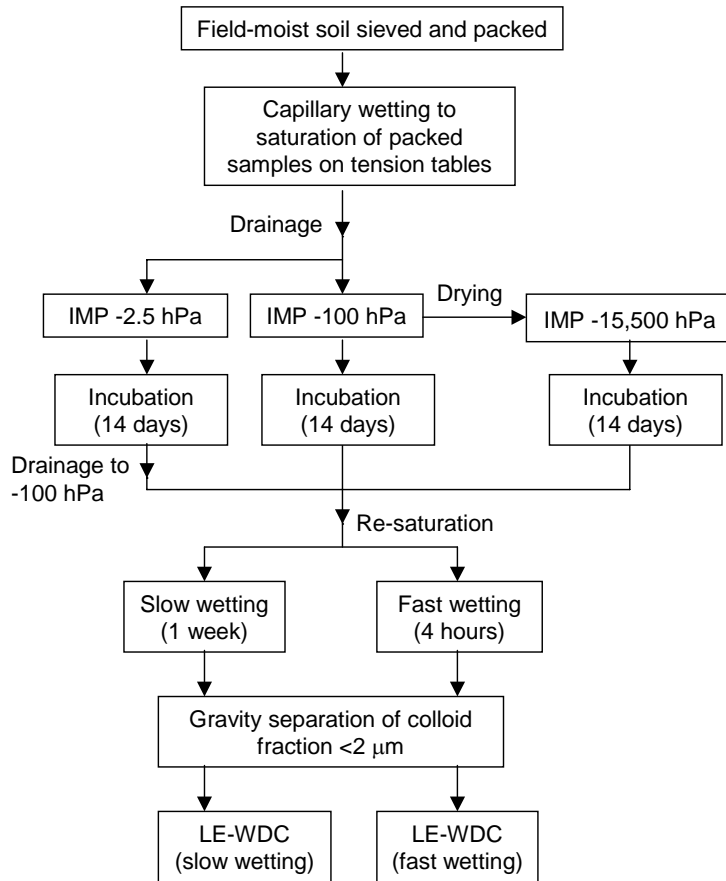


Figure 3.

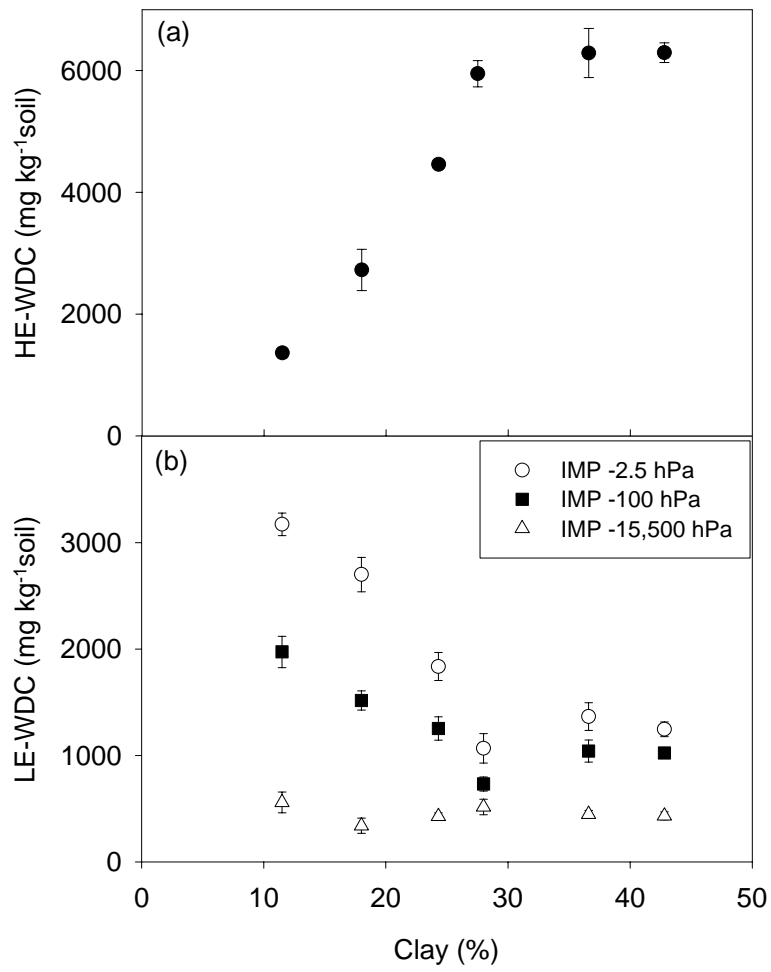


Figure 4.

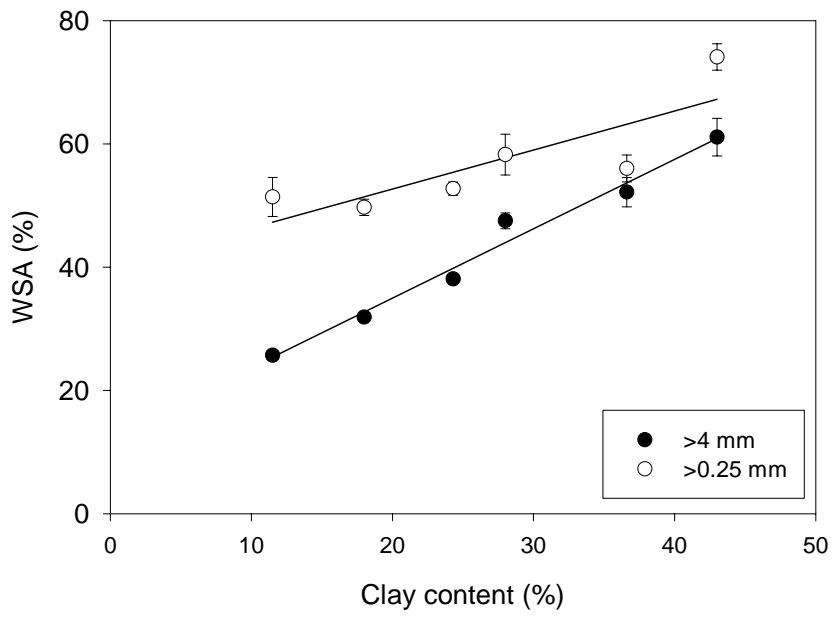


Figure 5.

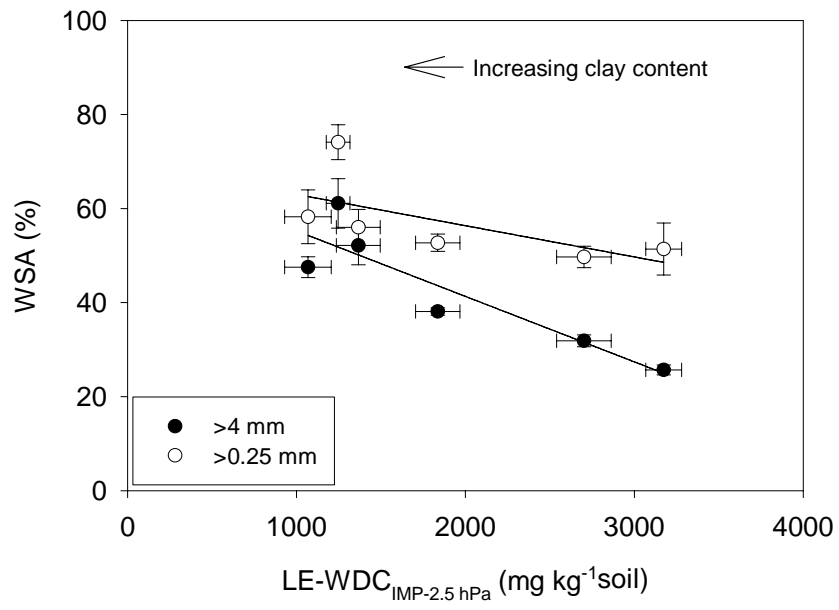


Figure 6.

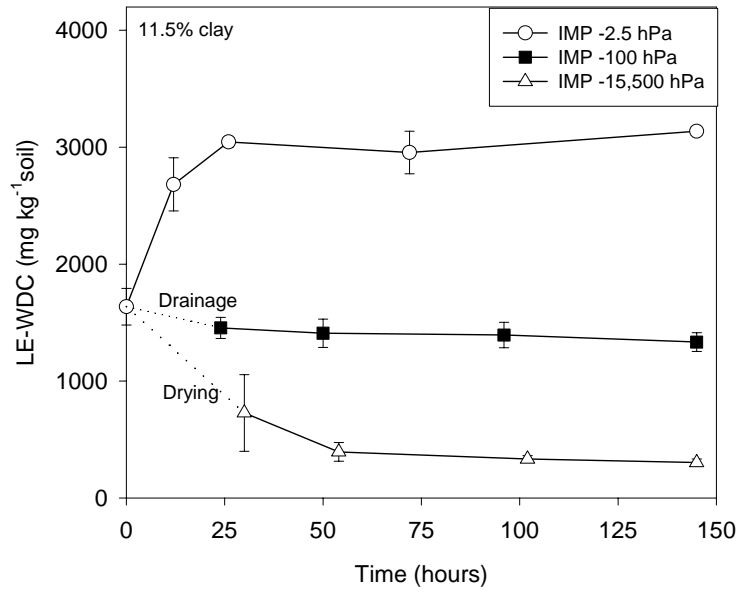
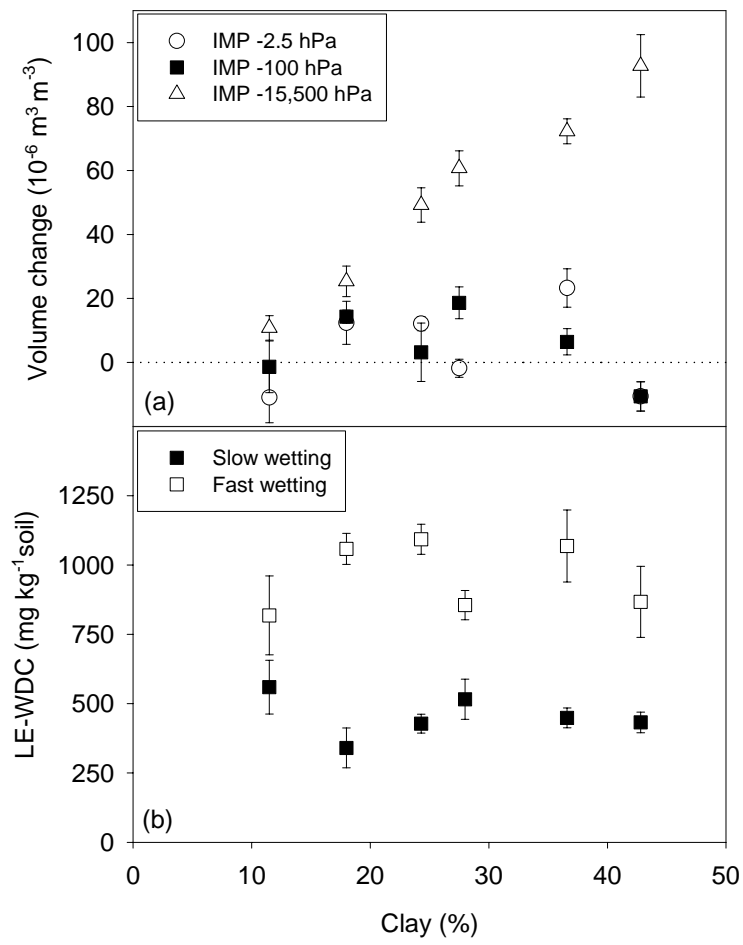


Figure 7.



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Colloid mobilization and transport in undisturbed soil columns. I. Pore structure characterization and tritium transport.

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Colloid mobilization and transport in undisturbed soil columns. I. Pore structure characterization and tritium transport.

ABSTRACT

While it is recognized that preferential flow may increase the transport of colloids, less is known about the actual role of preferential flow on *in situ* colloid mobilization. Changes in pore structure upon soil exposure to drying-rewetting may additionally affect colloid mobilization. Information about the pore structure and the active flow volume, as well as the changes in these properties, are therefore important when investigating colloid mobilization. We investigate the pore structure characteristics and the transport of tritium ($^3\text{H}_2\text{O}$) during steady unsaturated flow conditions. A total of 54 soil columns sampled along a natural clay gradient representing six clay contents (12, 18, 24, 28, 37, and 43% clay) were equilibrated to three different initial matric potentials (IMP), $\psi = -2.5, -100$ and $-15,500$ hPa. Pore structure characteristics were deduced from water retention characteristics and measurements of air-filled porosity and air permeability. Tracer experiments were conducted at 1 mm h^{-1} and with a suction of 5 hPa. A mobile-immobile region model (MIM), and a three-region model (2MIM) with two mobile and one immobile region were used for describing the breakthrough curves (BTCs). The 2MIM model was able to fit the data well, and predict the existence of two mobile flow regions, most pronounced at higher clay content. The 12% clay soil exhibited matrix-dominated flow behavior probably attributed to a large fraction of drained pores disconnecting the rapidly conducting flow system. Soils with $\geq 18\%$ clay exhibited asymmetrical BTCs with early breakthrough and tailing, and an increasing amount of immobile water indicating preferential flow. Drying and rewetting significantly reduced the degree of preferential flow, due to changes in the pore structure.

List of abbreviations:

BTC: Breakthrough curves; CDE: Convection-dispersion equation; CV: Coefficient of variance; EC: Electrical conductivity; IMP: Initial matric potential; MIM: Mobile-immobile model; 2MIM: two-mobile-immobile model; SAR: Sodium adsorption ratio; WSA: Water stable aggregates

INTRODUCTION

Both the *in situ* mobilization and the subsequent transport of mobilized colloids depend on the pore size, geometry and continuity of the actively conducting pore system. Investigations have shown that structural macropores may provide preferential flow pathways for water flow and suspended colloids (Smith et al., 1985; Camobreco et al., 1996). The flow velocities within these preferential flow paths can be orders of magnitude higher than the surrounding matrix, and they thereby constitute a risk for rapid transport of colloids and contaminants to drain and groundwater. The volume fraction of active pores and the continuity of these pores have a major influence on water flow and transport of suspended colloids (White, 1985). Smith et al. (1985) found that when the continuity of macropores was destroyed by disturbing part or all of the column the recovery of *E.coli* was much reduced. In contrast, to the well-known role of structural macropores on colloid transport, less is known about the actual role of soil structure and preferential flow on *in situ* colloid mobilization. Soil structure and the changes in structure upon soil exposure to external and internal stresses such as drying and rewetting may be very important with respect to *in situ* mobilization of colloids. The pore structure controls the active flow pathways of water and thereby the contact area between the infiltrating water and colloids. Changes in soil structure such as drying and rewetting phenomena may affect colloid mobilization by changing the cohesive forces between colloids, exposing new surfaces, and by changing the active flow volume.

It is generally recognized that soil structure and physical non-equilibrium (PNE) flow conditions (channeling, short-circuiting, bypassing, preferential flow or partial displacement) of water and solutes are highly related (e.g. Beven and Germann, 1982; White, 1985). Preferential flow results from different convective velocities among mobile and immobile water regions, and preferential flow has been demonstrated in aggregated packed soils (Biggar

and Nielsen, 1962; van Genuchten and Wierenga, 1977) as well as undisturbed soils (Seyfried and Rao, 1987; Gaber *et al.*, 1995; Langner *et al.*, 1999). The immobile or stagnant water has typically been related to thin liquid films around soil particles, dead-end pores, nonmoving intraaggregate water, or relatively isolated regions associated with unsaturated flow (see review by Nielsen *et al.*, 1986).

The water retention characteristics have been used as a quantitative measure of soil structure since the pore-size distribution can be derived from the water retention curve. Estimates of the pore-size distribution are, however, not necessarily related to the efficiency of pores in conducting water (e.g. Beven and Germann, 1982; White, 1985). Approaches to identify the functional porosity have involved dye studies (Bouma and Wösten, 1979; Seyfried and Rao, 1987), or visualizing preferential flow by x-ray computer assisted tomography (CAT) scanning (Perret *et al.*, 1999; Vanderborght *et al.*, 2002) or single photon emission computed tomography (SPECT) scanning (Perret *et al.*, 2000). In addition, measurements of soil air permeability have been identified as a valuable tool for characterizing soil structure (Ball, 1988; Blackwell *et al.*, 1990; Granovsky and McCoy, 1997; Moldrup *et al.*, 2001). The air permeability expresses the soils capacity to conduct air by convection, and measuring air-flow at pressure potentials where water has drained from the pores of interest allows examination of the pore network. Pore continuity and tortuosity may also be inferred from relationships among air permeability and air-filled porosity as suggested by Groenevelt *et al.*, 1984. Several studies have indicated that continuity of the actively conducting pores is probably more important than volume and number of macropores in controlling water flow (Ball, 1988), and tracer infiltration (Douglas *et al.*, 1980; Allaire-Leung *et al.*, 2000).

Several attempts have been made to account for the non-equilibrium nature of the solute breakthrough in undisturbed soils (e.g. reviews by Nielsen *et al.*, 1986; Brusseau and Rao, 1990). A widely used approach has been to modify the convection-dispersion equation (CDE) to account for the partition of the water phase into mobile and immobile regions, where convective-dispersive transport is restricted to the mobile region and a diffusive exchange of solute exists between the mobile and immobile region (van Genuchten and Wierenga, 1976). The applicability of the mobile-immobile (MIM) model to laboratory scale transport processes has been demonstrated by van Genuchten and Wierenga (1977, aggregated clay loam), Gaudet *et al.*, (1977; unsaturated sand), Gaber *et al.* (1995; saturated and unsaturated, undisturbed silt loam), and Langner *et al.* (1999; saturated and unsaturated, undisturbed silt loam). Other studies have demonstrated that the compartmentalization of soil-water into only two regions was insufficient to account for the range of pore-water velocities encountered (Seyfried and Rao, 1987 (undisturbed clay loam); Li and Ghodrati, 1995 (silt loam containing macropores)). In an attempt to account for the very broad range of pore-water velocities encountered in structured soils Morisawa *et al.*, (1986) suggested a “three-region” model (c.f. Brusseau and Rao, 1989).

The primary objective of this study was to use undisturbed soil columns, sampled along a naturally occurring clay gradient with clay contents ranging from 12 to 43%, to examine: (i) the pore structure characteristics based on measurements of the pore-size distribution, air-filled porosity and air permeability, (ii) the active flow volume based on tritium ($^3\text{H}_2\text{O}$) breakthrough curves (BTC) and parameter estimates deduced from model fit using the mobile-immobile model approach or an extended two mobile – one immobile model approach, and (iii) evaluate the changes in pore structure characteristics and the active flow volume upon soil exposure to drainage and drying-rewetting based on measurements conducted on soils with different initial

matric potentials. These results were additionally used to evaluate the role of soil structure and preferential flow on *in-situ* colloid mobilization in a companion paper (Kjaergaard *et al.*, 2004a).

MATERIALS AND METHODS

Field site and soil characteristics

Intact soil columns of topsoil were excavated in the early spring 2001 from 1 m² areas at 10-18 cm depth, at six sites along a naturally occurring clay gradient from an arable field, Lerbjerg, Denmark (56°22'N, 9°59'E). The clay gradient and the relative locations of the sampling sites was described and illustrated in a previous paper (Kjaergaard *et al.*, 2004b). The soil is developed on morainic deposits from the Weichsel Glacial Age, and the site has been under conventionally tilled winter wheat for several years. Primary minerals quartz, micas and feldspars dominated the sand and silt fractions, while the clay fraction was dominated by secondary minerals illite (20-30%), smectite – predominantly montmorillonite (10-30%), and vermiculite (10-20%) (Schjønning *et al.*, 1999).

At the sampling sites the top 10 cm of soil and vegetation was removed, and the soil cores were excavated by manually pressing a steel cylinder (10 cm diameter, 8 cm length) into the soil, and removing surrounding soil. The intact soil cores were gently cut planar at each end, sealed, transported to the lab in lined plastic boxes, and stored at 2°C at field-moist conditions (water content close to field-capacity ~ -100 hPa). Bulk samples from the sampling area were air-dried, sieved at 2 mm and used for analysis of soil characteristics (Table 1). Soil texture was determined using a combination of wet-sieving and the hydrometer method. Total C was determined on a LECO Carbon Analyzer coupled to an infrared CO₂ detector. Soil pH was

determined in 0.01 M CaCl₂ with 1:2.5 (w:w) soil:electrolyte suspension. The content of calcite was measured gas-volumetrically.

