PREFACE

The present dissertation including three enclosed articles is submitted in partial fulfilment of the requirements for the Doctor of Philosophy (Ph.D.) degree. The work was carried out at the Danish Institute of Agricultural Sciences, Dept. of Agroecology, Foulum and was funded by the Danish Research Agency (FREJA programme). I have been matriculated as a Ph.D. student at Aalborg University with Assoc. Professor Per Moldrup, Aalborg University and Senior Scientist Lis Wollesen de Jonge, Danish institute of Agricultural Sciences, as my supervisors.

I thank my supervisors Per Moldrup and Lis Wollesen de Jonge for their encouragement and guidance for this work. The experimental work was done at the Department of Agroecology, Danish Institute Agricultural Sciences. I thank the department for providing the facilities for conducting my experimental work. I thank Per Schjønning and Lars Munkholm, Danish Institute of Agricultural Science for providing the soil samples for the experimental work and Kristian Keiding and Lisbeth Wybrandt, Aalborg University for conducting characterizations of colloid suspensions. I also thank all the technical staff at the research groups for Soil Physics and Chemistry and for organic matter and Microbial Ecology for their help with the laboratory work. A special thank goes to Palle Jørgensen, Lene Skovmose, Bodil Christensen, and Michael Koppelgaard for your help and patience. I also want to thank Margit Schacht for improving the English of my papers and Anne Sehested for always being helpful when I most needed it. I also thank all my other colleges at research centre Foulum for the warm, friendly and slightly sarcastic working environment you provide.

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Mette Lægdsmand

ENGLISH SUMMARY

Strongly sorbing chemicals may be transported to surface waters, drains and groundwater by sorption to colloids in the soil. The degree of colloid-facilitated transport of a chemical is determined by the overall mobility of the colloids in the soil and the sorption affinity of the chemical for the mobile colloids.

The overall mobility of soil colloids is determined by the release of colloids from the soil aggregates, the transport of the colloids, and the recapture of colloids. The content of organic matter in the soil may affect the processes of release and recapture of colloids in two ways: The strength of aggregates in wet condition is increased with higher organic matter content leading to reduced area of contact between water and aggregate and hereby a lower release. The colloid stability is generally increased with higher degree of organic coating leading to increased release and reduced recapture of colloids. Ionic strength and valence of major cations in the pore water influence the stability of colloids and hereby also the release and recapture of the colloids in the soil.

The sorption affinity of hydrophobic organic chemicals (HOC) to the mobile colloids will be affected by the content and quality of organic matter. Ionic strength and valence of the cations in the porewater affect the structure of the organic matter and it is possible that the sorption affinity of HOC for the colloid associated organic matter also may be affected.

The effect of organic matter and solution chemistry on the colloid mobility and the sorption affinity of HOC for the mobile colloids were investigated. Two soils with different content of indigenous organic matter were used for the experiments. One was from an organic dairy farm (*Manured soil*) and the other had been grown without addition of manure for 20 years (*Depleted soil*). Pyrene was used as a model chemical for the colloid-facilitated transport. Colloidal mobility was studied using different procedures: batch release of colloids from soil aggregates, leaching of colloids from columns packed with aggregates, and comprehensive mathematical modeling of colloid leaching. The sorption affinity of pyrene was studied using batch sorption experiments with three different fractions of the colloids in the two soils.

It was investigated how the amount of organic matter affected the amount and quality of colloids released from aggregates in batch experiments by three different degrees of aggregate break-down. The amount of colloids that could be released from the aggregates was highly dependent on the degree of aggregate break-down. With a higher degree of aggregate break-down the amount of released colloids was higher and the amount of associated organic matter was lower. With chemical/mechanical dispersion and for the mechanical breakdown of the aggregates, colloids of medium size (0.3 - 1 μm) were dispersed with release of fine colloids (below 0.3 μm) and organic matter. No fine colloids were released from the aggregates by spontaneous release. The medium size colloids were microaggregates being held together by organic matter. The amount of colloids released from *Manured soil* by batch methods were lower than from the *Depleted soil*. This points to the structural stability as the controlling factor in the release of colloids from aggregates with batch methods.