Pretreatment of soil columns

The experiment included six clay contents (11.5, 18, 24.3, 27.5, 36.6 and 42.8%), and three initial matric potentials (IMP) $\psi = -2.5, -100$ and $-15,500$ hPa, which cover the moisture conditions from near saturation to the crop wilting point. The experiment was carried out with three replicates of each combination giving a total of 54 columns. The pretreatment procedure of the soil columns is illustrated in Figure 1. Initially the columns were saturated with electrolyte solution, having a chemical composition identical to natural rainwater (electrical conductivity (EC) at 0.025 mS cm^{-1} and sodium adsorption ratio (SAR) at 0.736) by slow capillary infiltration on tension tables, and allowed to equilibrate for 48 hours. After initial saturation, one third of the samples were drained to -2.5 hPa (at column bottom) and two third were drained to -100 hPa (at column bottom) on tension tables, and allowed to equilibrate for one week. Half of the samples drained to -100 hPa were subsequently dried by passing through dry air until the samples reached a gravimetric water content corresponding to a soil matric potential of $-15,500$ hPa. The water content at $-15,500$ hPa was estimated using water retention data from Schjønning *et al.*, (1999). After drainage and drying all samples were weighed, sealed and allowed to equilibrate for 14 days at 10°C . Water loss at IMP -2.5 hPa was prevented by incubating the samples in containers with a water saturated atmosphere, and water gain at IMP $-15,500$ hPa was prevented by incubating the samples in containers with silica gel. Soils were re-weighed after the 14 days incubation period.

Column setup and tracer experiment

After incubation the soil columns were installed in the irrigation and effluent sampling system as illustrated in Figure 2. A cloth was placed on the top of the soil core to avoid erosion by raindrop impact. The column rested on a 2 mm stainless steel grid supporting the soil core. A nylon mono-filament screening fabric with 31 μm mesh openings allowed application of a constant negative pressure, as well as collecting leached colloidal suspensions. A suction of 5 hPa was applied to the lower boundary of the soil via the collection chamber. Suction was held constant by connecting the collection chamber to a Mariotte device. Column effluent was collected continuously every hour by installing a two-piece pressure controlled open-closing device on a rubber tube. Irrigation water was applied from an irrigation device containing nine hypodermic needles (0.5 mm inner diameter) placed 2.5 mm apart, with a distance from the hypodermic needles to the soil surface of 4 mm. Soils were irrigated at low intensity 1 mm h^{-1} (7.5 ml h^{-1}) with an electrolyte solution, having a chemical composition identical to natural rainwater (EC 0.025 mS cm^{-1} and SAR 0.736). Irrigation intensity was controlled by a peristaltic precision pump (HOH Water Technology, Denmark). All experiments were carried out at a constant temperature of 20°C .

Initially soil columns with different IMP were irrigated until steady out-flow at -5 hPa was established. At steady out-flow, the influent was switched to a one-hour pulse application of 7.5 ml water marked with tritium, hereafter referred to as tritium, $^3\text{H}_2\text{O}$ (specific activity 1.11 MBq L^{-1}). Effluent fractions of 7.5 ml were sampled continuously every hour for the first 6-8 h after pulse application followed by steadily decreasing sampling. The experiment continued for about 4-5 pore volumes. Corresponding influent and effluent fractions were analyzed for tritium using liquid scintillation counting, and the results were used to construct tritium breakthrough curves (BTC). The BTCs were plotted as the relative concentration (C/C_0)

against number of eluted pore volumes (V/V_0), where C is the measured effluent activity of tritium (cps volume^{-1}), C_0 is the measured influent activity, V is the out-flow volume (m^3), and V_0 is the water-filled porosity ($\text{m}^3 \text{ m}^{-3}$) at -5 hPa. In order to ensure mass recovery, C_0 was adjusted so the applied mass of tritium was consistent with the mass recovered in the effluent.

Immediately after finishing the leaching experiment column weights were measured and the columns allowed draining to -100 hPa on tension tables and reweighed again. Column dry weight was determined after oven drying at 105°C. Sample volume was measured with a calliper. Bulk density, ρ_b , was estimated from sample volume and the dry weight, and total porosity calculated from the bulk density, using values of particle density between 2.64-2.68 measured by Schjønning *et al.* (2003).

Pore structure characterization

Air permeability (k_a) and air-filled porosity (ϵ_a) was measured directly on the soil cores at $\psi = -2.5$, -100 and -15,500 hPa immediately before the leaching experiment, at -5 hPa immediately after the leaching experiment, and after final drainage to -100 hPa (Fig. 1). Air permeability was measured with an air permeameter (Iversen *et al.*, 2001) using the steady state method of Grover (1955). Air-filled porosity was measured using an air-pycnometer (Vomocil, 1965). From preliminary investigations we found that soil columns with no measurable air permeability at -100 hPa, did not allow any flux of water. Based on these experiences, air permeability was measured at all columns at field-moist conditions (~ -100 hPa), and columns with no measurable air permeability were disregarded. Among the 25 soil columns sampled at each of the six 1 m^2 areas, no columns were disregarded at 12% clay, while a maximum of 12 columns were disregarded at 43% clay.

Measurements of air permeability, air-filled porosity and estimates of gas diffusivity (D/D_0) allowed calculation of some soil structure characterizing parameters. Schjønning *et al.* (1999, 2002) and Moldrup *et al.* (2001) used the equivalent pore diameter (d) of the drained pores, as derived from the parallel tube fluid flow model by Millington and Quirk (1964) and Ball (1981), as a soil structure characterizing parameter:

$$d = 2 \sqrt{\frac{8k_a}{D/D_0}} \quad [1]$$

where D is the gas diffusion coefficient in soil ($\text{cm}^3 \text{ soil air cm}^{-1} \text{ soil h}^{-1}$), and D_0 is the gas diffusion coefficient in air ($\text{cm}^2 \text{ h}^{-1}$). Moldrup *et al.* (2000) found a highly significant relationship ($r^2=0.98$) for D/D_0 as a function of ε at -100 hPa soil matric potential:

$$\frac{D_{100}}{D_0} = 2\varepsilon_{a,100}^3 + 0.04\varepsilon_{a,100} \quad [2]$$

where D_{100} is the gas diffusion coefficient at -100 hPa, and $\varepsilon_{a,100}$ is the air-filled porosity at -100 hPa. Inserting Eq. [2] into Eq. [1] allows estimation of the equivalent pore diameter at -100 hPa (d_{100}) from measurements of only $\varepsilon_{a,100}$ and $k_{a,100}$. Measurements of $\varepsilon_{a,100}$ and $k_{a,100}$ and estimates of D/D_0 additionally allowed calculation of the number of air-filled pores (n_{100}) in a soil transect (Ball, 1981; Schjønning *et al.* (1999, 2002):

$$n_{100} = \frac{\varepsilon_{a,100}^{0.5} (D_{100}/D_0)^{1.5}}{8\pi k_{a,100}} \quad [3]$$

RESULTS AND DISCUSSION

Pore structure characteristics

The total porosity of the soils increased with increasing clay content (Table 1). The water retention characteristics reflected the differences in the pore-size distribution (Fig. 3a), with an increase in the fraction of pores $<0.2 \mu\text{m}$ from 26% at 12% clay to 51% at 43% clay. The fraction of pores between 0.2 to $30 \mu\text{m}$ deviated less among the soils, constituting from 41-53% of the total porosity. The volume of pores $\geq 30 \mu\text{m}$ significantly decreased with increasing clay content, constituting 33% of the total pore volume at 12% clay to 3% at 45% clay. The fraction of pores $>600 \mu\text{m}$, which represents the pore volume drained at the 5 hPa-suction applied during the leaching experiment, constituted 12% of the total porosity at 12% clay, declining to 7% at 18% clay, and 1% at 24% clay. In the higher clay soils ($\geq 28\%$) it was not possible to identify the existence of pores $>600 \mu\text{m}$ based on the soil-water retention characteristics indicating that the possible volume of this pore-size fraction is very small.

The differences in the pore-size distribution were also reflected by the measurement of air permeability at the specific matric potentials (Fig. 3b). At a matric potential of -2.5 hPa, k_a was generally low for all soils ($2\text{-}12 \mu\text{m}^2$), indicating a very low but existing amount of continuous air-filled pores. Increasing the matric potential to -100 hPa increased k_a at 12 and 18% clay ($24\text{-}28 \mu\text{m}^2$) in agreement with the larger fraction of pores $>30 \mu\text{m}$, while k_a remained at the same low level ($2\text{-}8 \mu\text{m}^2$) for the higher clay soils ($\geq 24\%$). At a matric potential of -15,500 hPa, the low values of k_a at high clay content ($19 \mu\text{m}^2$ at 43% clay) and the increasing k_a with decreasing clay content ($118 \mu\text{m}^2$ at 12% clay), clearly reflected the differences in the size distribution and continuity of air-filled pores.

Changes in soil structure following drainage and drying-rewetting are shown in Figure 4. For soils kept at -2.5 hPa prior to the experiment, only final measurement at -100 hPa was achieved, as these soils were not at -100 hPa before the tracer experiments. Both the fraction of pores $>30 \mu\text{m}$ ($\epsilon_{a,100}$) (Fig. 4a,b,c), and the air permeability (Fig. 4d,e,f) decreased with increasing clay content. Generally, drying to -15,500 hPa and rewetting increased the fraction of pores $>30 \mu\text{m}$ (Fig. 4c) and the air permeability of this pore fraction (Fig. 4f). This agreed with the results of Reeve *et al.* (1980) showing a close correlation between total clay content and shrinkage. Increasing porosity is generally associated with drying and rewetting (e.g. Pardini *et al.*, 1996; Czarnes *et al.*, 2000).

The estimated equivalent pore diameter displayed values of d ranging between 200 and 700 μm (Fig. 4g,h,i). These values of equivalent pore diameter were consistent with values of d_{100} (250-500 μm) obtained from the similar soils using measurements of air permeability and gas diffusivity (Moldrup *et al.*, 2001). Moldrup *et al.* (2001) compared the d_{100} values from the undisturbed soils with d_{100} values from sieved and repacked soils having d_{100} values around 50 μm , and sieved and repacked soils that was allowed to generate structure during 17 month having d_{100} values between 100 and 250 μm . These results indicated a rather well developed pore structure in these undisturbed soil columns with rather high values of d for all clay soils. Drying the soils to -15,500 hPa and rewetting generally resulted in a decrease in d_{100} (Fig. 4i), probably as a result of the swelling upon rewetting. The estimated number of pores $>30 \mu\text{m}$ generally decreased with increasing clay content (Fig. 4j,k,l). Large variability in n_{100} among samples was observed at 12% clay, with values of n_{100} ranging between 17 and 150. Drying the soils to -15,500 hPa and rewetting generally resulted in an increase in the number of pores $>30 \mu\text{m}$ (Fig. 4l).

Tritium breakthrough characteristics

The transport parameters (mean values) for each combination of clay and IMP are summarized in Table 2. The soil water content (θ) at steady out-flow increased with clay content, as a result of the differences in the pore-size distribution, resulting in a relative saturation ranging from 88 at 12% clay to around 100% at $\geq 24\%$ clay, indicating a very low (not measurable) fraction of pores $>600 \mu\text{m}$ in the high clay soils. There seemed to be no effect of IMP on the relative saturation. The average Darcy flux velocity (q) among all soil columns was rather constant at 2.5 cm day^{-1} .

Results of the tritium BTCs at 12, 18, 28 and 43% clay are shown in Figure 5. The transport behavior at 24 and 37% clay was similar to the 28 and 43% clay soils. BTCs obtained at 12% clay (Fig. 5a-c) attained almost symmetrical behavior, and only small variations were observed in the shape of the BTCs among the replicates. Peak arrivals were observed slightly after one pore volume, indicating that tritium was retarded in these soils. Tritium has often been used as a conservative tracer, however, several studies suggested that tritium may exhibit some retardation in soils, and retardation factors of 1.02 to 1.26 has been reported (e.g. Seyfried and Rao, 1987; Jacobsen *et al.*, 1992; Gaber *et al.*, 1995). Retardation of tritium due to isotopic exchange between tritium and hydroxyls in the crystal-lattice was reported by Heemstra *et al.* (1961), and supported by findings of Stewart and Barker (1973) showing that tritium isotopic exchange was especially pronounced in vermiculite and certain types of montmorillonite.

At higher clay content, the BTCs illustrated the well-known features of non-equilibrium behavior, with asymmetrical shapes of the BTC, early appearance of tritium in the effluent, and tailing indicating the presence of an immobile region of pore water (Fig. 5 d-l). Large variations were generally observed in the shape of the BTCs among the replicates, with

increasing tendency for double peaks as the clay content increased. The asymmetry of BTCs with early breakthrough and pronounced tailing indicates that solutes are transported relatively rapidly by convection through the soil by a small fraction of the soil water, accompanied by diffusive mass transfer of solute between the mobile and immobile regions (Seyfried and Rao, 1987; Gaber *et al.*, 1995; Langner *et al.*, 1999).

The effect of drainage or drying-rewetting (IMP) depended on soil clay content, with no variations at 12% clay. At higher clay contents ($\geq 18\%$) significant changes in the shape and position of the BTCs were generally observed after drying and rewetting (IMP -15,500 hPa), while only minor effects of IMP -100 hPa were observed. At 18% clay the BTCs at IMP -15,500 hPa adopted almost symmetrical behavior (Fig. 5f), and this was also the case at 24% clay (data not shown). At higher clay content the non-equilibrium behavior was still evident, but the position of the BTCs were generally changed with significant later peak arrival. With decreasing initial matric potential the differences among the clay contents were significantly reduced. Estimating the number of pore volumes eluted at the 12.5% and 50% $^3\text{H}_2\text{O}$ -displacement (Table 2) revealed that increasing clay content and high initial matric potential both reduced the number of pore volumes eluted at 12.5% and 50% $^3\text{H}_2\text{O}$ -displacement, indicating a higher degree of preferential transport.

Three-region model (2MIM) for tritium transport

In this study, several BTCs exhibited distinct double-peaks. Even though the MIM-model has been used to describe the existence of double-peaks (e.g. Mortensen, 2001), the second peak being a consequence of diffusive exchange between the mobile and immobile region, we found that the MIM-model was not able to describe the existence of double-peaks well (Fig. 6b-f). To describe the transport of tritium in these soils we assumed that the water phase conceptually

consisted of three separate physical pore regions: (i) a region with rapid water flow (e.g. in the larger interaggregate pores), θ_{m1} (m^3m^{-3}), (ii) a region with moderate water flow (in the smaller interaggregate pores), θ_{m2} (m^3m^{-3}), and (iii) a region with immobile water (in the intraaggregate pores), θ_{im} (m^3m^{-3}). The two mobile regions are assumed to have independent pore water velocities (v_1, v_2 , (cm h^{-1})) and dispersion coefficients (D_1, D_2 ($\text{cm}^2 \text{h}^{-1}$)). The dispersion coefficients are calculated using:

$$D_{m1} = v_{m1}\tau_{m1} \quad [4a]$$

$$D_{m2} = v_{m2}\tau_{m2} \quad [4b]$$

where τ_{m1} and τ_{m2} are the independent dispersivity coefficients in the mobile regions (cm). If the input flux of water per cross sectional area of column (the Darcy velocity, q , (cm h^{-1})) is known the value of θ_{m2} is given as:

$$\theta_{m2} = \frac{q - v_{m1}\theta_{m1}}{v_{m2}} \quad [5]$$

First order diffusional mass transfer of tritium is assumed between each mobile region and the immobile region. Direct transfer between the two mobile regions is not included in the model, as mass transfer will occur indirectly via the immobile region. The mass transfer coefficients for each mobile region (α_{m1}, α_{m2} (h^{-1})) were also assumed independent and functions of the pore water velocity (De Smedt and Wierenga, 1979; Wierenga and van Genuchten, 1989). The α values were calculated as:

$$\alpha_{m1} = v_{m1}K \quad [6a]$$

$$\alpha_{m2} = v_{m2}\kappa \quad [6b]$$

where κ (cm^{-1}) is a constant assumed identical for both mobile regions. The overall governing differential equations for $^3\text{H}_2\text{O}$ transport are:

$$\frac{\partial C_{m1}}{\partial t} = \frac{D_{m1}}{R} \frac{\partial^2 C_{m1}}{\partial x^2} - \frac{v_{m1}}{R} \frac{\partial C_{m1}}{\partial x} + \frac{\alpha_{m1}}{R} (C_{im} - C_{m1}) \quad [7a]$$

$$\frac{\partial C_{m2}}{\partial t} = \frac{D_{m2}}{R} \frac{\partial^2 C_{m2}}{\partial x^2} - \frac{v_{m2}}{R} \frac{\partial C_{m2}}{\partial x} + \frac{\alpha_{m2}}{R} (C_{im} - C_{m2}) \quad [7b]$$

$$\frac{\partial C_{im}}{\partial t} = -\frac{\theta_{m1}}{\theta_{im}} \frac{\alpha_{m1}}{R} (C_{im} - C_{m1}) - \frac{\theta_{m2}}{\theta_{im}} \frac{\alpha_{m2}}{R} (C_{im} - C_{m2}) \quad [7c]$$

where R is the retardation factor assuming linear equilibrium sorption ($R = 1 + \rho_b K_d / \theta$) of tritium and C denotes the activity (cps volume⁻¹) of tritium in the three regions. It is assumed that R has the same value in all regions. The equations were solved in Microsoft ExcelTM using a forward time backward space finite difference scheme corrected for second-order numerical errors (Moldrup *et al.* 1994). A time step of 0.025 h and a spatial step of 0.0058 m were used.

The curve-fitted parameter values for each combination of clay and IMP are summarized in Table 3. With θ and q measured during transport experiments, parameters θ_{m1} , v_1 , v_2 , τ_1 , τ_2 , κ and R are fitted from the BTCs by minimizing the sum of squared deviations (SSD) between measured and predicted $^3\text{H}_2\text{O}$ concentrations. The fitting procedure was done by manually selecting initial values for the parameters to be fitted and then using Microsoft ExcelTM to optimize the parameter values while minimizing the SSD. The optimal values of the parameters θ_{m2} and θ_{im} can be calculated once optimal values for the fitted parameters are found. Based on the observed retardation of tritium, the retardation factor (R) was estimated from the 12% clay

showing the latest breakthrough. The tritium BTC in the 12% clays was fitted using only one mobile region (MIM model, e.g., following the approach by Parker and van Genuchten (1984) in their CXTFIT model, or by Gaber *et al.* (1995)). The retardation factor was fitted from the BTC allowing the values of the other input parameters (θ_{mi} , v , τ , κ) to assume optimal values. From the curve fitting a retardation factor of 1.2 was found, and it was assumed that R had the same value in all regions in all clay soils. Two mobile regions (2MIM model) were considered for all soils with $\geq 18\%$ clay, and with a fixed R-value at 1.2, six parameters needed to be fitted for the 2MIM model.

Selected BTCs with calculated best fit (least sum of squares) are presented in Figure 6, using either the MIM (Fig 6a) or the 2MIM (Fig. 6b-f). In general the models were able to fit the data quite well. The BTC behavior resulting in double peaks indicated the existence of two mobile water regions, a region with very rapid water flow resulting in the first peak, and a region with moderate water flow resulting in the second peak, and tailing indicating diffusive mass transfer between the immobile and mobile regions. For some soils, especially at lower clay content or after drying and rewetting (IMP -15,500 hPa), the contribution of the rapid mobile water was low, resulting in BTC behavior with a left-skewed shoulder (Fig. 6b). Other soils exhibit pronounced breakthrough of tritium in the rapid mobile water, resulting in a very distinct peak with right-skewed shoulder, and with a minimum of tailing, indicating negligible mass transfer between the mobile and immobile water regions (Fig. 6d). In most cases the BTCs exhibited two distinct peaks, differing in the quantitative influence of the rapid mobile water, with marked dominance (Fig. 6e), moderate dominance (Fig. 6f) or minor dominance (Fig. 6c). The existence of double peaks indicates that the application of the 2MIM model may give a more accurate representation of the transport conditions compared to the simpler MIM approach. The MIM has usually been applied to columns with packed soil aggregates (van Genuchten

and Wierenga, 1976; Rao et al., 1980; Brusseau and Rao, 1990) where the interpretation of the model parameters, including the mobile water fraction and the mass transfer coefficient, is relatively straightforward. The interpretation of these parameters from studies on intact structured soils is more complicated (Seyfried and Rao, 1987). Given the large number of parameters in the 2MIM model, the interpretation of their physical relevance should be done with caution.

The model results revealed that the fraction of immobile water generally increased with clay content and decreased with decreasing IMP (Table 3). This agrees with the interpretations based on the shapes of the BTCs, with the lowest values of θ_{im} obtained for those soil columns showing the highest degree of symmetry in the BTCs. The matrix-dominated flow behavior of the BTCs at 12% clay is surprising, as these soils cores actually contained a very large fraction of large pores. The active flow volume is, however, determined both by the effective pore continuity, the pore-water velocity and the steady state soil-water content. The combination of a lower relative saturation and a higher volume of large pores that may have resulted in a disconnection of the rapidly conducting pore network in the 12% clay soils, and the relative low convective velocity consequently resulted in negligible amounts of immobile water. This agrees with the results of Seyfried and Rao (1987) reporting increasingly symmetrical shapes of tritium BTCs, when increasing soil-water tension from 0 to 2 kPa in an undisturbed clay loam. Langner *et al.* (1999) additionally reported increasing equilibrium behavior when increasing soil-water tension from 0 to 10 hPa. In contrast, studies performed on packed sand columns demonstrated that tailing in BTC increased with increasing soil-water tension (Nielsen and Biggar, 1961; Gaudet *et al.*, 1977; DeSmedt and Wierenga, 1984). However, as noted by Brusseau and Rao (1990) homogeneous porous media with a narrow pore-size distribution,

may be more susceptible to isolation of immobile regions when the soil-water content decreases, because of the lack of continuous pores with smaller diameter.

The observed changes in the BTCs after drying and rewetting (IMP -15,500 hPa) is a consequence of the changes in soil structure caused by shrinkage and swelling upon drying and rewetting. Shrinkage and swelling increased the porosity and the number of pores $>30 \mu\text{m}$ and decreased the equivalent pore diameter. This agrees with the results from Bouma and Wösten (1979) concluding that the increased porosity resulting from shrinkage and swelling was composed of a larger volume of finer pores, while the large pores were closed upon swelling. When the larger pores are closed the progressively finer pores increase their relative contribution to the flow and the pore-water velocity distribution is narrowed, which explains the displacement of the BTCs at IMP -15,500 hPa, and the apparent reduction in the values of θ_{im} (Table 3). It is noted that two estimates of mobile water seem not well estimated by the 2MIM-model θ_{m2} at 18% clay (IMP -15.500 hPa) and θ_{m1} at 24% clay (IMP -15.500 hPa). In both these cases the drying-rewetting have resulted in flow behavior approaching matrix-dominated flow (Fig. 5f), indicating only one mobile water region and a better fit would have been obtained with the simpler MIM-model.

Linking pore structural characteristics and preferential flow

The amount of immobile water is conceptually related to the pore-water velocity distribution and thereby the pore-size distribution of the water-filled pores. The pore-size distribution and the continuity of the water-filled pore system are probably key factors controlling the transport behavior of tritium in these soils. The water retention characteristics revealed that the 24-43% clay soils resembled each other with respect to a very low fraction of pores $>30 \mu\text{m}$ and a not-measurable fraction of pores $>600 \mu\text{m}$, resulting in an effective saturation at or close to 100%

at the applied pressure potential of -5 hPa. These soils additionally resembled each other with respect to: (i) pore structure characteristics (a low air permeability, and a very low number of pores $>30\ \mu\text{m}$ having a rather high equivalent diameter), and (ii) the tracer breakthrough characteristics demonstrating a very rapid breakthrough and less pronounced tailing (12.5% $^3\text{H}_2\text{O}$ -displacement and the amount of immobile water). A high continuity of a few large pores with relatively little diffusive exchange between mobile and immobile water regions was probably responsible for the very early tritium breakthrough observed for these soils.

The soils low in clay (12 and 18% clay) differed from the higher clay soils by a larger fraction of pores $>30\ \mu\text{m}$, and additionally a large fraction of pores $>600\ \mu\text{m}$ drained during the leaching experiment, causing a lower relative saturation (between 86 and 96%). The existence of air-filled pores probably resulted in disconnection of the rapidly conducting pore system, narrowing the pore-size distribution and the amount of immobile water, consequently resulting in reduced degree of preferential flow. This was most pronounced for the 12% clay soil, resulting in the matrix- dominated flow behavior.

The analysis of the dependence of moisture history on soil structural characteristics revealed that the drying to -15,500 hPa and rewetting prior to the tracer experiment increased the porosity and number of pores $>30\ \mu\text{m}$ but decreased the equivalent pore diameter indicating closing of the largest pores and a reduction in the pore-water velocity distribution. This change in soil structure resulted in a significant increase in the number of eluted pore volumes at 12.5% and 50% $^3\text{H}_2\text{O}$ -displacement and reduced the amount of immobile water for all clay soils except the 12% clay which was not affected by the drying and rewetting. The changes in the pore structure characteristics following the drying and rewetting was thereby directly reflected in the tritium transport behavior.

CONCLUSIONS

The investigation of the influence of soil structure on the susceptibility of preferential flow revealed that: (i) The occurrence of preferential flow was not related to the volume fraction of large pores, as drainage of pores $>600\ \mu\text{m}$ at the applied suction of 5 hPa probably disconnected the rapidly conducting pore-system resulting in matrix-dominated flow behavior at 12% clay. (ii) At the higher clay soils ($\geq 24\%$ clay) a high degree of preferential flow seemed to relate to the existence of few large continuous water-filled pores, resulting in very high pore-water velocities in the rapid mobile water region and consequently rapid leaching of tritium. (iii) Drying the soils to the crop wilting point (-15,500 hPa) and rewetting prior to the tracer experiment significantly reduced the degree of preferential flow as a result of an increased porosity dominated by pores with a minor equivalent pore diameter.

The extended three-region solute transport model (2MIM) was able to fit the measured tritium breakthrough curves well, and supported the existence of two mobile flow domains, most pronounced for the higher clay soils and the low initial matric potentials. In perspective, efforts should be directed towards better understanding and describing the influence of soil matric potential on the continuity of the actively conducting pore system, and linking model parameters with soil structural properties.

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Table 1. Basic characteristics of Lerbjerg soils.

Soil	Texture class (μm)			Organic-C g kg ⁻¹	CaCO ₃ g kg ⁻¹	pH _{CaCl2}	Bulk density† Mg m ⁻³	Porosity‡ m ³ m ⁻³
	< 2 g kg ⁻¹	2-20 g kg ⁻¹	20-2000 g kg ⁻¹					
L1	115	65	820	10.9	0	6.6	1.61	0.39
L2	180	85	735	16.7	0	6.7	1.58	0.40
L3	243	113	644	15.5	0	7.2	1.49	0.44
L4	275	125	600	17.1	0	7.4	1.49	0.45
L5	366	99	535	15.5	9.8	7.5	1.42	0.47
L6	428	108	464	17.4	16.9	7.5	1.34	0.50

† Mean measured bulk density for undisturbed soil cores (n = 9), CV = 2-3%

‡ Calculated porosity for undisturbed soil cores (n = 9) from measurements of particle density.

Table 2. Mean measured transport parameters for each combination of clay and initial matric potential (IMP) (n = 3).

Clay %	IMP hPa	Porosity †	Soil-water content ‡	Relative saturation	Darcy flux §	³ H ₂ O-displacement §	
		θ_s m ³ m ⁻³	θ m ³ m ⁻³	θ/θ_s -	q cm day ⁻¹	12.5% V/V ₀	50% V/V ₀
12	-2.5	0.393	0.360	0.92	2.63 (0.03)	0.71 (0.03)	1.09 (0.03)
12	-100	0.394	0.338	0.86	2.44 (0.04)	0.52 (0.05)	1.03 (0.07)
12	-15,500	0.387	0.335	0.87	2.48 (0.05)	0.67 (0.02)	1.08 (0.06)
18	-2.5	0.398	0.375	0.94	2.56 (0.01)	0.23 (0.08)	0.70 (0.18)
18	-100	0.397	0.381	0.96	2.55 (0.04)	0.29 (0.04)	0.88 (0.06)
18	-15,500	0.409	0.364	0.89	2.54 (0.01)	0.63 (0.04)	1.11 (0.02)
24	-2.5	0.430	0.435	1.01	2.53 ¶	0.04 ¶	0.18 ¶
24	-100	0.446	0.443	0.99	2.29 (0.02) #	0.14 (0.004) #	0.54 (0.01) #
24	-15,500	0.439	0.425	0.97	2.45 (0.07)	0.39 (0.09)	0.83 (0.12)
28	-2.5	0.429	0.432	1.01	2.47 (0.02)	0.07 (0.02)	0.32 (0.05)
28	-100	0.426	0.465	1.09	2.61 (0.05)	0.08 (0.02)	0.36 (0.10)
28	-15,500	0.445	0.438	0.99	2.55 (0.06)	0.20 (0.08)	0.55 (0.12)
37	-2.5	0.474	0.483	1.02	2.46 (0.01) #	0.06 (0.02) #	0.37 (0.10) #
37	-100	0.469	0.480	1.02	2.49 ¶	0.10 ¶	0.42 ¶
37	-15,500	0.470	0.479	1.02	2.44 (0.04)	0.29 (0.04)	0.69 (0.05)
43	-2.5	0.504	0.502	1.00	2.54 (0.07) #	0.05 (0.003) #	0.34 (0.05) #
43	-100	0.495	0.505	1.02	2.52 (0.03) #	0.09 (0.03) #	0.40 (0.10) #
43	-15,500	0.504	0.517	1.03	2.48 (0.03)	0.27 (0.08)	0.70 (0.11)

† Mean calculated porosity for undisturbed soil cores from measurements of particle density, CV = 0.4-5.7%

‡ Mean measured soil-water content, CV = 2-6%

§ Values in parentheses indicate standard errors of estimates

¶ Only one measurement due to clogging and ponding of columns (n=1)

Only two measurements due to clogging and ponding of columns (n=2)

1

2 Table 3. Curve-fitted transport parameters for each combination of clay and initial matric potential (IMP) (n = 3)

Soil	IMP hPa	θ_{m1} $m^3 m^{-3}$	θ_{m2} $m^3 m^{-3}$	θ_{im} $m^3 m^{-3}$	v_1 $cm day^{-1}$	v_2 $cm day^{-1}$	τ_1 cm	τ_2 cm	α_1 day^{-1}	α_2 day^{-1}
12	-2.5	-	0.29 - 0.35	0.020 - 0.052	-	7.44 - 8.88	-	0.27 - 0.85		0.26 - 0.29
12	-100	-	0.29 - 0.35	0.005 - 0.040	-	6.96 - 8.16	-	0.84 - 2.7		0.014 - 0.12
12	-15,500	-	0.31 - 0.35	0.004 - 0.042	-	7.44 - 8.16	-	0.31 - 0.87		0.029 - 0.12
18	-2.5	0.006 - 0.025	0.15 - 0.34	0.031 - 0.20	18.2 - 64.8	6.24 - 14.6	1.7 - 4.7	1.5 - 4.0	0.14 - 0.86	0.058 - 0.23
18	-100	0.013 - 0.13	0.20 - 0.34	0.030 - 0.080	8.40 - 28.8	6.48 - 7.44	2.8 - 8.6	1.7 - 2.3	0.14 - 0.58	0.029 - 0.14
18	-15,500	0.27 - 0.35	0 - 0.069	0.0003 - 0.009	7.20 - 7.68	0 - 6.48	0.80 - 1.7	0.16 - 0.94	0 - 0.58	0 - 0.29
24	-2.5	0.023 †	0.090 †	0.31 †	55.2 †	13.9 †	0.62 †	1.5 †	0.58†	0.14†
24	-100	0.022 - 0.027	0.12 - 0.20‡	0.22 - 0.26‡	24.0 - 36.0‡	9.12 - 11.5‡	0.15 - 2.1‡	0.45 - 0.84‡	1.15 - 2.59‡	0.58 - 0.86‡
24	-15,500	0.004 - 0.082	0.23 - 0.36	0.053 - 0.14	0.35 - 0.64	5.76 - 7.44	4.0 - 9.1	0.99 - 2.3	0.0023 - 0.29	0.0012 - 0.29
28	-2.5	0.014 - 0.023	0.087 - 0.11	0.31 - 0.33	8.40 - 64.8	14.2 - 18.2	0.47 - 2.7	0.75 - 2.0	0.58 - 2.76	0.26 - 0.86
28	-100	0.013 - 0.036	0.073 - 0.20	0.24 - 0.37	43.2 - 50.4	10.3 - 11.8	2.3 - 3.4	0.77 - 2.9	0.58 - 1.73	0.12 - 0.58
28	-15,500	0.009 - 0.043	0.16 - 0.24	0.13 - 0.26	15.6 - 48.0	7.68 - 11.3	0.44 - 0.67	0.62 - 1.7	0.58 - 1.15	0.26
37	-2.5	0.015 - 0.018‡	0.097 - 0.17‡	0.29 - 0.36‡	43.2 - 67.2‡	9.84 - 14.6‡	2.4 - 3.1‡	1.3 - 1.8‡	1.44 - 2.02‡	0.29 - 0.43‡
37	-100	0.043 †	0.15 †	0.27 †	26.4 †	8.64 †	5.0 †	2.2 †	0.58†	0.17†
37	-15,500	0.031 - 0.062	0.17 - 0.27	0.15 - 0.26	8.88 - 21.6	7.44 - 8.88	0.94 - 2.5	1.2 - 2.3	0.20 - 0.86	0.14 - 0.29
43	-2.5	0.013 - 0.017‡	0.097 - 0.14‡	0.34 - 0.38‡	55.2 - 69.6‡	11.3 - 15.4‡	2.1 - 2.9‡	0.75 - 0.93‡	1.15 - 3.36‡	0.23 - 0.58‡
43	-100	0.017 - 0.018‡	0.11 - 0.19‡	0.30 - 0.37‡	40.8 - 52.8‡	9.84 - 14.4‡	1.3 - 2.7‡	0.92 - 1.0‡	1.15 - 2.02‡	0.29 - 0.58‡
43	-15,500	0.020 - 0.035	0.14 - 0.35	0.14 - 0.34	13.9 - 26.4	5.76 - 11.8	1.5 - 2.6	1.1 - 2.0	0.26 - 2.02	0.086 - 0.86

3

4 † Only one measurement due to clogging and ponding of columns

5 ‡ Only two measurements due to clogging and ponding of columns

6

1 **FIGURE CAPTIONS**

2 Fig. 1. Illustration of pretreatment procedures and tracer experiment.

3

4 Fig. 2. Fig. 1. Experimental setup consisting of soil column (10 cm in diameter, 8 cm length),
5 irrigation device connected to a precision pump, column base with a nylon mono-filament screening
6 fabric (31 μm), resting on a 2 mm stainless steel grid, collection vacuum chamber with outlet
7 connected to a Mariotte device controlling the suction, rubber tube with two-piece pressure
8 controlled open-closing device, and fraction collector.

9

10 Fig. 3. Response of matric potential on (a) water retention characteristics, and (b) air permeability.
11 Equivalent pore diameter of (a) water occupied, and (b) air-filled pores corresponding to the applied
12 pressure potential is illustrated at the second x-axis. Error bars: $\pm\text{SE}$.

13

14 Fig. 4. Pore structure characteristics determined at -100 hPa as a function of clay content and initial
15 matric potential (IMP) before (initial) and after (final) the tracer experiment: (a-c) measured air-
16 filled porosity, $\varepsilon_{a,100}$, (d-f) measured air permeability, $k_{a,100}$, (g-i) estimated equivalent pore
17 diameter, d_{100} , and (j-l) estimated number of pores $\geq 30 \mu\text{m}$, n_{100} . Error bars: $\pm\text{SE}$ correspond to
18 measurements on three replicate columns for each clay soil.

19

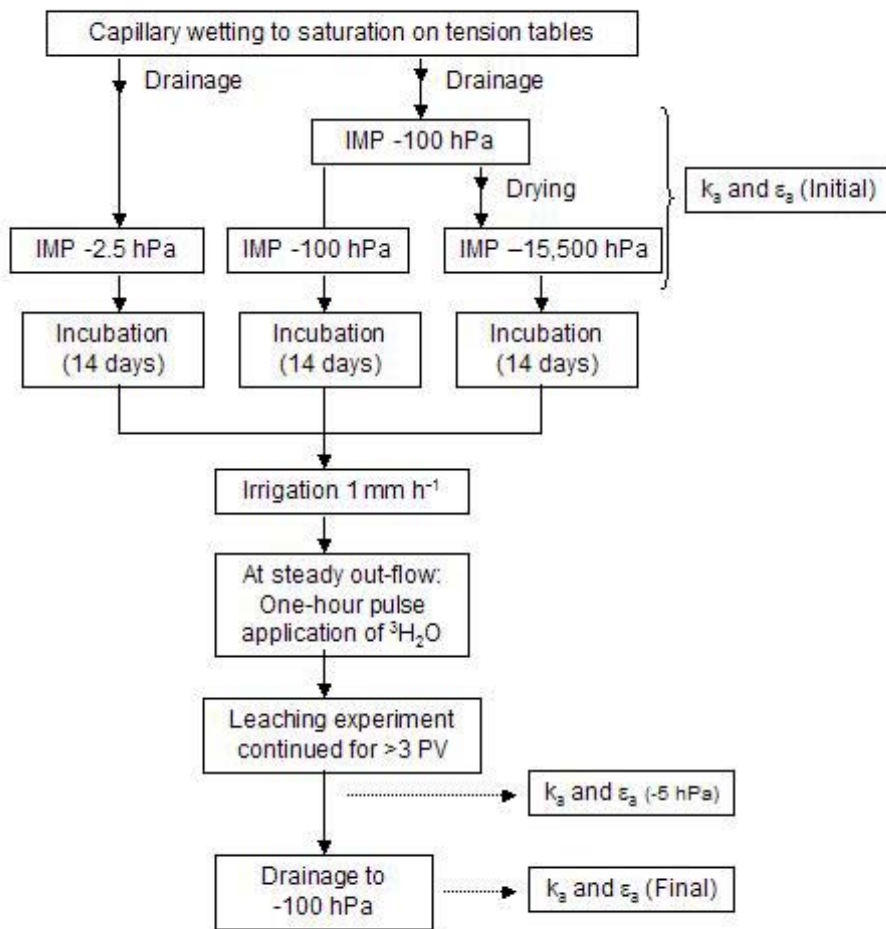
20 Fig. 5. Tritium ($^3\text{H}_2\text{O}$) breakthrough curves plotted as relative concentration (C/C_0) against number
21 of eluted pore volumes (V/V_0) as a function of clay content and initial matric potential (IMP) of
22 -2.5, -100 and -15,500 hPa. Dotted line marks one pore volume. Replicates corresponding to
23 measurements on three replicate columns are represented by different symbols.

24

1 Fig. 6. Selected tritium ($^3\text{H}_2\text{O}$) breakthrough curves plotted as relative concentration (C/C_0) against
2 number of eluted pore volumes (V/V_0) with calculated best fit using either (a) the mobile-immobile
3 model (MIM), or (b-f) the two mobile – one immobile model (2MIM) and the mobile-immobile
4 model (MIM). Note that two different x- and y-axis are used.