The effect of indigenous organic matter and irrigation water chemistry on leaching of colloids form columns packed with natural soil aggregates from the two soils was investigated. Also the effect of irrigation intensity was investigated on the *Manured soil*. The amount of colloids leached from the columns was strongly dependent on the ionic strength of the infiltrating water. The valence of the

major cation of the infiltrating water only affected the leaching slightly. More colloids were leached from columns packed with aggregates from the *Manured soil* compared with the *Depleted soil*. This indicate that the amount of colloids leached from the aggregates were more dependent on the colloid stability than on the structural stability.

A mathematical model describing the leaching of colloids from an aggregated soil under different irrigation ionic strength was developed. The model was successfully calibrated to fit the observed leaching of colloids from columns packed with aggregates and irrigated with three levels of ionic strength. Each soil was calibrated separately. The *Manured soil* had a higher release of colloids from the aggregate surfaces at high ionic strength and a higher sorption capacity of the air-water interfaces for colloids, compared with the *Depleted soil*. The air-water interface was an important source of mobile colloids in the *Manured soil*. In the *Depleted soil* the air-water interface was less important. The model simulated the diffusion controlled steady-state leaching with two additional irrigation intensities on the *Manured soil*. The sensitivity of the model was highest towards changes in parameters determining the diffusion through stagnant water surrounding the aggregates and the capacity of the air-water interface for sorption/desorption of colloids.

Sorption of pyrene to mobile colloids was investigated. The effect of the release process of the mobile colloids, water chemistry and the indigenous organic matter content of the original soil was examined. It was also investigated if the observed differences had significant effect on the amount of pyrene that could be leached from an aggregated soil. This was done by simulating the leaching of pyrene by a static leaching model. Both the release process and the ionic strength and valence of cation had significant effect on the Freundlich isotherms. The sorption capacity of the organic matter (K_{oc}) was highest for colloids released under chemical/mechanical breakdown of aggregates and the non-linearity was higher. The amount of pyrene sorbed to colloids in KCl was higher than in $CaCl_2$. The indigenous organic matter content of the original soil only affected the K_{oc} for the spontaneously released colloids. Model simulation with a static leaching model indicated that the release process of the colloids could influence the total leaching of pyrene. Furthermore, it was demonstrated that the major transport mechanism for pyrene in the soils was colloid-facilitated transport when the total pyrene concentration was low and transport facilitated by dissolved organic matter when the concentration was high.

The results indicated that the transport of HOC in natural soils most likely will increase with higher organic matter content of the soil, due to a higher leaching of colloids and dissolved organic matter, a higher amount of colloid-associated organic matter of the colloids released, and a higher K_{oc} of the colloid-associated organic matter. Low ionic strength will probably increase the transport of HOC in natural soils due to a higher leaching of colloids and a slightly higher leaching of DOM. Monovalent cations will increase the leaching due to a higher K_{oc}.

DANISH SUMMARY (DANSK RESUME)

Stærkt sorberende stoffer kan transporteres til overfladevand, dræn og grundvand ved binding til kolloider i jorden. Graden af kolloidfaciliteret transport af et stof afhænger af mobiliteten af kolloiderne og stoffets sorptionsaffinitet for de mobile kolloider.

Den overordnede mobilitet af kolloiderne afhænger af frigivelsen fra aggregater i jorden, transporten af kolloiderne og hvordan kolloiderne indfanges igen. Indholdet af organisk stof påvirker frigivelse og indfangning af kolloider på to måder: Den strukturelle stabilitet af våde aggregater bliver større med højere indhold af organisk stof. Det fører til et mindre kontaktareal mellem vand og aggregat og hermed til lavere frigivelse af kolloider. Kolloidstabiliteten er generelt forøget med højere grad af organisk coating. Dette fører til større frigivelse af kolloider og mindre indfangning. Ionstyrken og valensen af kationer i porevandet påvirker stabiliteten af kolloider og hermed også frigivelse og indfangning af kolloider i jorden.