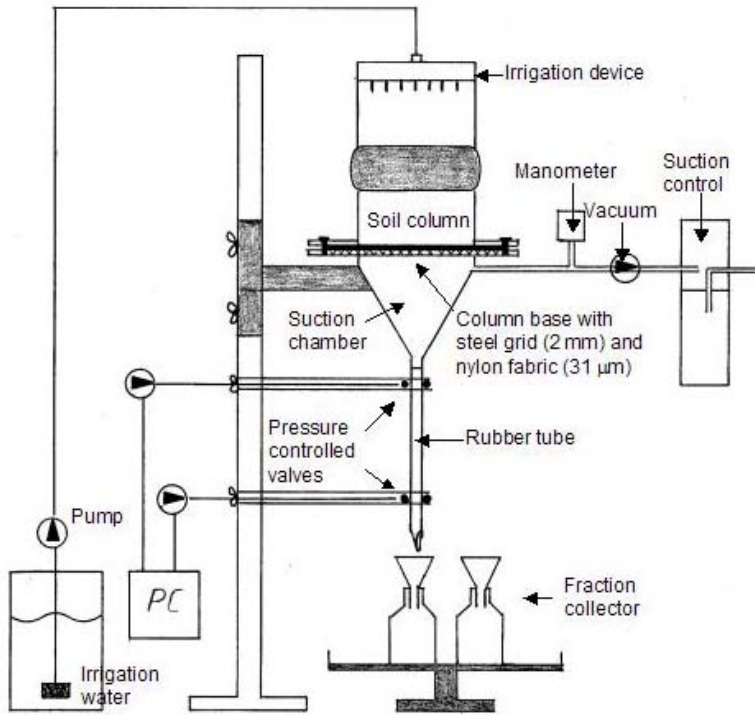
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1 **Figure 1.**



2

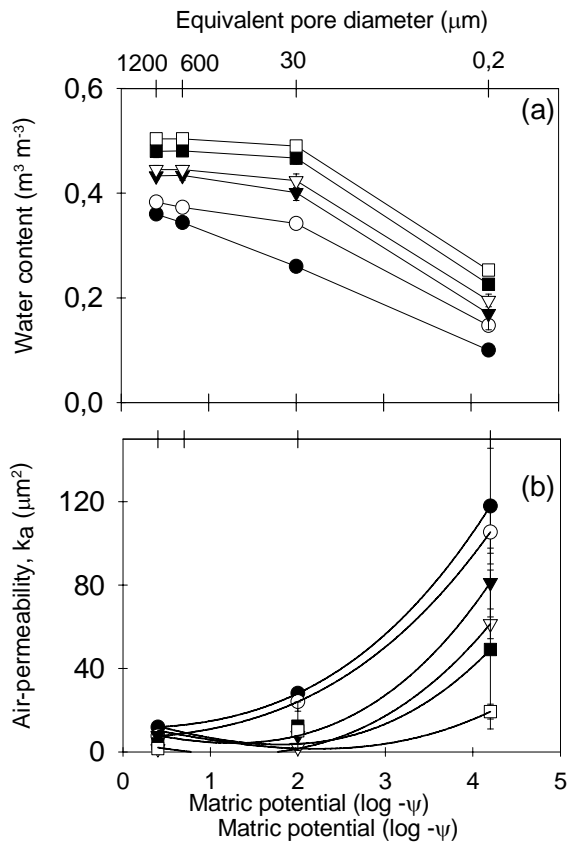
1 **Figure 2.**



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4

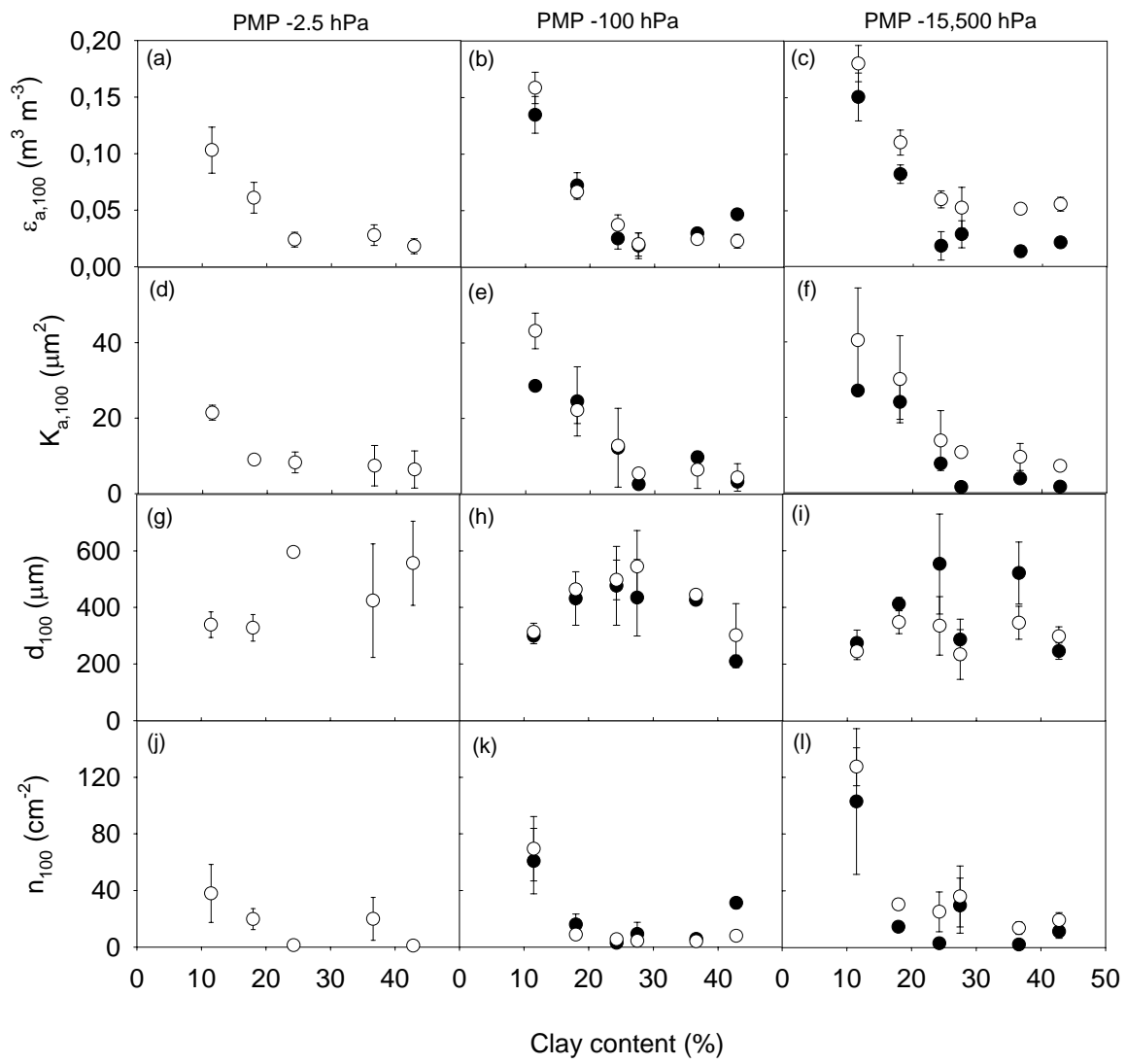
1 **Figure 3.**

2



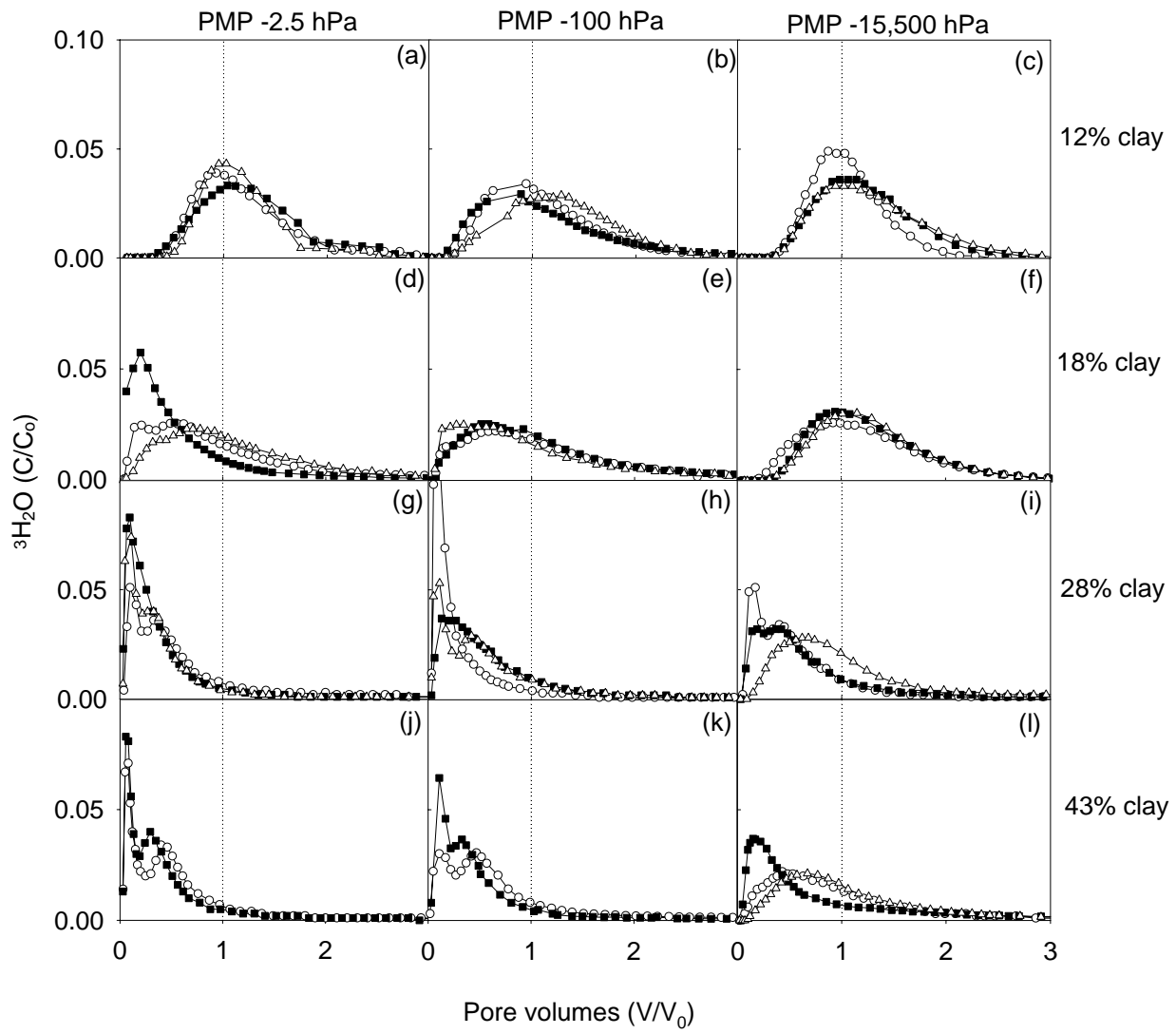
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1 **Figure 4.**



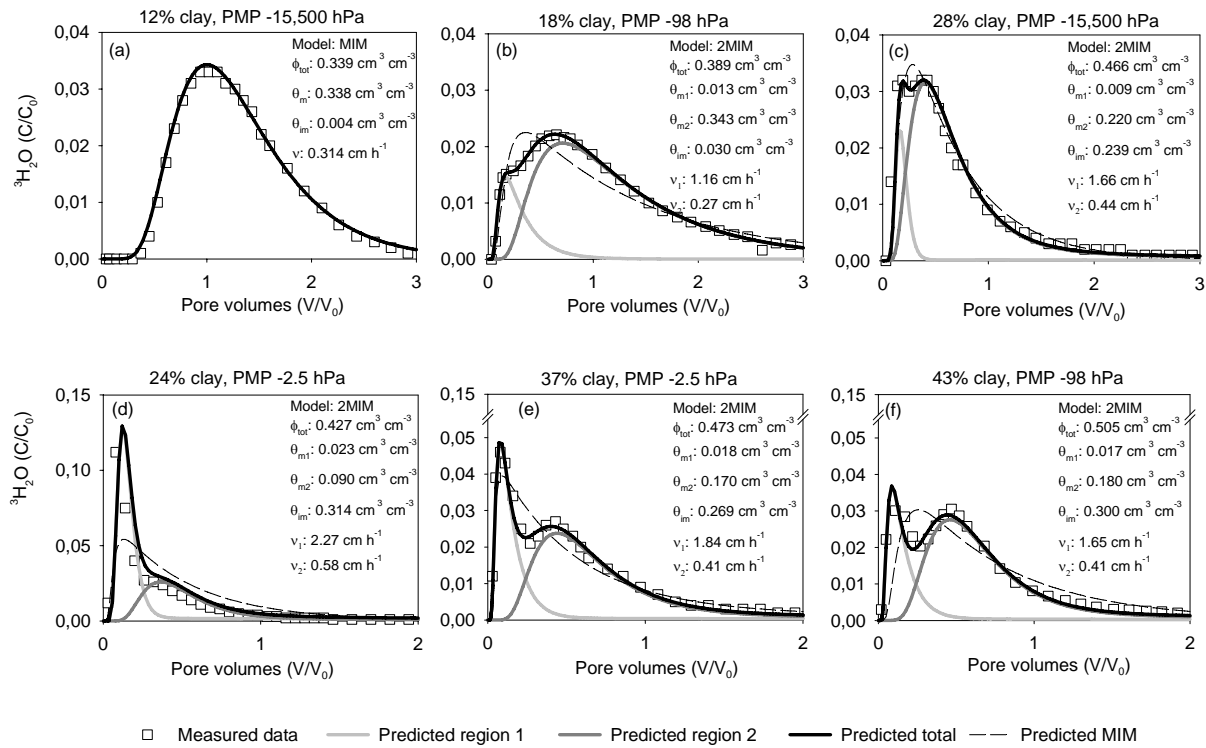
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1 **Figure 5.**



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Figure 6.



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Colloid mobilization and transport in undisturbed soil columns. II. The role of colloid dispersibility and preferential flow

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Colloid mobilization and transport in undisturbed soil columns. II. The role of colloid dispersibility and preferential flow

ABSTRACT

This study investigates *in situ* colloid mobilization and leaching from unsaturated, undisturbed soil columns in order to evaluate the processes controlling colloid mobilization in structured soils. A total of 54 soil columns sampled along a natural clay gradient representing six clay contents (12, 18, 24, 28, 37 and 43% clay) were equilibrated to three different initial matric potentials (IMP) $\psi = -2.5$ (wet), -100 (moderate wet) and $-15,500$ hPa (dry) followed by five days of irrigation at 1 mm h^{-1} and applying a suction of 5 hPa at the lower boundary. The results revealed that: (i) colloid leaching from the initially wet and moderate wet soils decreased with increasing clay content, (ii) colloid leaching from the initially dry soils was low and independent of clay content, (iii) the leaching of total organic carbon (TOC) consisted mainly of dissolved organic carbon (DOC), and drying to $-15,500$ hPa increased the leaching of carbon. *In situ* colloid mobilization and leaching was related to measurements of low-energy water-dispersible colloids (LE-WDC). Results indicate that *in situ* colloid mobilization from the initially wet and moderate wet 12% clay soils subjected to matrix- dominated flow behavior, was controlled mainly by the time-dependent increase in colloid dispersion, while colloid mobilization from the initially dry soils was limited by the strong and persistent association created during the drying. At the more clayey soils, which were dominated by preferential flow, a lower displacement of high-ionic strength soil-water with low-ionic strength rainwater may contribute to the inherently lower dispersibility in controlling colloid mobilization.

List of abbreviations:

BTC: Breakthrough curve; DOC: Dissolved organic carbon; EC: Electrical conductivity; IMP: Initial matric potential; LE-WDC: Low-energy water-dispersible colloids; POC: Particulate organic carbon; SAR: Sodium adsorption ratio; TOC: Total organic carbon; WDC: Water-dispersible colloids.

INTRODUCTION

It is generally recognized that mobile soil colloids may facilitate the transport of strongly sorbing contaminants through the vadose zone (de Jonge et al., 1998, 2000; Sprague et al., 2000; Villholth et al., 2000; Petersen et al., 2003). Results from field studies have demonstrated that soil colloids may be released to drainage water in high concentrations during rainfall events (Ryan et al., 1998; El-Farhan et al., 2000; Villholth et al., 2000; Petersen et al., 2003). Most of our present knowledge concerning the mechanisms of colloid mobilization and transport has been obtained from saturated model systems or repacked soil (e.g. review by Ryan and Elimelech, 1996; Kretzschmar et al., 1999). Such studies have demonstrated that colloid mobilization is directly controlled by solution ionic strength and pH affecting the electrostatic repulsion between colloids (e.g. Grolimund and Borkovec, 1999; Flury et al., 2002). Additionally, physical perturbations such as hydrodynamic shear stress generated by the flowing water (Kaplan et al., 1993), flow transients such as temporal variability in moisture content and the movement of air-water interfaces (Saiers and Lenhart, 2003), and colloid diffusion (Ryan and Gschwend, 1994) has been suggested to control the mobilization and transport of colloids in these systems.

Natural structured soils differ from the homogeneous systems in two important aspects: (i) the complex association of colloids in aggregates of varying size and stability determining the inherent ability of colloids to disperse in response to infiltration of low-ionic strength rainwater, and (ii) the profound effect of pore structure on the active flow volume of the infiltrating water, affecting both *in situ* colloid mobilization and the subsequent transport of mobilized colloids. Dispersion is the ultimate state of aggregate breakdown that results in release of colloids as a consequence of expanding double layers and dominating repulsive forces as described by the DLVO theory (Derjaguin and Landau, 1948; Verwey and Overbeek,

1948). The fraction of colloids that disperses in water (water-dispersible colloids, WDC) has been used as an input parameter for predicting colloid leaching and colloid-facilitated transport through the vadose zone (Jarvis et al., 1999; Villholth et al., 2000). Besides the well-documented importance of clay mineralogy (e.g. Frenkel et al., 1978; Seta and Karathanasis, 1996) and solution chemistry (e.g. Rengasamy, 1983), total clay content (e.g. Pojasok and Kay, 1990; Brubaker et al., 1992; Kjaergaard et al., 2004a), soil matric potential (e.g. Pojasok and Kay, 1990; Kjaergaard et al., 2004a) and management in terms of crop sequence, application of organic manures, soil tillage and field traffic (e.g. Watts et al., 1996a,b; Schjønning et al., 2002) affect the dispersibility of colloids from aggregates.

It is well known that structural macropores may provide preferential pathways for water flow and suspended colloids (e.g. Smith et al., 1985; Camobrecco et al., 1996), but only few studies have investigated the actual *in situ* colloid mobilization and transport in undisturbed soil columns (Jacobsen et al., 1997; de Jonge et al., 1998; 2000; Lægdsmand et al., 1999; Schelde et al., 2002; de Jonge et al., 2004) or in field studies (Ryan et al., 1998; El-Farhan et al., 2000; Villholth et al., 2000; Petersen et al., 2003). These studies have verified the importance of solution ionic strength and pH in colloid mobilization in structured soils (de Jonge et al., 1998), while the importance of physical perturbations is less clear. Several studies have evaluated the role of colloid mobilization by hydraulic shear following rapid infiltration of water (Jacobsen et al., 1997; Ryan et al., 1998; Schelde et al., 2002; Petersen et al., 2003), and these studies all indicated that *in situ* colloid mobilization in structured soils is not governed by shear stress. The importance of flow transients was demonstrated by El-Farhan et al. (2000) who observed that all peak particle concentrations occurred near either the rising or falling limb of the water flux hydrograph. The authors attributed this to the movement of air-water interfaces during imbibition and drainage, but Schelde et al. (2002) concluded in their study that this was not a

dominant process in controlling colloid mobilization. Jacobsen et al. (1997) suggested that the amount of mobilized particles was limited by colloid diffusion, and Schelde et al. (2002) additionally demonstrated that colloid mobilization in structured soils was a time-dependent and possibly a diffusion-limited process. Most of the studies performed on undisturbed soil columns have attributed the macropores as the source of *in situ* mobilized colloids, but the lack of knowledge concerning the diffusive displacement of high-ionic strength resident water with low-ionic strength rainwater between immobile and mobile water regions does not elucidate the actual role of preferential flow on *in situ* colloid mobilization.

The primary objective of this study was to further evaluate the processes controlling *in situ* colloid mobilization in structured soils. In structured soils inter- and intraaggregate porosity affects the accessibility of the colloids to the infiltrating water and ion diffusion. Based on the conceptual perception that most colloids are associated in aggregates, we hypothesize that *in situ* mobilization of colloids may be controlled by: (i) the diffusive displacement of high-ionic strength intraaggregate water with low-ionic strength infiltration water (Fig. 1a), (ii) the actual dispersibility of the colloids (Fig. 1b), and (iii) the diffusion of colloids from the immobile intraaggregate water to the mobile convective water (Fig. 1c). In this study we investigate colloid mobilization and transport in undisturbed soil columns exposed to a low and frequently occurring irrigation intensity and applying a weak suction to the lower boundary of the soil column, simulating a situation of water infiltration through the upper unsaturated soil horizon where the macropores are not necessarily fully functional. Focus is on total clay content and initial matric potential as key parameters affecting *in situ* colloid mobilization and transport due to the influence of these parameters on colloid dispersibility, shrinkage-swelling phenomena, the active flow volume, and in promoting transient flow conditions along wetting fronts when water infiltrates dry soils.

MATERIALS AND METHODS

Field site and soil characteristics

Intact columns of topsoil were excavated at 10-18 cm depth at six sites along a naturally occurring clay gradient from an arable field at Lerbjerg, Denmark. Site description, sampling procedures and physical characteristics are presented in Kjaergaard et al. (2004b). Basic chemical characteristics of the six sites are presented in Table 1. Exchangeable cations and cation exchange capacity (CEC) on these soils was determined by Schjønning et al. (1999) as the NH_4^+ -equivalents found in the leachate following saturation with NH_4^+ (NH_4OAc , pH 7) (Kalra and Maynard, 1991). Sodium-adsorption ratio (SAR) were calculated from the concentrations of Ca^{2+} , Mg^{2+} and Na^+ in the leachate.

Pretreatment of soil columns

Pretreatment of the soil columns prior to the leaching experiment is described in detail in the companion paper Kjaergaard et al. (2004b). In short, the investigation included six clay contents, 11.5, 18, 24.3, 27.5, 36.6 and 42.8%, and three initial matric potentials (IMP), $\psi = -2.5$, -100 and $-15,500$ hPa, ranging from near saturation to the crop wilting point. The experiment was carried out with three replicates of each combination. The pretreatment procedure involved: (i) saturation of the soil columns by slow capillary wetting on tension tables with electrolyte solution having a chemical composition similar to natural rainwater, (ii) drainage to -2.5 hPa and -100 hPa on tension tables and drying to $-15,500$ hPa by passing through dry air, and (iii) incubation for 14 days at 10°C .

Column leaching experiment and analysis of colloid suspensions

The soil column setup and details of the experimental procedure is explained and illustrated in the companion paper Kjaergaard et al. (2004b). In short, the leaching experiment involved irrigation at 1 mm h^{-1} with an electrolyte solution, having a chemical composition similar to natural rainwater and sampling of effluent at a suction of 5 hPa applied to the lower boundary of the soil. A cloth was placed on the top of the soil core to avoid erosion by raindrop impact. Effluent fractions of 15 ml were collected continuously, weighed and analyzed for colloid concentration, electric conductivity (EC), pH and total organic carbon (TOC). Colloid concentration was determined by turbidity using a Hach 2100AN turbidimeter (Hach, Loveland, CO). Turbidity values (expressed in nephelometric turbidity units, NTU) were converted to colloid concentration using regression equations based on suspensions of low-energy input water-dispersible colloids (LE-WDC) separated from each clay soil. The procedure for separating LE-WDC is described by Kjaergaard et al. (2004a). Calibration curves were made from stock LE-WDC suspension for each clay soil. A linear correlation existed between colloid concentration and turbidity at turbidity values ≤ 100 NTU, while non-linearity was observed for all clay soils at colloid concentrations above 100 NTU. Electric conductivity was measured directly in all samples, and suspension pH was measured on every 10th sample. Total organic carbon was measured in all samples by carbon combustion using a Total Organic Carbon Analyzer (TOC-5000A, Shimadzu) equipped with a suspended particle kit and coupled to an auto sampler with magnetic stirring. The fraction of leached particulate organic carbon (POC_{leached}) was estimated from the ratio of POC:LE-WDC measured by Kjaergaard et al. (2004a), assuming that the fraction of colloids leached (Col_{leached}) resembles the fraction of LE-WDC:

$$POC_{\text{leached}} = \frac{POC}{LE-WDC} \times Col_{\text{leached}} \quad [1]$$

The fraction of dissolved organic carbon (DOC) was calculated as the difference between TOC and POC. Leached colloid concentration, TOC and POC is plotted against number of eluted pore volumes (V/V_0) where V is the out-flow volume (m^3), and V_0 is the water-filled porosity ($m^3 m^{-3}$) at -5 hPa.

RESULTS

Initial conditions and active flow volume

The development of effluent flow rate as a function of time after initiation of rainwater irrigation to the soils with different initial matric potentials is illustrated for 12 and 43% clay in Figure 2. Before application of a 5 hPa suction the soils were allowed to wet up by irrigating with low-ionic strength rainwater at 1 mm h^{-1} until effluent was collected from the soils. Soils incubated at -2.5 hPa were initially close to saturation and effluent was collected after about 2-3 hours of irrigation (Fig. 2a,d). For the soils incubated at -100 hPa the pore-size fraction $\geq 30 \mu\text{m}$ was initially drained, and the soils were allowed to moisten by irrigating with rainwater (Fig. 2b,e). This implies that when leaching started from these soils, the resident soil-water in the pore fraction $\geq 30 \mu\text{m}$ had already been displaced by more dilute low-ionic strength rainwater compared to the soils at IMP -2.5 hPa. Effluent was collected after 2-6 hours irrigation. When a 5 hPa suction was applied to the bottom of the soil columns, a steep increase in effluent flow-rate was observed reflecting the drainage of pores with an equivalent diameter larger than $600 \mu\text{m}$. After application of suction the effluent flow rate rapidly stabilized in the range $\pm 0.5 \text{ ml h}^{-1}$ from the mean. The rapid stabilization of the effluent flow rate for the soils incubated at IMP -2.5 hPa and -100 hPa indicates that no further wetting of the soil columns took place after application of suction.

For the soils at IMP -15,500 hPa wetting took place during the first part of the experiment (Fig. 2c,f). For these soils the pore-size fraction $\geq 0.2 \mu\text{m}$ was initially drained, and 8-12 hours of irrigation was applied to the heavy clay soil (43% clay) compared to 20-22 hours irrigation to the 12% clay soils before effluent was collected. When suction was applied to the 12% clay soils, there was a small increase in effluent flow rate followed by a moderate, rapid build-up of the flow rate to a constant out-flow, except for one of the replicates that had a markedly lower effluent flow. No increase in effluent flow rate was observed when suction was applied to the high clay soil (43% clay), and the flow rate increased steadily during the next 21-25 hours until a constant out-flow occurred (Fig. 2f).

A thorough analysis of the active flow volume in these soil columns in terms of tritium ($^3\text{H}_2\text{O}$) breakthrough experiments was presented by Kjaergaard et al. (2004b). Here it was found that the 12% clay soils exhibit matrix-dominated flow behavior, while soils with $\geq 18\%$ clay exhibit an increasing degree of preferential flow with increasing clay content. This is illustrated by the number of pore volumes eluted when 12.5% of the applied tritium has been leached (Fig. 3). Drying to -15,500 hPa and re-wetting significantly reduced the degree of preferential flow for all soils (Fig. 3) and resulted in matrix dominated flow behaviour at 18 and 24% clay. No differences in the BTC's were found between soils with IMP -2.5 and -100 hPa.

Mobilization and leaching of colloids and organic carbon

Clay content and initial matric potential affected both the effluent concentration of colloids and the general leaching pattern as illustrated at 12, 18, 28 and 43% clay with IMP -2.5, -100 and -15,500 hPa (Fig. 4). The leaching pattern at 24 and 37% clay was similar to the leaching pattern at 28 and 43% clay. Two important features should be noted from these leaching

curves. First, at lower clay content (<24% clay) colloid leaching differed among clay contents and initial matric potentials with respect to both leaching pattern and colloid concentration (Fig. 4a-f). Colloid leaching from the initially wet (IMP -2.5 hPa) and moderate wet (IMP -100 hPa) soils increased during at least part of the experiment with maximum effluent concentrations observed from the moderate wet soils. In contrast colloid concentration from the initially dry soils (IMP -15,500 hPa) decreased continuously to a constant low value (5-20 mg L⁻¹) after about two pore volumes of leaching. Colloid leaching from the wet and moderate wet 12% clay soils seemed to have reached the maximum concentration after one to three pore volumes of leaching (Figure 4a,b), while it was less clear if colloid leaching from the wet and moderate wet 18% clay soils reached a maximum concentration within three pore volumes of leaching (Figure 4d,e). At the higher clay soils (≥24% clay) colloid leaching generally displayed similar behavior among clay contents and the different initial matric potentials with rapidly decreasing effluent concentrations to constant low values below 20 mg L⁻¹ within the first pore volume of leaching (Fig. 4g-l).

Leaching of TOC from the initially wet and moderate wet 12 and 18% clay soils was fairly constant (15-40 mg L⁻¹) during the course of the experiment (Fig. 5a,b,d,e). In contrast, leaching of TOC from the initially dry soils displayed a very high initial concentration followed by a gradual decline (Fig. 5c,f). The increase in leaching of carbon following drying may be a consequence of microbial death and lysis of microbial cells (Denef et al., 2001). At the higher clay soils (≥24% clay) high initial concentrations (30-70 mg L⁻¹) were generally observed from all soils, declining to fairly constant values (15-40 mg L⁻¹) within one pore volume of leaching (Fig. 5g-l). The estimated amount of POC clearly indicated that DOC constituted the main fraction of carbon leached from all soils irrespective of initial moisture conditions, with POC contributing to less than 10% of the total amount of carbon leached.

These results are in agreement with results of Lægdsmand et al. (1999) who demonstrated that 83-99% of all TOC leached from an undisturbed sandy loam soil is present as DOC.

The average accumulated amount of colloids and carbon leached after three pore volumes is depicted in Figure 6 as a function of clay content and initial matric potential. From the accumulated leaching of colloids (Fig. 6a) some important features should be noticed: (i) For initially wet and moderate wet soils, the accumulated mass of colloid leached decreased with increasing clay content from 49 mg (IMP -2.5 hPa) and 74 mg (IMP -100 hPa) at 12% clay to a minimum of 7-19 mg at $\geq 24\%$ clay. (ii) Leaching of colloids from initially dry soils was low (11-24 mg) and independent of clay content. (iii) Initial matric potential affected colloid leaching only at lower clay contents (12 and 18% clay), and the largest amounts of colloids were leached from initially moderate wet soils. From the accumulated leaching of carbon (Fig. 6b) two important features should be noticed: (i) For initially wet and moderate wet soils the accumulated leaching of carbon (16-23 mg) was independent of clay content and initial matric potential, and (ii) carbon leaching from the initially dry soil generally increased (25-49 mg), and this increase was more pronounced at lower clay contents ($\leq 24\%$ clay) compared to higher clay contents.

DISCUSSION

The role of flow transients and preferential flow

Most studies investigating *in situ* colloid mobilization from structured soils have reported high initial concentrations followed by a rapid decline to constant low concentrations (Jacobsen et al., 1997; Ryan et al., 1998; Schelde et al., 2002; de Jonge et al., 2004). This has been suggested to be caused by creation of shear stress by the first flow of water, or flow transients such as temporal variability in moisture content, pore water velocity and preferential sorption

of colloids to moving air-water interfaces (Saiers and Lenhart, 2003). Several studies have evaluated the possible role of hydraulic shear following rapid infiltration of water on *in situ* colloid mobilization (Kaplan et al., 1993; Jacobsen et al., 1997; Ryan et al., 1998; Petersen et al., 2003). Kaplan et al. (1993) suggested that colloid mobilization by hydraulic shear was a possible mechanism of colloid release in reconstructed soil pedons, but no studies on natural undisturbed soils have supported this suggestion. Jacobsen et al. (1997), Ryan et al. (1998) and Petersen et al. (2003) observed no or negative correlations between infiltration velocity and particle concentration, indicating that the *in situ* mobilization in structured soils was not controlled by hydraulic shear. Examining the effect of flow interruptions on colloid mobilization from undisturbed sandy loam soil columns Schelde et al. (2002) clearly demonstrated that colloid mobilization in their experiments was not controlled by hydrodynamic shear, but was a time-dependent and possibly a diffusion-limited process.

In the present study the high initial flush of colloids followed by a rapid decline to a constant low level observed mainly at clay contents $\geq 24\%$ clay (Fig. 4 g-l) coincides with the application of suction and the simultaneous drainage of pores with an equivalent diameter larger than 600 μm . Thus, it is highly likely that the initial flush of colloids we observed at the beginning of the leaching experiment, in agreement with other studies (Jacobsen et al., 1997; Ryan et al., 1998; Schelde et al., 2002) resulted from the build-up of colloid concentration in the mobile region during non-flow periods allowing time for colloid diffusion from immobile to mobile water as suggested by Schelde et al. (2002). The combination of a high degree of preferential flow (i.e. a large fraction of immobile water) and the rapid decline to constant low concentrations at clay contents $\geq 24\%$ clay, may indicate that the supply of colloids was limited at least partly by either a low-diffusive displacement of high-ionic strength soil-water with low ionic strength rainwater impeding colloid dispersion, or by colloid diffusion from immobile to

mobile water. In contrast, the matrix-dominated flow behavior at 12% clay and a minor degree of preferential flow at 18% clay combined with the increase in colloid leaching, at least during part of the experiment, suggests that the larger active flow volume results in a larger source area of colloids, that may partly explain the higher colloid leaching in these soils.

High initial flush of colloids has also been attributed to flushing of colloids sorbed to moving air-water interface (e.g. El-Farhan et al., 2000). El-Farhan et al. (2000) attributed peaks in particle concentrations occurring near the rising or falling limb of the water flux hydrograph to the movement of air-water interfaces during imbibition and drainage. Not considered by these authors was that changes in pore water velocity during imbibition and drainage have changed the active flow volume and thereby the source area of colloids. At present no studies on undisturbed structured soils have documented the actual role of colloid transport by moving air-water interfaces. Schelde et al. (2002) concluded that even if air-water interfaces contributed to the initial flush of colloids, this was not a dominant process in colloid mobilization compared to the time-dependent and rate-limiting processes of colloid release. In this study, the observed decline in colloid concentration coinciding with the rewetting of the initially dry soils at 12 and 18% clay does not agree with the suggestion that transient flow regimes should increase colloid mobilization.

The observed leaching patterns with either increasing or declining colloid concentrations indicate the role of the active flow volume on *in situ* colloid mobilization, but it was not possible to explain the differences in colloid leaching behavior observed for the replicate soil columns at 12% clay, nor to explain the differences in colloid leaching between different initial matric potentials at 12% clay from the knowledge of the active flow volume in these soils (Kjaergaard et al., 2004b). The differentiation of replicate soil columns with respect to leaching

pattern, and the differences among soils with different initial matric potentials suggest differences in aggregate stability and colloid dispersibility.

The role of colloid dispersibility

Investigation of colloid dispersibility (Kjaergaard et al., 2004a) demonstrated that the amount of LE-WDC decreased with increasing clay content as a result of increased aggregate stability, and decreased with decreasing initial matric potential as a consequence of increased interparticle bonding or cementation upon drainage and drying (Fig. 6c). When drying was severe (IMP -15,500 hPa) colloid dispersibility was low and independent of clay content, and the response of colloid dispersibility to drainage and drying persisted even after one week of slow re-wetting. These results may at least partly explain the observed decline in colloid leaching as clay content increases from the initially wet and moderate wet soils, and the clay-independent leaching after drying to -15,500 hPa (Fig. 6a). Several possible mechanisms of colloid mobilization may explain the initial high leaching of colloids when rewetting the dry soils (Fig. 4). First, when dry aggregates are rewetted, they may break down by a combination of physicochemical dispersion and slaking, which is disintegration caused by compression of entrapped air during wetting (Le Bissonnais, 1996). The results from Kjaergaard *et al.* (2004a) documented that the amount of LE-WDC from these soils significantly increased as a result of aggregate breakdown by slaking upon fast rewetting. Second, it is possible that the initial high leaching of DOC (Fig. 5) may facilitate the mobilization of mineral colloids. The rapid depletion of mobile colloids indicates, however, that the drying has introduced very strong associations among colloids, and these associations are not easily broken even after prolonged leaching of low-ionic strength rainwater.

The measurements of LE-WDC documented that colloid dispersibility decreased as the initial matric potential decreased (Fig. 6c), but the actual mobilization and leaching of colloids from the undisturbed soil columns was largest from the initially moderate wet soils (Fig. 4 and 6a). The explanation for this deviation is differences in the pre-treatment procedure between the two types of experiments. As explained earlier in this paper, when leaching started from the initially moderate wet undisturbed soil columns the soil-water in the pore fraction $\geq 30 \mu\text{m}$ was already displaced with more dilute low-ionic strength rainwater compared to the initially wet soils. This implied that the initially moderate wet soils were already more dispersed, explaining the higher colloid leaching from these soils (Fig. 4b,e). When measuring LE-WDC the soil samples incubated at -2.5 hPa were shortly drained to -100 hPa prior to measurement and subsequently re-saturated with low-ionic strength water, in order to have similar treatments with respect to changes in electrolyte composition for the samples at -2.5 and -100 hPa (Kjaergaard et al., 2004a). This means that the measurements of LE-WDC reflect the sole effect of initial soil-water content on colloid dispersion, while differences in colloid leaching between initially wet and moderate wet samples are influenced by differences in the initial pore water ionic strength.

Measurements of LE-WDC (Fig. 6c) also demonstrated an effect of initial matric potential on colloid dispersibility for all clay soils. The accumulated colloid leaching (Fig. 5a), however, showed no effect of initial matric potential at higher clay contents ($\geq 24\%$). This is probably a consequence of pores $>30 \mu\text{m}$ constituting a decreasing fraction of the pore volume with increasing clay content (Kjaergaard et al., 2004b), which consequently minimizes the effect of drainage of this pore fraction.

Mechanisms for *in situ* colloid mobilization

To evaluate the time-dependency of colloid mobilization, the cumulative mass of colloids has been plotted against the square root of time for the different initial matric potentials at 12, 18 and 28% clay (Fig. 7). In addition, the time-dependent changes in the electric conductivity of the effluent water are illustrated. Generally, the curves for accumulated colloid mass leached seemed non-linear within the first part but attained linearity after some time, indicating that colloid mobilization after some leaching is rate-limited. Several authors have demonstrated that colloid leaching in structured soils is time-dependent and possibly limited by diffusion (Jacobsen et al., 1997; Lægdsmand et al., 1999; Schelde et al., 2002). However, dispersion of colloids from aggregates may also be time-dependent in a dynamic system, where the ionic strength of the intraaggregate soil-water gradually decreases due to continued infiltration and displacement of high-ionic strength soil-water with low-ionic strength rainwater.

The results presented in this study and the above discussions lead to the conclusion that different mechanisms may be responsible for controlling colloid mobilization and leaching depending on both the clay content and the initial matric potential. In our experimental system we found the following interpretation of the different processes controlling colloid mobilization: (i) At 12% clay (IMP -2.5 and -100 hPa), displacement of high-ionic strength resident water with low-ionic strength rainwater gradually increases colloid mobilization as leaching approaches one pore volume. As a result of the matrix-dominated flow behavior all resident soil-water was displaced after about one pore volume of leaching and colloid mobilization was clearly time-dependent. The steeper slope of the IMP -100 hPa leaching curves (Fig. 7b) indicates that these soils were initially more dispersed compared to the soils at IMP -2.5 hPa (Fig. 7a). This suggests that colloid mobilization at IMP -2.5 hPa may be limited by colloid dispersion from aggregates, with a gradual increase in colloid mobilization as

irrigation with low-ionic strength rainwater continues. At IMP -15,500 hPa colloid mobilization was impeded by the strong associations resulting from the drying. (ii) At 18% clay (IMP -2.5 and -100 hPa) the colloid dispersibility was reduced compared to the 12% clay soils, and the preferential flow behavior suggests that a lower diffusive displacement of high ionic-strength intraaggregate water with low-ionic strength rainwater may have contributed to the reduced colloid leaching. Again the steeper slopes of the IMP -100 hPa leaching curves having initially lower pore-water ionic strength supported this assumption. At IMP -15,500 hPa colloid dispersion was impeded by the strong associations resulting from the drying. At higher clay content (28% clay), colloid mobilization was partly limited by the inherent low dispersibility (Fig. 6c) resulting from either a high volume of clay (IMP -2.5 and -100 hPa) or stronger colloid associations upon drying (-15,500 hPa), and partly by a low diffusive displacement of high ionic-strength intraaggregate water with low-ionic strength rainwater. In addition, colloid diffusion from immobile to mobile water may limit colloid leaching. We could not single out the importance of diffusion-limited displacement of high-ionic strength resident water with low-ionic strength rainwater, nor the eventually diffusion-limited transfer of colloids from the immobile to mobile water regions, since the stronger cohesive forces already impeded colloid dispersibility.

We find that straining was not likely to cause the reduced leaching of colloids from the higher clay soils. First, measurements of LE-WDC showed that the inherent dispersibility of these soils was already very low (Fig. 6c), and second, the results from the $^3\text{H}_2\text{O}$ -BTCs indicated that only a minor fraction of large pores contributed to the active flow volume of these soils minimizing the possibility of significant straining (Kjaergaard et al., 2004b). In contrast, it is important to note that we observed the largest colloid leaching from soils having matrix-dominated flow behavior, suggesting that colloid transport is not exclusively related to large

structural macropores. The role of preferential flow deduced from this study may also explain the general observed colloid leaching behavior from structured soils (e.g. Jacobsen et al., 1997; Ryan et al., 1998; Schelde et al., 2002). In these studies preferential flow was promoted by zero-tension lower boundaries and high irrigation intensities promoting a high degree of preferential flow, which may consequently result in the macropores being the primary source of mobile colloids and lead to a rapid depletion in effluent colloid concentration. During declining flow intensities (e.g. El-Farhan et al., 2000) or non-flow periods (e.g. Schelde et al. 2002) the rate of ion displacement among immobile and mobile water regions would increase, resulting in supply or replenishment of mobile colloids.

CONCLUSION

The results from this study have revealed the complexity in the process of colloid mobilization with respect to the interacting effect of inherent (soil clay content) and dynamic (ionic strength, initial matric potential and degree of preferential flow) soil properties. From this study the primary factor controlling *in situ* colloid mobilization in structured soils seemed to be the ability of colloids to disperse in response to low-ionic strength rainwater. Accumulated colloid leaching was largest when both the colloid dispersibility and the diffusive displacement of high-ionic strength resident water with low-ionic strength rainwater were high. The results supported the hypothesis that *in situ* colloid mobilization in structured soils may be limited by either/or: (i) the time-dependent increase in colloid dispersion due to continued infiltration of low-ionic strength rainwater (IMP -2.5 at 12 and 18% clay), (ii) a low diffusive displacement of high-ionic strength resident water with low-ionic strength rainwater (IMP -2.5 and -100 hPa at 18% clay), and (iii) a combination of low diffusive displacement of high-ionic strength resident water with low-ionic strength rainwater and reduced colloid dispersibility induced by

either a high volume of clay ($\geq 24\%$ clay) or stronger colloid associations upon drying (IMP - 15,500 hPa for all soils).