Sorptionsaffiniteten af hydrofobe organiske stoffer (HOC) for kolloider bestemmes både af mængde og kvalitet af det organiske stof. Ionstyrken og valensen af kationer i jordvæsken påvirker strukturen af det organiske stof og hermed muligvis også sorptionsaffiniteten af HOC for det organiske stof der er associeret med kolloiderne.

Effekten af organisk stof og vandkemi på mobiliteten af kolloider og sorptionsaffinitet af HOC for de mobile kolloider er undersøgt. To jorde med forskelligt naturligt organisk stof indhold blev brugt til det eksperimentelle arbejde. Den ene er udtaget på en økologisk malkekvægsbedrift (Organisk gødet jord) og den anden have blevet dyrket uden organisk gødning i 20 år (Uorganisk gødet jord). Pyren blev brugt som modelstof for den kolloidfaciliterede transport. Mobiliteten af kolloider blev undersøgt ved brug af forskellige teknikker: frigivelse af kolloider i batch forsøg, udvaskning af kolloider fra kolonner pakket med aggregater og matematisk modellering af kolloid udvaskning. Sorptionsaffiniteten af pyren blev undersøgt med tre forskellige fraktioner af kolloiderne i de to jorde.

Mængden og kvaliteten af kolloider frigivet ved tre forskellige grader af aggregat nedbrydning i batch forsøg blev undersøgt. Mængden af kolloider der kunne frigives var stærkt afhængig af aggregat nedbrydningen. Med en større grad af nedbrydning af aggregater kunne flere kolloider frigives og mængden af associeret organisk stof var mindre. Ved kemisk/mekanisk nedbrydning og ved mekanisk nedbrydning af aggregater blev kolloider i mellem størrelse (0.3 - 1 μm) nedbrudt under frigivelse af organisk stof og fine kolloider (< 0.3 μm). De helt små kolloider fandtes ikke når der kun forekom spontan frigivelse af kolloider. Dette kan tolkes som at mellem kolloider var mikroaggregater der blev holdt sammen af organisk stof. Mængden af kolloider frigivet fra den organisk gødede jord ved batch metoder var lavere end fra den uorganisk gødede jord. Det peger på at den strukturelle stabilitet styrer hvor mange kolloider der kan frigives ved batch metoder.

Det er blevet undersøgt hvilken effekt organisk stof og vandkemi har på udvaskning af kolloider fra umættede kolonner pakket med aggregater fra de to jorde. Desuden blev effekten af vandingsintensitet undersøgt på den organisk gødede jord. Mængden af kolloider der kunne udvaskes fra kolonner pakket med aggregater, var stærkt afhængigt af ionstyrken af det infiltrerende vand. Valensen af kationer i det infiltrerende vand havde også en effekt der dog kun indfandt sig langsomt. Hvis indholdet af organisk stof i aggregaterne var højt, så var den udvaskede mængde af

kolloider også høj. Dette tyder på at mængden af kolloider der kunne udvaskes blev bestemt af kolloidstabiliteten mere end af den strukturelle stabilitet.