Finally, colloid dispersibility should be considered a key parameter when developing predictive models for *in situ* colloid mobilization and colloid-facilitated transport in the vadose zone. The agreements between the LE-WDC estimates and the actual mobilization of colloids indicates that measurements of LE-WDC may be a valuable tool for risk assessments with respect to colloid mobilization.

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Table 1. Basic characteristics of Lerbjerg soils.

Location	Texture class (μm)			Organic-C g kg ⁻¹	CaCO ₃ g kg ⁻¹	pH _{CaCl2}	CEC† mmol _c kg ⁻¹	SAR‡ %
	< 2 ----- g kg ⁻¹	2 -20 g kg ⁻¹	20 - 200 ----- g kg ⁻¹					
L1	115	65	820	10.9	0	6.6	114	0.044
L2	180	85	735	16.7	0	6.7	150	0.036
L3	243	113	644	15.5	0	7.2	181	0.035
L4	275	125	600	17.1	0	7.4	229	0.030
L5	366	99	535	15.5	9.8	7.5	264	0.036
L6	428	108	464	17.4	16.9	7.5	325	0.035

† CEC: Cation exchange capacity (data from Schjøning et al., 1999)

‡ SAR: Sodium adsorption ratio [SAR = Na/(Ca+Mg)^{0.5}, concentration in mmol L⁻¹]

FIGURE CAPTIONS

Fig. 1. Conceptualization of the processes involved in colloid mobilization in structured soils (a) the diffusive displacement of high-ionic strength intraaggregate water with low-ionic strength infiltration water, (b) the actual dispersibility of the colloids, and (c) the diffusion of colloids from the immobile intraaggregate water to the mobile convective water.

Fig. 2. Examples of development of effluent out-flow rates as a function of time after initiation of rainwater irrigation at 12 and 43% clay with initial matric potentials (IMP) of -2.5, -100 and -15,500 hPa.

Fig. 3. Average values of early tritium breakthrough, expressed as the number of pore volumes eluted when 12.5% of the applied tritium has been leached. Error bars: \pm SE.

Fig. 4. Effluent colloid concentration against number of eluted pore volumes (V/V_0) as a function of clay content and initial matric potential (IMP). Replicate columns are represented by different symbols.

Fig. 5. Measured total organic carbon TOC (filled symbols) and estimated particulate organic carbon POC (unfilled symbols) against number of eluted pore volumes (V/V_0) as a function of clay content and initial matric potential (IMP). Replicate columns are represented by different symbols.

Fig. 6. Effect of clay content and initial matric potential (IMP) on (a) accumulated colloid mass leached after three pore volumes, (b) accumulated total organic carbon (TOC) leached after

three pore volumes, and (c) amount of low-energy water-dispersible colloids (LE-WDC) from Kjaergaard et al., 2004a. Error bars: \pm SE.

Fig. 7. Plot of accumulated colloid mass (filled symbols) and electric conductivity EC (open symbols) against square root of time for 12, 18 and 28% clay and initial matric potential (IMP) of -2.5, -100 and -15,500 hPa. Dotted lines mark leaching of one pore volume. Replicates are represented by different symbols.

Figure 1

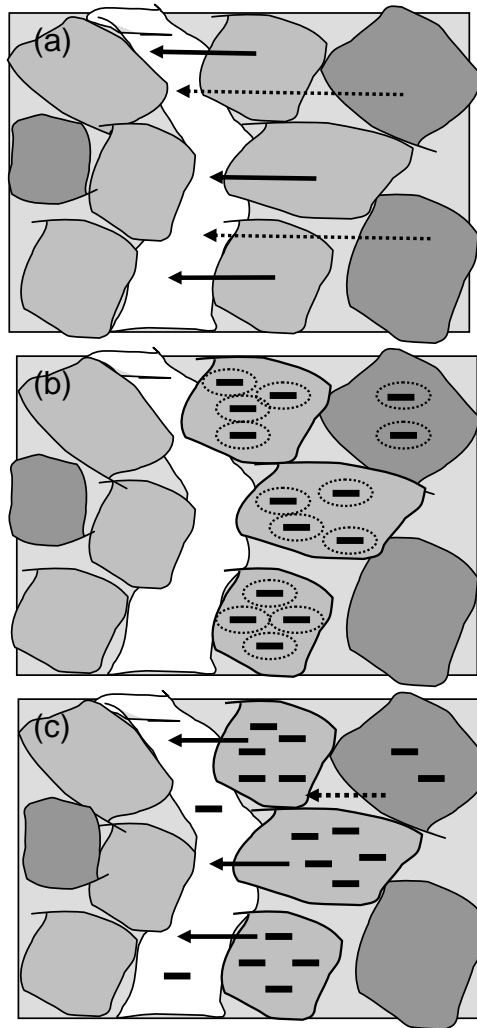


Figure 2

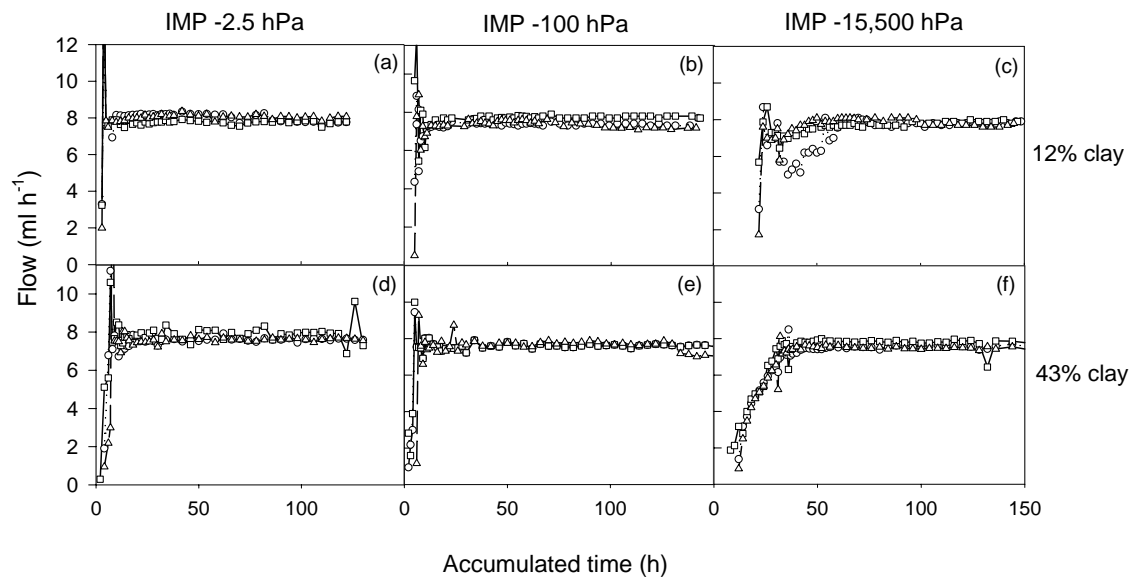


Figure 3.

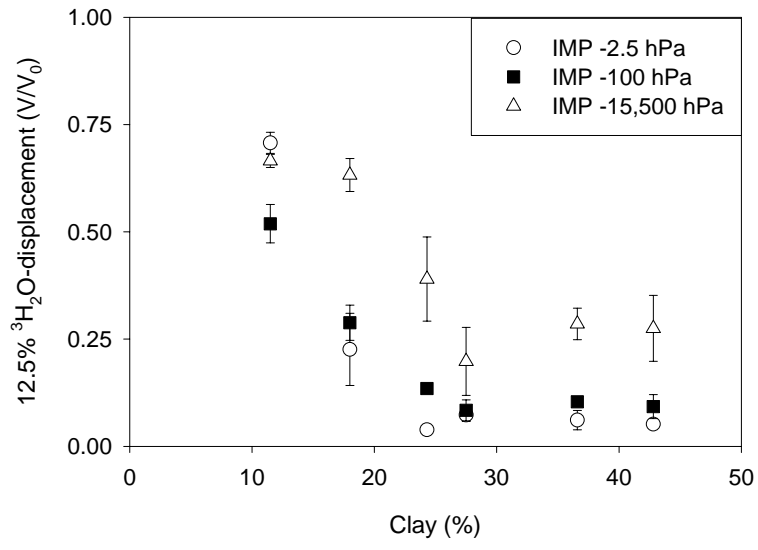


Figure 4

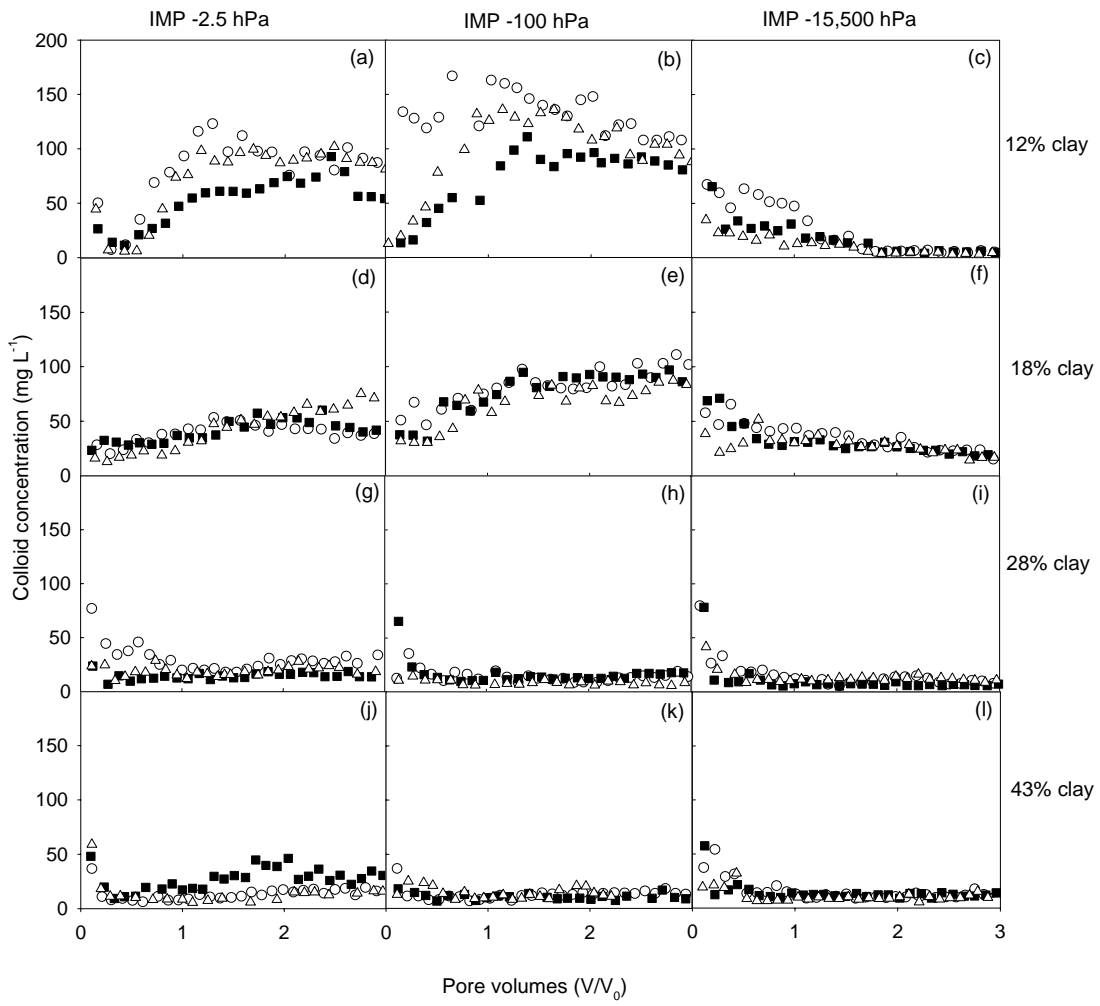


Figure 5.

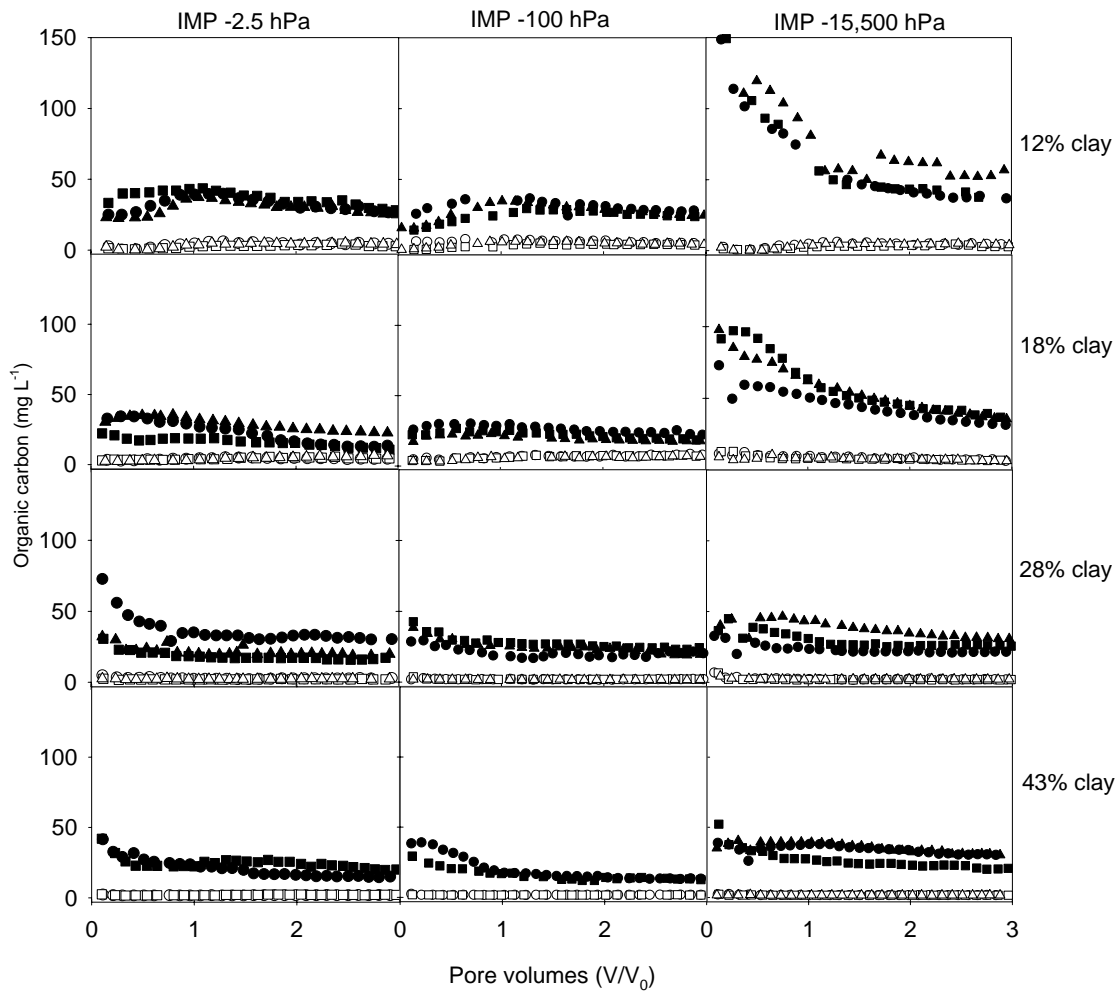


Figure 6.

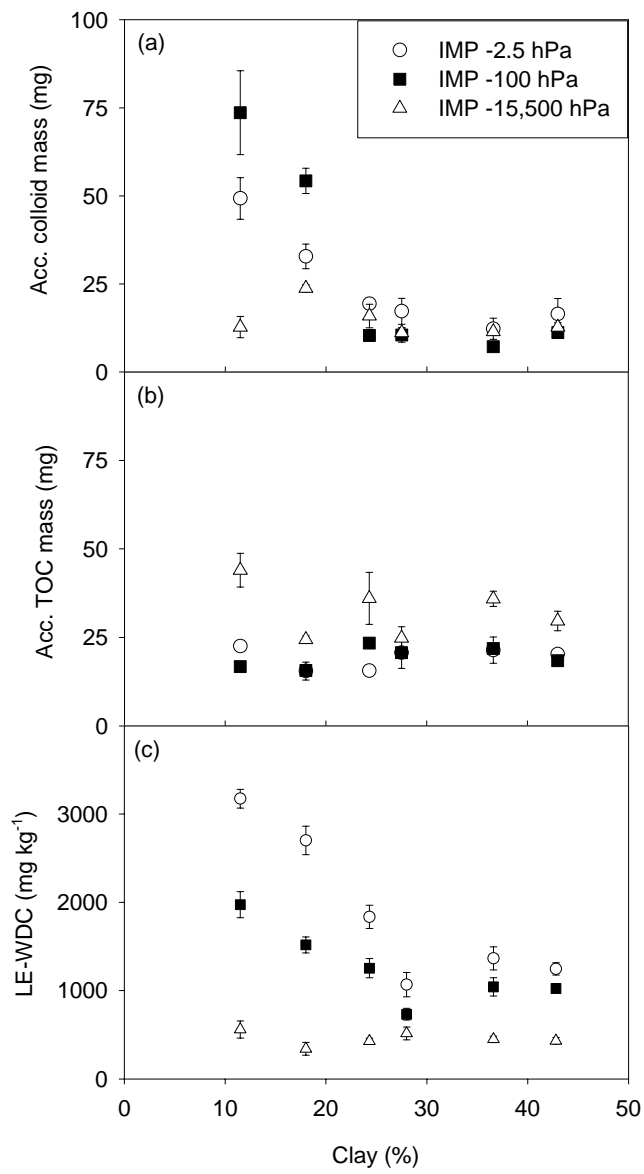
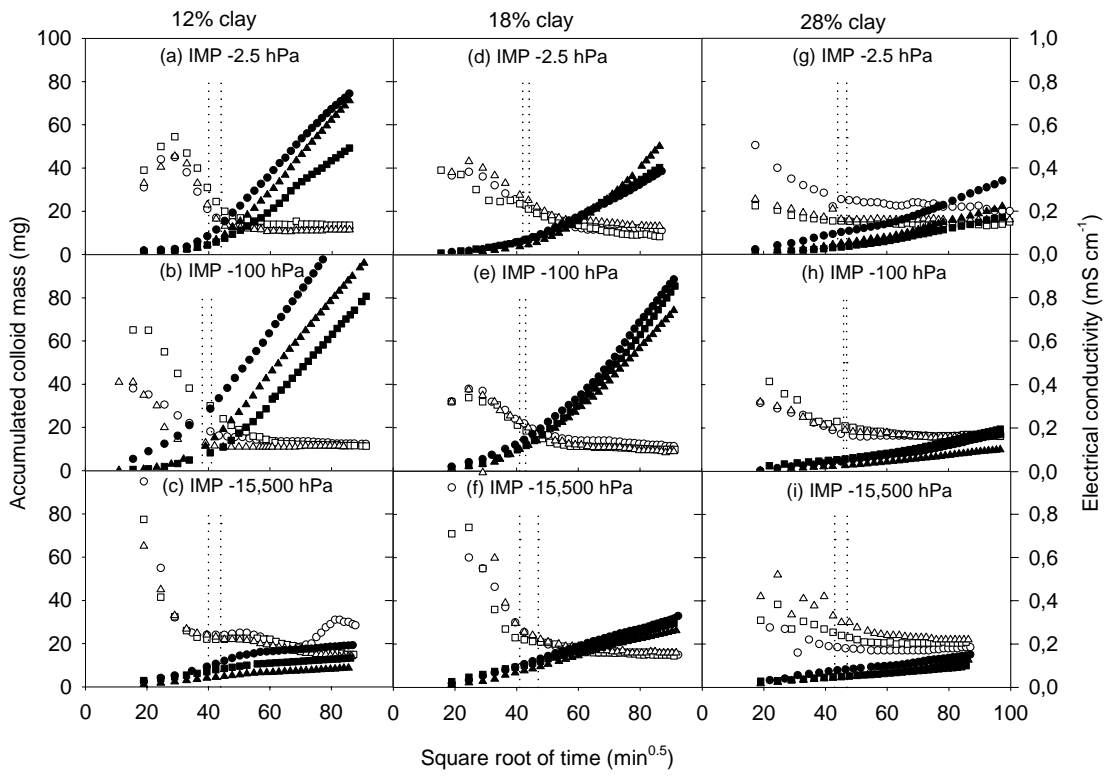


Figure 7



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Stability and physicochemical properties of water-dispersible colloids from macropore deposits
and bulk horizons of an Agrudalf

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Stability and physicochemical properties of water-dispersible colloids from macropore deposits and bulk horizons of an Agrudalf

ABSTRACT

Mobility of colloids depends in part on the release from aggregates and the stability in suspension. This study determined the soil dispersibility of the different horizons in a Typic Agrudalf. Water-dispersible colloids (WDC) from bulk horizons and macropore deposits were characterized for mineralogy and physical chemical properties. The effect of solution pH and ionic strength on ζ -potential and flocculation behavior was evaluated using dynamic light scattering, and the role of colloid associated organic carbon (OC) and sesquioxides were elucidated. The soil dispersibility did not reflect the contrasting physicochemical conditions, but was directly correlated with total clay content. Generally, WDC were enriched in OC and sesquioxides. WDC from the Ap-horizon and from macropore deposits differed markedly from the remaining WDC-fractions due to a significantly higher content of OC (14-35 g kg⁻¹), Al_{CBD} (9.3-10.6 g kg⁻¹) and a much smaller N₂-adsorption surface area (14-25 m² g⁻¹). Treatment with Na₂S₂O₈ for removal of OC increased the surface area by 171-225%, indicating surface coatings of OC. The contribution of OC to the colloidal stability was inferred from: (i) a more negative ζ -potential and larger suspension stability of WDC with larger content of OC, and (ii) reduced negative ζ -potential as well as suspension stability after OC removal. Large variations were observed in the flocculation behavior for WDC with rather similar mineralogical composition. A two-fold increase of the initial particle diameter occurred at an electric conductivity of 91 μ S cm⁻¹ for the least stable colloids and at 1023 μ S cm⁻¹ for the most stable and OC-rich colloids. The effect of solution pH on flocculation was significant only at pH below 4.5.

List of abbreviations:

EC: Electric conductivity; EM: Electrophoretic mobility; MM: Macropore matrix; MP: Macropore deposits; NOM: Natural organic matter; OC: Organic carbon; PSD: Particle-size distribution; WDC: Water-dispersible colloids.

INTRODUCTION

A large number of inorganic and organic soil contaminants are associated with colloids. The fate of these contaminants and consequently their impact on the environment are thus strongly dependent on the nature and behavior of the colloids. The ability of mobile colloids to facilitate the transport of strongly sorbing contaminants, such as pesticides, phosphorous and heavy metals by acting as contaminant carriers has been documented from several laboratory studies (Grolimund et al., 1996; Seta and Karathanasis, 1997; de Jonge et al., 1998, 2000). In addition, results from field studies have demonstrated that soil colloids and associated contaminants may be released to drainage water in high concentrations during rainfall events (e.g. Villholth et al., 2000; Petersen et al., 2003). Thus, mobilization and transport of colloids increases the risk of leaching of strongly sorbing environmental contaminants generally regarded as immobile.

In the vadose zone the majority of colloids are associated in aggregates and released following aggregate breakdown (Le Bissonnais, 1996). Physical-chemical dispersion is the ultimate state of breakdown that results in release of colloids as a consequence of expanding double layers and dominating repulsive forces as described by the DLVO theory (Derjaguin and Landau, 1948; Verwey and Overbeek, 1948). It is generally recognized that the fraction of clay that disperses in water (water-dispersible colloids, WDC) has been found related to soil erodibility (e.g. Brubaker et al., 1992), and WDC has also been used as input parameter for predicting colloid leaching through the vadose zone (Jarvis et al., 1999). From regression analysis comparing a range of soil factors, several studies have identified total clay content as one of the most important properties in determining the amount of WDC (e.g. Pojasok and Kay, 1990; Brubaker et al., 1992). Seta and Karathanasis (1996), however, did not find any correlation between total clay content and the amount of WDC investigating subsurface alfisols, mollisols and ultisols. They argued that the Fe, Al and kaolinite content accounted for most of the

variability in WDC. It is generally recognized that soils dominated by 2:1-layer minerals are dispersed more readily than those dominated by sesquioxides and 1:1-layer minerals (Yaron and Thomas, 1968). The higher dispersibility of soils dominated by 2:1-layer minerals has been attributed to a higher charge density, but Seta and Karathanasis (1996) concluded that the mineralogical composition and surface charge did not explain differences in colloid dispersibility among illitic, montmorillonitic and mixed Alfisols. In natural field soils, the effect of mineralogy may, however, be influenced by the presence of surface adsorbed organic carbon which may mask the direct importance of clay mineralogy. Experimental evidence has suggested that natural organic matter (NOM) adsorbed to soil colloids stabilizes colloid suspensions due to both electrostatic and steric mechanisms (e.g. Kretzschmar et al., 1993; Kaplan et al., 1997; Kretzschmar et al., 1998), and organic coatings have been found to induce colloid stability by steric hindrance at high ionic strength conditions (Hunter, 1987).

Once colloids have been dispersed, they can be transported through natural porous media at a greater velocity than conservative dissolved tracers (Kretzschmar et al., 1995), the transportability being determined both by the pore size of the actively conducting flow pathways and the size and stability of the dispersed colloids in the soil solution. When soil-water containing suspended colloids infiltrates deeper soil layers with changing chemical environment, continued mobility depends on the ability of colloids to resist flocculation and sedimentation. Identification and quantification of the solution and colloidal properties controlling the stability of the potentially mobile colloids is consequently of importance when predicting the susceptibility for colloid leaching to drainage and groundwater.

In Danish clayey till soils where the clay fraction is dominated by 2:1-layer silicates, dispersion and translocation of clay colloids is a natural process and a key phenomenon, resulting in the

development of illuvial subsurface horizons with a higher clay content compared to the upper eluvial horizons. Furthermore, micromorphological features showing deposits of clay skins on ped faces and at the interface of water conducting pores represents evidence of colloid translocation. Conducting a micromorphological analysis of a Typic Agrudalf (Flakkebjerg, Denmark), Rasmussen et al. (2001) observed well-developed clay coatings at the interface of fractures, interaggregatepores and biopores. These observations indicated a pronounced colloidal transport to the depth of 170 cm. The objectives of this study were to: (i) determine the soil dispersibility of the different horizons in the soil profile, (ii) determine the mineralogy and physicochemical properties of WDC isolated from macropore deposits and bulk horizons, and (iii) determine the effect of solution ionic strength and pH and evaluate the role of organic carbon on colloid stability based on measurements of ζ -potential and particle-size distributions.

MATERIALS AND METHODS

Field site and soil characteristics

The investigated soil originates from a site located on a flat glacial plain at Flakkebjerg, Denmark. The top-till is developed on morainic deposits from the Weichsel Glacial Age, and the site has been cultivated for centuries. The soil profile was excavated to a depth of approximately 150 cm, and bulk soil material was sampled over the entire horizon from each horizon in the profile. Intact structures for preparation of thin sections and colloid characterization were collected around pores with visible clay and organic deposits in the BC_{tg} horizon. Special samples comprising macropore deposits (MP-BC_{tg}) and underlying macropore matrix material (MM-BC_{tg}) were separated using a scalpel. Thin sections were prepared from polyester resin impregnated intact structures (Dalsgaard et al., 1981; Murphy 1986). Thin sections were examined with a petrologic microscope (Carl Zeiss Jena – Jenapol). All bulk soil samples were air-dried, gently crushed, sieved at 2 mm, and used for all analysis.

Particle-size distribution of the <2 mm fraction was measured using the Andreasen pipette method after dispersion in sodium pyrophosphate. The content of calcite if present was measured gas-volumetrically. Soil pH was measured in water in a 1:8 soil:water suspension, this soil:solution ratio was used as it represents the same soil:solution ratio used for fractionation of WDC. Cation-exchange capacity at pH 8.1 was determined using the ammonium acetate method (Chapman, 1965). Sodium adsorption ratio (SAR) was calculated from the concentrations of Ca^{2+} , Mg^{2+} and Na^+ in the leachate. Iron (Fe_{CBD} , Fe_{ox}) and aluminium (Al_{CBD} , Al_{ox}) were analyzed after extraction by citrate-bicarbonate-dithionite (CBD) (Mehra and Jackson, 1960), and oxalate (ox) (Schwertmann, 1964). The CBD-treatment was repeated twice to ensure complete removal of oxides. All analysis were made in duplicate except for soil texture. Average values are presented in Table 1.

Fractionation of water-dispersible colloids

The fraction of WDC was separated from the air-dried and sieved bulk samples (Ap, Btg₂ and BCtg) and special samples (MP-BCtg and MM-BCtg) by shaking in deionized water at a 1:8 (w/w) soil:water ratio for 16 h on a reciprocal shaker at 60 rpm. After dispersion, the fraction <20 μm was separated and decanted from the soil suspension by gravity sedimentation. Further fractionation of the decanted suspension in particle size fractions 0.2-2 μm and <0.2 μm was accomplished by centrifugal particle size analysis (Slater and Cohen, 1962).

Each WDC fraction was divided into three portions: One remained intact, the second was treated once with sodium peroxodisulphate (OX) for oxidative removal of organic matter (Meier and Menegatti, 1997), and the third portion received the $\text{Na}_2\text{S}_2\text{O}_8$ treatment followed by a treatment with citrate-bicarbonate-dithionite (CBD) for removal of Fe- and Al-oxides (Mehra and Jackson, 1960). The treatments are subsequently referred to as Intact, OX and OX+CBD.

Oxidation using $\text{Na}_2\text{S}_2\text{O}_8$ was chosen because it is more effective in removing organic matter from clays than procedures employing H_2O_2 , and because it imparts minimum destruction of the inorganic mineral phase (Meier and Menegatti, 1997). All WDC fractions were subsequently saturated with Ca^{2+} by five centrifugal washes with 1 M CaCl_2 . Excess electrolytes were removed by centrifugal washes with deionized water until the electric conductivity (EC) of the supernatant was $\leq 10 \mu\text{S cm}^{-1}$. The WDC-suspensions were stored in polyethylene containers at 4°C until use. The concentration of solids in each colloidal suspension was determined in triplicate as suspension dry weight, after oven drying at 100°C . Subsamples of each WDC fraction were saturated with Mg^{2+} and K^+ , using the same procedure as with CaCl_2 . These samples were subsequently air-dried and used for mineralogical and chemical analysis.

Characterization of water-dispersible colloid fractions

Iron (Fe_{CBD}) and aluminum (Al_{CBD}) were extracted in triplicate from the intact WDC-fractions by CBD treatment (Mehra and Jackson, 1960), and determined using atomic absorption spectroscopy (AAS). Total C and N were determined in duplicate for Intact and OX-treated WDC-fractions using a Europe Scientific mass spectrometer. The mineralogy of the OX+CBD treated fractions was investigated by powder X-ray diffraction (XRD) using a Siemens D 5000 diffractometer and applying $\text{Co-K}\alpha$ radiation at a scanning speed of $0.24^\circ 2\theta \text{ min}^{-1}$. Both unoriented and oriented Mg^{2+} , Mg^{2+} -ethylene-glycol and K^+ saturated specimens were examined, the latter additionally at 350 and 550°C . Powder X-ray diffractograms of the colloid fractions were obtained and semi-quantitative estimation of the clay mineral composition was accomplished according to the procedure described by Ernstsén (1998). Specific surface areas were determined through N_2 -adsorption using a single-point BET method.

Electrophoretic mobility and flocculation behavior

Electrophoretic mobility (EM) and particle-size distributions (PSD) of WDC-suspensions were measured by laser Doppler velocimetry-photon correlation spectroscopy (LDV-PCS) using a Zetasizer3000 instrument (Malvern Instruments, Malvern, England). Measurements of electrophoretic mobility and particle-size distributions were calibrated using latex standards supplied by Malvern Instruments. The mean hydrodynamic diameter (d_H) of colloids and flocs, which by definition is inversely proportional to their diffusion coefficient, is obtained from a cumulant analysis of the autocorrelation function of the scattered light intensity. Zeta potentials (ζ) were estimated from EM measurements (μ) using Helmholtz-Smoluchowski's equation. All analyzes were carried out at $20 \pm 0.5^\circ\text{C}$, and triplicate measurements were recorded for each sample.

Analysis was performed on the Intact, OX and OX+CBD treated WDC-fractions as a function of pH and electric conductivity of CaCl_2 suspensions. Colloidal suspensions for EM and particle-size distribution analysis were prepared from stock suspensions. The stock suspension was diluted in 6 different CaCl_2 concentrations bracketing an EC from 10-1200 $\mu\text{S cm}^{-1}$ to provide colloid mass concentrations of 25 mg L^{-1} for EM measurements and of 100 mg L^{-1} for particle-size distribution measurements. Colloid stability as a function of pH was measured in a background electrolyte concentration of 0.35 mM CaCl_2 (corresponding to an EC of 78 $\mu\text{S cm}^{-1}$), where pH was adjusted to initial values of 3.5, 4.5, 5.5, 6.5, 7.5 and 8.5 by addition of appropriate amounts of HCl or $\text{Ca}(\text{OH})_2$. Suspensions were allowed to equilibrate by shaking on a reciprocating shaker at 60 rpm for 20 h before measurements of either EM or PSD. The final suspension pH and EC was measured immediately before analysis.

Statistical analysis

Data were analyzed using General Linear Model's procedures for comparison (SAS Institute, 1990). Least significant differences at the 5% level of significance ($LSD_{0.95}$) were calculated.

RESULTS AND DISCUSSION

Characterization of the soil profile

The Flakkebjerg profile was classified as a loamy, mixed, mesic Typic Agrudalf (Soil Survey Staff, 1992). The profile was well-structured with several vertically oriented macropores penetrating to a depth of 150 cm. Eluviation of clay particles from the top-horizon was evident from clay skins on ped surfaces and at pore interfaces, and the enrichment of clay in the Btg- and BCtg-horizons (Table 1). A micromorphology image of an intact structure showing a typical macropore area with deposits of laminated clay colloids is presented in Figure 1.

The parent material was calcareous as indicated by the pH (6.2-8.3) and the presence of calcite (73.3 g kg^{-1}) in the BCtg horizon (Table 1). The $CEC_{8.1}$ was well correlated with clay content ($R^2=0.997$). Calcium was the dominating base cation resulting in very low sodium adsorption ratios. The organic carbon content was highest in the Ap-horizon (11.1 g kg^{-1}), but small amounts were found throughout the profile ($1.1\text{-}4.4 \text{ g kg}^{-1}$). The C:N ratio associated with the organic matter was close to 10 in the Ap-horizon, and decreased to approximately 6 in the lower horizons. The largest amount of Fe_{CBD} (12.0 g kg^{-1}) and Al_{CBD} (1.17 g kg^{-1}) were found in the Btg₁-horizon. The $Fe_{OX}:Fe_{CBD}$ ratio was in the range 0.10-0.47, with the highest value in the Ap-horizon exposed to the most intense weathering, while the iron oxides in the lower soil horizons were more crystalline. Mineralogical analysis of the bulk soil, as investigated by Rasmussen et al. (2001), showed the presence of smectite, illite, interstratified illite-smectite (I-

S), vermiculite, hydroxy interlayered vermiculite (HIV) and kaolinite, with smectite as the dominant clay mineral (40-65% of the clay minerals).

Colloid dispersibility

The percentage of WDC recovered from bulk samples increased down the profile, from 6.8% in the Ap-horizon, 10.7% in the Btg₂-horizon, to 17.9% in the BCtg-horizon (Table 2). These results demonstrated that from 46% (Btg₂-horizon) to more than 50% (Ap- and BCtg-horizon) of the total soil clay was found in the water-dispersible colloid fraction. The macropore deposits were found to be highly dispersible with 46.5% of the total mass fraction found in the WDC-fraction, compared to only 13.9% in the underlying matrix material (MM-BCtg). The largest amounts of WDC were generally found in the 0.2-2 µm size fractions, except for the macropore deposits, which were dominated by fine clay <0.2 µm. We would expect that differences in WDC between horizons would reflect contrasting mineralogical or soil physicochemical properties, but the high amount of WDC in the BCtg-horizon despite the presence of calcite, indicated that measurements of WDC did not reflect these characteristics. Instead we found that the mass of WDC in the bulk samples was strongly correlated with the content of total clay for all horizons sampled ($R^2=0.999$). This is in agreement with most other studies demonstrating a positive correlation between total clay content and the amount of WDC (e.g. Pojasok and Kay, 1990; Brubaker et al., 1992; Rasiah et al., 1992; Levy et al., 1993; Curtin et al., 1994). Common for these studies is the application of air-dry soil and the use of mechanical shaking in the measurement procedure. Results from Kjaergaard et al. (2004a) also demonstrated a positive correlation between clay content and WDC using air-dry soil and mechanical shaking, while employing a low-energy input separation procedure yielded a negative correlation between WDC and total clay content. Additionally, the low-energy input measurement of WDC was additionally very sensitive to initial soil conditions, and reflected

the actual leaching of colloids from intact soil cores (Kjaergaard et al., 2004b). The authors therefore recommended that separations of WDC, that should resemble potentially mobile colloids, should be based on low-energy input separation procedures. Based on this knowledge we expect that part of the separates of WDC obtained in this study and in other studies using intensive mechanical shaking, may represent some colloidal material that are not easily dispersed.

Characterization of water-dispersible colloids

Semiquantitative estimates of the relative content of clay minerals revealed that the mineralogy of the WDC in general were dominated by smectite or smectite+vermiculite, with smaller amounts of interstratified smectite-illite, illite, hydroxy-interlayered smectite/vermiculite and kaolinite (Table 2). This mineralogy corresponded to that of the total clay fraction of this soil (Rasmussen et al., 2001), indicating that there was no preferential dispersion of any clay mineral phase in the WDC-fractions. This could be attributed to the high-energy input in the WDC-separation procedure yielding WDC-separates constituting about 50% of the total clay fraction. The WDC-fractions showed enrichment in organic carbon (OC), compared to the bulk soil, with WDC from the Ap-horizon having the largest content of OC (26.1-35.3 g kg⁻¹), followed by the MP-BCtg fractions (13.8-17.9 g kg⁻¹). The natural organic matter (NOM) associated with the WDC from the BCtg₂ and BCtg fractions, generally had a low C:N-ratio (5.8-6.6), not very different from the C:N-ratios of the bulk soil material (6.1), reflecting the same type of organic carbon. In contrast a higher C:N-ratio (8.0-8.6) was observed for the WDC from the Ap-horizons, which differed markedly from the C:N-ratio of the bulk soil material (9.8), indicating other components of NOM in the WDC-fractions compared to the bulk soil.

Another characteristic feature concerning the composition of the WDC-fractions, was the enrichment of sesquioxides. The relatively large content of sesquioxides, in particular Al-oxides, in the WDC fraction was remarkable. Iron and aluminum are known to be strong flocculants (Goldberg et al., 1990; Seta and Karathanasis, 1996), and based on the general recognition of the flocculation power of sesquioxides, it cannot be expected that the oxides in the WDC appeared as free or surface exposed components, but rather screened by other components such as surface adsorbed organic matter. In the present case, the results indicate a positive correlation between the WDC content of Al and OC ($R^2=0.770$). Sesquioxides are indeed effective sorbents of humic substances, where specific adsorption via ligand exchange with protonated surface hydroxyl groups is the dominating binding mechanism (Murphy and Zachara, 1995). Shen (1999) reported results from scanning electron microscope (SEM) investigations, indicating the existence of a correlation between the atomic ratio of (Al+Fe):Si of soil colloid surfaces and the humic acid sorption capacity, where those soil colloids with larger values of the (Al+Fe):Si ratio were able to sorb humic acid more efficiently.

Measurements of N₂-BET specific surface area of the WDC fractions (Table 2) showed a variation in specific surface area from 14–69 m² g⁻¹. The lowest specific surface areas were observed for the Ap and MP-BCtg fractions, also having the largest contents of OC. The relatively low N₂-BET surface area combined with the large content of OC, indicate that organic matter dominates the surfaces of these WDC-fractions. Treatment with Na₂S₂O₈ removed 68-92% of the total OC from these WDC fractions, and resulted in an increase in specific surface area by 171-225 % (Table 3). This supported the hypothesis that the surfaces of these WDC were at least partly coated by OC, known to have extremely low (<1 m² g⁻¹) N₂-gas adsorbing surface areas (Chiou et al., 1990). Additional treatment with CBD for removal of

Fe- and Al-oxides decreased the specific surface area of the Ap fractions, but had less effect on the surface area of MP-BCtg fractions.