Der blev udviklet en model der kunne beskrive udvaskningen af kolloider fra en aggregeret jord under varierende ionstyrke. Modellen kunne kalibreres til at beskrive de observerede koncentrationer af kolloider udvasket med vand med tre forskellige ionstyrker. Hver jord blev kalibreret separat. Den organisk gødede jord havde en højere frigivelse af kolloider fra aggregat overfladerne og en større mængde kolloider til luft-vand skilleflader. Luft-vand skillefladen var en meget vigtig kilde til udvaskning af kolloider på den organisk gødede jord og mindre vigtig på den uorganisk gødede jord. Modellen kunne beskrive den diffusionsbegrænsede steady-state udvaskning under to andre niveauer af vandingsintensitet. Sensitiviteten af modellen var størst for ændringer i parametre for diffusionen i den immobile vandfilm der omgiver aggregaterne og for kapaciteten for sorption/desorption af kolloider til luft-vand skillefladen.

Det blev undersøgt om sorptionen af pyren til mobile kolloider afhang af frigivelses processen af de mobile kolloider, vandkemi og den oprindelige jords indhold af organisk stof og om de observerede effekter havde indflydelse på mængden af stærkt sorberende stoffer der kunne udvaskes fra en aggregeret jord. Både frigivelsesprocessen og ionstyrke og valens af kationer påvirkede sorptionsegenskaberne i form af Freundlich isothermer. Sorptionskapaciteten af det organiske stof (K_{oc}) var højere for kolloider der var frigivet under kemisk/mekanisk nedbrydning af aggregater og ikke-lineariteten af isothermerne var større. Sorptionen af pyren var større i KCl sammenlignet med $CaCl_2$. Indhold af organisk stof i den oprindelige jord havde kun effekt på sorptionsegenskaberne af de kolloider der blev frigivet spontant. Model simuleringer viste at der var en mærkbar effekt på den totale pyren transport af hvordan kolloiderne blev frigivet. De viste også at den vigtigste transport mekanisme for pyren var kolloid-faciliteret transport når koncentrationen af pyren i jorden var lav og at transporten overvejende var båret af organisk stof når koncentrationen af pyren i jorden var høj.

Resultaterne indikerede at transporten af HOC sandsynligvis stiger med stigende indhold af organisk stof, p.g.a en højere udvaskning af kolloider og opløst organisk stof, et højere indhold af organisk stof associeret med kolloiderne og en højere K_{oc} af HOC for det kolloidassocierede organiske stof. Lav ionstyrke vil sandsynligvis også forøge transporten af HOC i jorden, da udvaskningen af kolloider er højere og udvaskningen af opløst organisk stof er lidt højere. Monovalente kationer kan forøge transporten af HOC, da K_{oc} er højere.

LIST OF SUPPORTING PAPERS

Paper I:

Laegdsmand, M., L.W. de Jonge, P. Moldrup, and K. Keiding. 2004. Pyrene Sorption to Water Dispersible Colloids: Effect of Solution Chemistry and Organic Matter. Vadose Zone J. 3:451-461.

Paper II:

Laegdsmand, M., L.W. de Jonge, and P. Moldrup. 2005. Leaching of colloids and dissolved organic matter from columns packed with natural soil aggregates. Soil Sci. 170(1):13-27.

Paper III:

Laegdsmand, M., P. Moldrup and L.W. de Jonge. 2006. Modeling colloid leaching in unsaturated columns packed with natural soil aggregates. Eur. J. Soil Sci..DOI: 10.1111/j.1365-2389.2006.00854.x

TABLE OF CONTENTS

App. A: Soil sampling site and procedure

App. B: Leaching experiments of pyrene from aggregated soil

1. INTRODUCTION

Concern for the environment and human health has lead to research and monitoring of chemicals in soil and groundwater. The major concern has been the easily dissolved chemicals on the assumption that chemicals having a strong affinity to the stationary soil were immobile. However, strongly sorbing contaminants are found to have been transported over longer distances in soils than was expected from the affinity to the soil material and solubility alone (Rao et al., 1974, Coles and Ramspot, 1982; Enfield et al., 1982; Jury et al., 1986; Villholth et al., 2000). The phenomenon was first discovered in the 70s and has received increasing attention since. The enhanced transport of strongly sorbing pollutants has been attributed to sorption to small particles in the soil environment and subsequent transport of the complex of particle and pollutant. The processes of colloid-facilitated transport of pollutant in groundwater have been discussed and reviewed by e.g. McCarthy and Zachara (1989), Ryan and Elimelech (1996), and Kretzschmar et al. (1999).