ζ-potential and stability behavior of natural WDC

Increasing CaCl_2 concentration resulted in a marked decrease in the negative ζ -potential for all WDC fractions, from about -35 to -45 mV at $\text{EC} \sim 10 \mu\text{S cm}^{-1}$ to about -11 to -15 mV at $\text{EC} \sim 1200 \mu\text{S cm}^{-1}$ (Fig. 2a). The ζ -potential differed between the WDC-fractions, with the most negative ζ -potentials observed for the Ap fractions, followed by the MP-BCtg fractions. The reduction in negative ζ -potential with increasing EC can be explained by the compression of the diffuse double layer around charged surfaces, and a subsequent reduction in the electrical potential at the plane of shear (Hunter, 1981). In addition, increasing Ca^{2+} concentration in solution may result in increased Ca^{2+} binding to functional groups of colloid-bound humic substances, and a subsequent charge reduction (Amirbahman and Olson, 1995). The reduction in ζ -potential indicate reduction in the repulsive forces, and this was demonstrated in the stability behavior of the WDC. Increasing the CaCl_2 concentration resulted in flocculation, as confirmed by the relative increase in the mean hydrodynamic particle diameter (Fig. 2b). The increase in d_H differed between the WDC fractions, but the flocculation pattern revealed identical behavior. At low CaCl_2 concentrations the suspensions were stable and no flocculation occurred, but at a certain critical concentration, flocculation was initiated. The onset of flocculation differed among the WDC, and a two-fold increase of the initial particle diameter occurred at an EC of $91 \mu\text{S cm}^{-1}$ for the least stable Btg₂ colloids, 171 - $185 \mu\text{S cm}^{-1}$ for MP-BCtg, and at $1023 \mu\text{S cm}^{-1}$ for the most stable Ap colloids. The Btg₂ (0.2 - $2 \mu\text{m}$) fraction was very unstable and allowed only measurements at the lowest CaCl_2 concentrations before flocculation reached a level where further increase in particle size could not be measured due to sedimentation. The stability behavior of the WDC can, at least partly, be

explained by their respective ζ -potentials, the colloids having the most negative ζ -potential also revealed the largest resistance to flocculation (Fig. 2a,b). However, at higher CaCl_2 concentrations when the ζ -potential was reduced to a minimum level for all WDC fractions, steric stabilization forces from surface adsorbed organic matter may induce colloid stability at high ionic strengths conditions (Hunter, 1987).

In contrast to the marked influence of solution CaCl_2 concentration on the ζ -potential and stability behavior, the effect of solution pH was less pronounced. It appeared that the ζ -potential for the WDC was almost constant at pH 3.5 to 8; only the Ap (<0.2 μm) showed some reduction in the negative ζ -potential at pH <5 (Fig. 2c). The relative increase in the mean hydrodynamic particle diameter as a function of pH (Fig. 2d) showed that at pH 5-7, the colloidal suspensions were stable with no flocculation taking place. At pH <5 there was a relative increase in d_H for all colloid fractions except the Ap (<0.2 μm) reflecting flocculation, and at pH <4 the destabilization of the colloid suspension was marked for all fractions. Again, the Ap colloids appeared to be more resistant towards flocculation than the MP-BCtg colloids, and the Btg₂ colloids were significantly less stable. At pH >7 there was a slight decrease in d_H for some of the WDC indicating dispersion at higher pH. The effect of pH on the stability behavior can be explained as a result of protonization of pH-dependent charges sites on sesquioxides, humic substances and on the edge of layer silicates, and attraction between these positively charged surface sites and negatively charged layer silicates. Release of Al^{3+} at low pH may also contribute to flocculation. Furthermore, the changes in electric conductivity caused by the pH adjustment when adding HCl and $\text{Ca}(\text{OH})_2$ increases the ionic strength of the suspension. Theoretically we would expect this to additionally decrease the negative ζ -potential and increase flocculation at both low pH and high pH where the rise in ionic strength is largest.

Influence of NOM and sesquioxides on ζ -potential and stability behavior

The ζ -potential and stability behavior of the intact WDC fractions indicated that the stabilization of the suspended colloid fractions resulted from surface coverage by organic matter with high charge density. The OX-treatment for removal of NOM from Ap and MP-BCtg fractions had two significant effects on the resulting ζ -potential (Fig. 3). First, removal of NOM markedly reduced the negative ζ -potential, and second, removal of NOM caused the ζ -potential to become markedly affected by pH. The reduction in ζ -potential was more pronounced for the WDC fractions from MP-BCtg (43-54%) than from the Ap-horizon (17-26%), but the resulting pH-dependence of the ζ -potential showed similar patterns. As pH increased the reduction in ζ -potential, due to removal of NOM, became less marked, and at pH 7-8 the reduction in ζ -potential was only 17-18% for the MP-BCtg and 4% for the Ap (<0.2 μm). For the Ap (0.2-2 μm) removal of NOM at pH >6 resulted in an increase in the negative potential, reflecting an increase in the negative surface charge.

An explanation for this change in ζ -potential versus pH characteristics is that removal of NOM exposes a surface of sesquioxides with pH-dependent charge behavior. At low pH, the oxides will be dominantly positively charged, and therefore contribute to a marked decrease in negative ζ -potential, when removing surface adsorbed NOM. As pH increases the positive charge of the oxides is reduced, and hence the contribution of the sesquioxides to change in ζ -potential decreases. The anomalous behavior of Ap (0.2-2) at pH >6 may indicate the presence of sesquioxides with lower point of zero charge (PZC) than for the other samples.

The above considerations are supported by the increase in the negative ζ -potential for the OX+CBD treated fractions compared to the OX treated fractions (Fig. 3). Removal of sesquioxides from the Ap fractions increased the ζ -potential either to the level of the Intact WDC, or to even more negative potentials. For the MP-BCtg the removal of sesquioxides resulted in an increase in ζ -potential to an intermediary level for the MP-BCtg ($<0.2 \mu\text{m}$), while the resulting ζ -potential for the MP-BCtg ($0.2\text{-}2 \mu\text{m}$) was increased to the level of the Intact fraction at $\text{pH} \geq 5$. Oxidative removal of NOM from Ap fractions reduced the ζ -potential less than removal of NOM from the MP-BCtg fractions, despite the larger content of OC and the more negative ζ -potential of the Ap fractions. The reason for this cannot be deduced from this study, but it is likely to be related to the type and morphology of the underlying layer silicate and sesquioxide fraction.

The destabilizing effect of NOM removal on the WDC fractions was reflected in the flocculation behavior (Fig. 4). The OX-treated colloids rapidly flocculated even at high pH, whereas the suspensions of Intact colloids remained stable at pH above 4-5. The pH-dependence was extremely pronounced for the OX-treated colloids. An exception to this behavior was the Ap ($0.2\text{-}2 \mu\text{m}$) fraction where the NOM removal caused only a minor increase in the particle diameter. This is however in accordance with the less significant effect of NOM removal on the ζ -potential for this fraction. Furthermore removal of sesquioxides from the OX treated fractions resulted in a reduction in the average particle diameter. Smaller particle size of OX+CBD fractions results from loss of sesquioxides as “cement” gluing particles together, and the reduction in particle flocculation when surface coatings of positively charged sesquioxides are removed.

The larger stability of the NOM coated colloids suggests that NOM plays a significant role in stabilization of suspended colloids in this soil type dominated by 2:1-layer silicates. This is in agreement with results reported earlier for suspensions of natural variable charged soil colloids (Kretzschmar et al., 1993), and for artificial mixtures between variable charged minerals and humic acids (Jekel, 1986; Kretzschmar et al., 1998). This study demonstrated that for WDC with rather similar mineralogical composition, large variations were observed in the flocculation behavior. These findings clearly demonstrate that model predictions of colloid deposition based on colloid mineralogy may lead to erroneous conclusions. Also for colloid fractions where the stability behavior is controlled by surface adsorbed organic matter, large variation may occur in colloidal stability. This suggests that model predictions of colloid deposition should be based on direct examinations of colloid stability behavior.

CONCLUSIONS

This study demonstrated that colloid associated organic matter increased the suspension stability of natural water-dispersible colloids in a Typic Agrudalf dominated by 2:1-layer silicates. The contribution of OC to the colloidal stability was inferred from: (i) a more negative ζ -potential and larger suspension stability from WDC with larger content of OC, and (ii) reduced negative ζ -potential as well as suspension stability after OC removal. The presence of surface adsorbed organic matter presumably masked the underlying silicate and sesquioxides components, and consequently controlled the stability behavior of the WDC.

The average ζ -potential and stability behavior of natural WDC were strongly dependent on solution CaCl_2 concentration. Flocculation of WDC was directly related to ζ -potential measurements in the lower concentration range, while at higher CaCl_2 concentrations steric

stabilization forces may additionally explain the colloidal stability. Solution pH had less effect on the stability of the WDC, and flocculation was only significant at pH below 4.5.

This study demonstrated that a conventionally used method for separating water-dispersible colloids using air-dry soil and mechanical shaking yielded WDC-fractions that did not reflect differences in soil physical-chemical conditions, but was directly related to total clay content. We suggest that future investigations of WDC should consider separation procedures that may better resemble the easily dispersible colloid fraction.

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FIGURE CAPTIONS

Fig. 1. Micromorphology image (plane-polarized light) of an intact structure from the BCtg-horizon showing (a) macropore deposits (MP-BCtg) of laminated clay colloids, (b) macropore matrix (MM-BCtg), and (c) macropore area.

Fig. 2. Influence of CaCl_2 -concentration (EC) and pH on (a, c) ζ -potential, and (b, d) relative increase in mean hydrodynamic particle diameter (d_H) of water-dispersible colloids (WDC) from different soil horizons and colloidal size fractions.

Fig. 3. Effect of removal of organic matter (OX) and organic matter plus sesquioxides (OX + CBD) on the ζ -potential of water-dispersible colloids (WDC) from different soil horizons and colloidal size fractions as a function of pH. Error bars: $\pm\text{SE}$.

Fig. 4. Effect of removal of organic matter (OX) and organic matter plus sesquioxides (OX + CBD) on the mean hydrodynamic particle diameter (d_H) of water-dispersible colloids (WDC) from different soil horizons and colloidal size fractions as a function of pH. Error bars: $\pm\text{SE}$.

1 Table 1. Chemical and physical properties of the Flakkebjerg profile.

<u>Particle-size distribution (μm)</u>														
Horizon	Depth	< 2	2-20	20-2000	CaCO ₃	pH _{H2O}	OC	C:N- ratio	CEC _{8.1} †	SAR ‡	Fe _{CBD} §	Fe _{ox} ¶	Al _{CBD} §	Al _{ox} ¶
	cm	-----	g kg ⁻¹	-----	g kg ⁻¹		g kg ⁻¹		cmol _c kg ⁻¹		-----	g kg ⁻¹	-----	
<i>Ap</i>	0-24	133	216	651	0	6.51	11.1	9.8	10.8	0.034	5.98	2.82	0.86	0.68
AE	24-37	167	253	580	0	6.22	4.4	9.0	12.0	0.040	8.31	2.09	0.78	0.55
Btg ₁	37-65	202	269	529	0	6.73	2.8	8.6	13.5	0.042	12.0	1.14	1.17	0.67
Btg ₂	65-110	232	159	609	0	7.05	1.1	6.1	14.3	0.044	7.60	1.20	0.80	0.53
BCTg	110- 153	310	547	143	73.3	8.29	1.1	6.1	-	-	10.6	1.04	0.93	0.61

2 † Cation-exchange capacity at pH 8.1

3 ‡ Sodium adsorption ratio [SAR = Na/(Ca+Mg)^{0.5}, concentrations in mmol L⁻¹]

4 § CBD = Citrate-bicarbonate-dithionite extractable

5 ¶ Ox = Oxalate extractable

1 Table 2. Physico-chemical properties of water-dispersible colloids from the Flakkebjerg profile.

	WDC		OC	C:N-	Fe _{CBD}	Al _{CBD}	Surface area‡	ζ-potential §	Smectite	S-I #	Clay Mineralogy ¶			
	μm	%									g kg ⁻¹	ratio	g kg ⁻¹	m ² g ⁻¹
					†									
<i>Ap</i>	0.2-2	6.2	26.1	8.6	19.4	9.3	14	-20.7	48	17	11	9	5	10
	< 0.2	0.62	35.3	8.0	19.2	10.5	20	-24.2	44	21	19	3	7	6
<i>Btg₂</i>	0.2-2	9.7	4.5	6.2	14.6	4.9	47	-16.8	46	23	12	8	5	7
	< 0.2	3.0	5.1	5.8	20.8	6.3	67	-14.1	46	27	10	5	8	4
<i>BCtg</i>	0.2-2	15.3	3.8	6.6	18.0	3.9	44	ND	32	9	32	12	7	8
	< 0.2	2.6	6.3	6.5	28.4	7.3	69	ND	57	17	16	3	5	2
<i>MP-BCtg</i>	0.2-2	20.9	17.9	7.7	20.1	10.6	23	-17.3	24	23	35	4	9	5
	< 0.2	25.6	13.8	6.5	24.0	10.0	25	-16.6	43	18	15	1	17	6
<i>MM-BCtg</i>	0.2-2	12.0	4.3	7.4	18.2	1.9	ND§§	-13.9	52‡‡	11	‡‡	20	10	7
	< 0.2	1.9	10.1	7.4	31.4	4.9	ND	-13.3	72	11	7	2	4	3
<i>LSD_{0.95}</i>		-	0.12	0.13	1.15	0.82	-	0.62	-	-	-	-	-	-

2 † CBD = Citrate-bicarbonate-dithionite extractable.

3 ‡ N₂-BET specific surface area

4 § ζ-potential determined at [CaCl₂] = 0.35 mM and pH ~ 6.5

5 ¶ Mineralogical composition of the WDC-fractions determined by semi-quantitative analysis

- 1 # S-I: Interstratified smectite-illite
- 2 †† HIM: Hydroxy-interlayered vermiculit / smectite
- 3 ‡‡ The content of smectite+vermiculite is 52%
- 4 §§ ND = Not determined

1
 2 Table 3. Effect of removal of organic carbon (OX) and organic carbon+sesquioxides
 3 (OX+CBD) on specific surface area and particle diameter of water-dispersible colloids.

WDC	μm	Treatment	Organic carbon	Specific surface [†]	Particle diameter [‡]
			g kg^{-1}	$\text{m}^2 \text{g}^{-1}$	nm
Ap	0.2-2	Intact	26.1	14	879
		OX	2.1	38	770
		OX+CBD	2.1	30	632
	<0.2	Intact	35.3	20	591
		OX	11.4	61	500
		OX+CBD	11.4	51	454
MP-BCtg	0.2-2	Intact	17.9	23	751
		OX	3.4	64	808
		OX+CBD	3.4	62	506
	<0.2	Intact	13.8	24	339
		OX	4.1	78	491
		OX+CBD	4.1	82	335

4 [†] N₂-BET specific surface area

5 [‡] Mean hydrodynamic particle diameter determined at $\text{EC} \leq 10 \mu\text{m S cm}^{-1}$

Figure 1

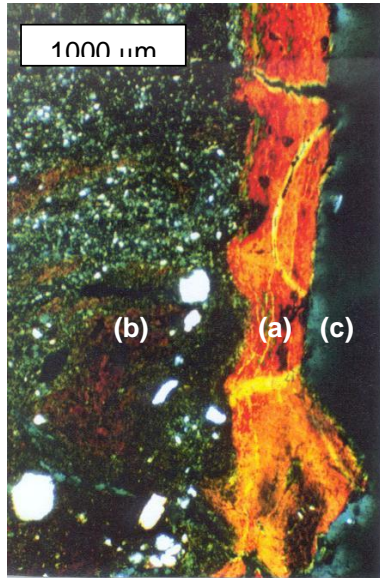


Figure 2

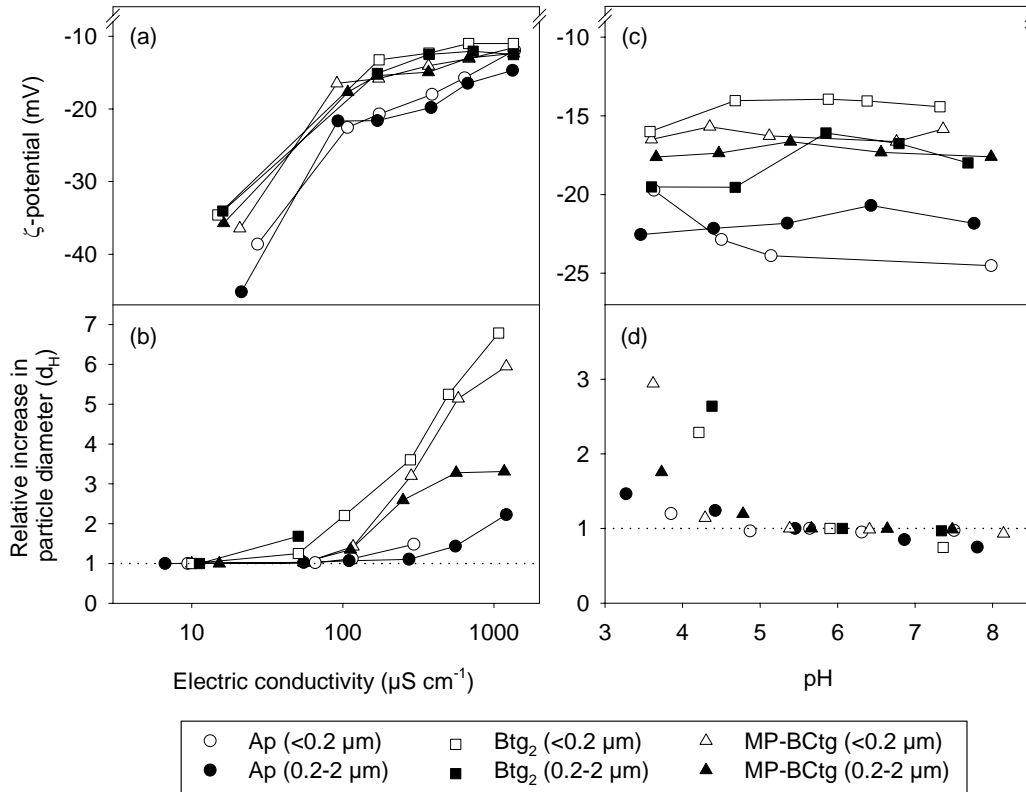


Figure 3

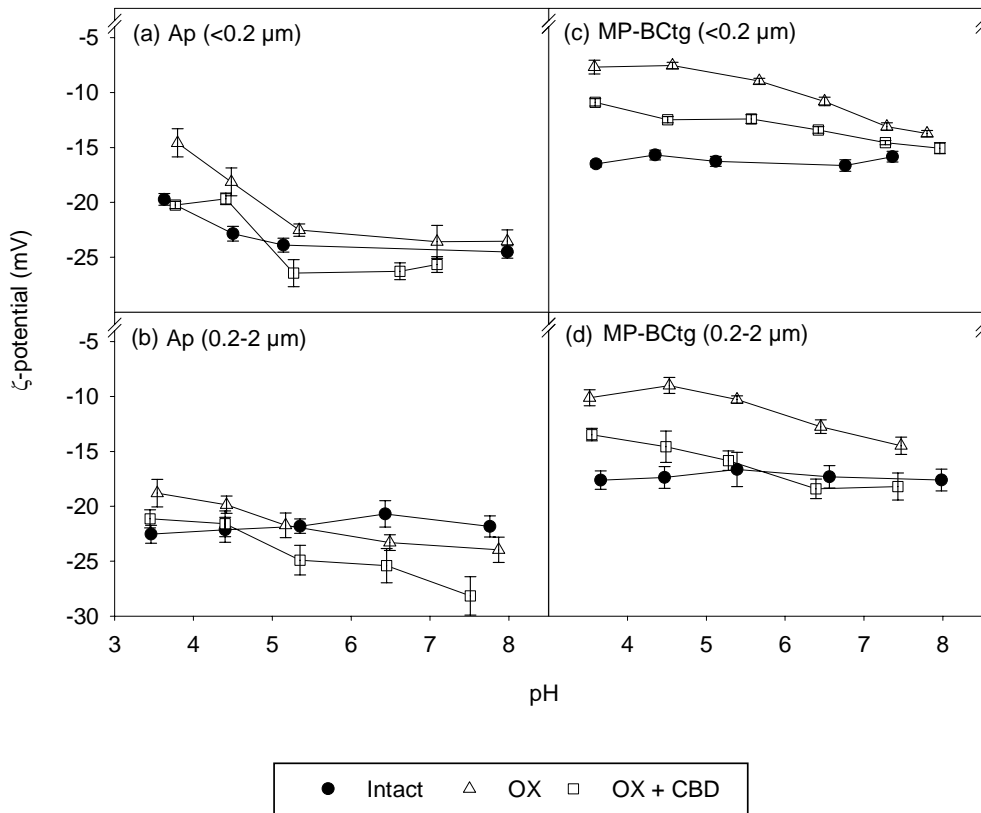


Figure 4