Colloid-facilitated transport has been demonstrated as a possible transport mechanism for polyaromatic hydrocarbons (PAHs) (Roy and Dzombak, 1997), strongly sorbing pesticides (Vinten et al., 1983; Seta and Karathanasis, 1996; de Jonge 1998; de Jonge et al., 2000; Barton and Karathanasis, 2003; Petersen et al., 2003), heavy metals (Amrhein et al., 1993; Roy and Dzombak, 1997; Denaix et al. 2001; Um and Papelis, 2002; Barton and Karathanasis, 2003), radionuclides (Saiers and Hornberger, 1999; Flury et al., 2002), and phosphorus (Uusitalo et al., 2001; de Jonge et al., 2004). These chemical compounds generally have low solubility, but they have different chemical and physical properties. PAHs are preferentially sorbed to the organic matter on the colloids and heavy-metals, radionuclides, and phosphorus are bound both to the organic and the inorganic parts of the colloids. These differences in sorption properties define the colloids of interest for the facilitated transport.

Following the proposal of the colloid-facilitated transport as an important mechanism for the transport of strongly sorbing chemicals in soils and sediments, efforts have been made to establish the theoretical basis for the colloid-facilitated transport. In the beginning the major concern was the leaching of toxic chemicals from buried deposits to drinking water reservoirs. This directed the research towards the saturated porous media (e.g. Kretzschmar et al., 1995; Liu et al., 1995; Ryan and Elimelech, 1996; Grolimund et al., 1998; Elimelech and O'Melia, 1990; Toran and Palumbo, 1991). These studies have provided solid understanding of the processes of deposition of colloids on grains, entrapment of colloids in smaller pores (pore straining), and the size exclusion of the colloids from the fine pores of the soil. Later, colloid-facilitated transport has been proposed as a dominating transport process of chemicals from surface-applied sources. This has moved some of the attention to the mobilization and transport of colloids in the unsaturated porous media (e.g. Kaplan et al., 1993; Corapcioglu and Choi, 1996; Wan and Tokunaga, 1997; Choi and Corapcioglu, 1997; Gamerdinger and Kaplan, 2001; Saiers and Lenhart, 2003(a); Saiers and Lenhart, 2003(b)). These studies have provided knowledge of sorption of colloids at the air-water interface, entrapment behind thin liquid films (film straining), and the release of colloids due to changes in saturation. The understanding of the processes affecting the release and transport of colloids in natural unsaturated topsoil is still weak. Laboratory and field experiments have been conducted on unsaturated structured soils (e.g. Seta and Karathanasis, 1997; Jacobsen et al., 1997, Jarvis et al., 1999, Laegdsmand et al., 2000, Villholth at al., 2000, Gamerdinger and Kaplan, 2001; Schelde et al., 2002), but the preferential flow causes problems in the analysis of the results. The heterogeneous structure of the topsoil gives a very high variability on results from intact soil masking the differences between treatments.

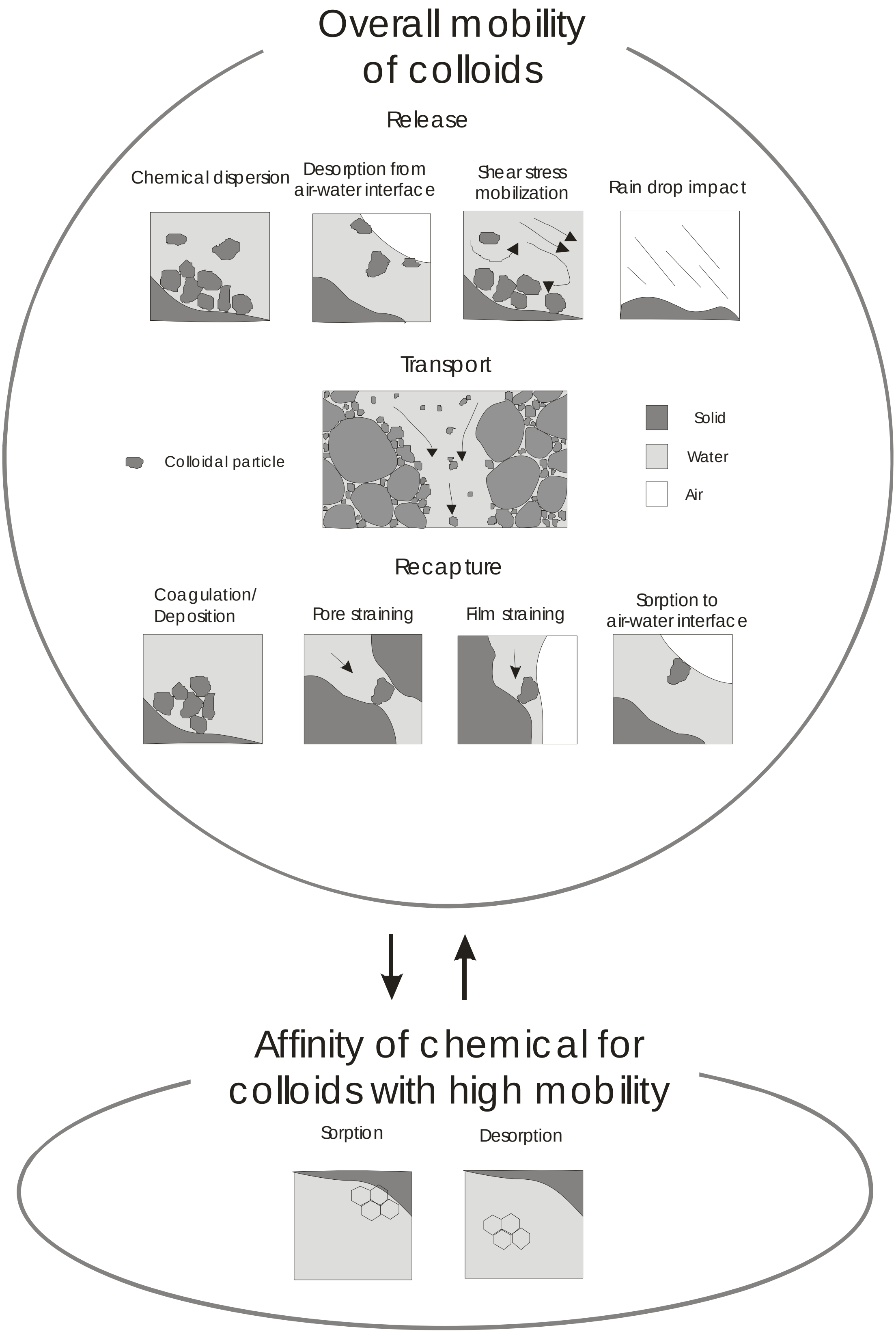

Figure 1: The processes of the colloid-facilitated transport**.** Mobility and affinity.

Two major issues determine the extent of colloid-facilitated transport: (i) the overall mobility of the colloidal particles involved in the transport and (ii) the sorption affinity of the chemical to the mobile colloids or the potentially mobile colloids (Figure 1). The overall mobility is determined by the extent of colloid release, the transport of the colloid through the pores of the soil and the extent of recapture of the colloids. The colloidal particles may become released from within the soil by chemical dispersion and desorption from the interface between the air and water phases and from the surface of the soil by shear stress in overland erosive flow and by the mechanical impact of raindrops. Once the colloids are released into the soil water, transport may occur. Colloids are excluded from smallest pores in the soil due to the size of the colloidal particles. The colloids may be transported along with the water through the pores of the soil until they are recaptured. The recapture may be due to the coagulation of colloids or by chemical deposition of colloids to the stationary phase of the soil, physical straining in a small pore or a thin water film or sorption onto the interface between air and water. Sorption and desorption of contaminants to soil colloids may occur while colloids are in suspension or while attached either to a soil aggregate or to air-water interfaces. Only the sorption to colloids with a high mobility is interesting when the colloid-facilitated transport is to be quantified.

The topsoil is the source of the surface-applied pollutants and of mobile colloids found in groundwater and drainwater (Mercier et al., 2000). If colloid-facilitated transport is to be integrated in the risk assessment when new agrochemicals are legalized or when waste products (e.g. sewage sludge, ash or industrial waste) are permitted for deposition on agricultural soils, knowledge about the processes in the topsoil is essential. The topsoil differ from the sandy groundwater aquifer: (i) water flow in the topsoil is dominated by preferential flow due to extensive turbation by soil fauna and tillage, (ii) flow is unsaturated, (iii) the chemistry of the porewater is changing dynamically with the infiltration of low ionic strength rainwater, (iv) colloids are generally present in large amounts (for clay soils the source of colloids is unlimited), and (v) the topsoil generally contain a large amount of organic matter.

1.1. OBJECTIVES

The main objective of this thesis was to investigate the processes of colloid-facilitated transport with regard to the surface-applied chemicals in agricultural soils. The work focuses on the topsoil processes, since there is a lack of knowledge about the processes in this particular area. Two important issues formed the centre of the investigation. One was the indigenous organic matter content of the soil. This was studied using two soils with similar geological history and textural composition and different managements through a longer period of time, leading to different organic matter contents. Soil characteristics and sampling are described in App. A. The soil with the high organic matter content will be referred to as *Manured soil* and the soil with the low organic matter content as *Depleted soil* in the following. Another issue was the chemistry of soil water. This was studied using three levels of ionic strength and two different cations (Ca^{2+} and K^{+}). Pyrene, a four-ringed PAH, has been used as a model substance for the sorption of hydrophobic organic compounds (HOCs) to the colloids, and for the colloid-facilitated transport of HOCs.

The following aspects concerning colloid-facilitated transport will be presented in this thesis:

Soil colloids and their release from soil aggregates
The objectives were:

- to evaluate how the amount of indigenous organic matter in the soil affect the amount and properties of the colloids released from the aggregates
- to evaluate how different degrees of disruption of the aggregates influence the amount and properties of the colloids released from the aggregates

Traditionally, the potential of a soil to disperse has been evaluated by batch dispersion methods. Soil aggregates are immersed in water and rotated and the amount of colloids released is considered as an estimate for the amount of dispersible colloids of this particular soil. In this study, three different batch methods were used to release colloids from soil aggregates. The three methods involved three different degrees of aggregate disruption. The *TC* method involved total chemical/mechanical disruption of the soil aggregates, the *WDC* method involved mechanical breakdown of the aggregates, and the *SWDC* method involved spontaneous release of colloids from the aggregates with a low degree of mechanical breakdown. The colloid suspensions released by the three different methods were characterized.

Leaching of colloids from soil
The objectives were:

- to investigate how indigenous organic matter content affects the leaching of colloids from aggregated soil
- to investigate how the chemistry of the irrigation water affects the leaching of colloids
- to investigate how the irrigation intensity affects the leaching of colloids

Release, transport, and recapture of colloids are dominated by preferential flow in intact soil. The flow paths of the water in soil are complex and may only be investigated by means of bulk measurements (e.g. hydraulic conductivity or tracer experiments). To be able to investigate single chemical and physical factors affecting the leaching, a simpler system than intact soil has to be used. Leaching experiments were conducted on columns packed with aggregates under unsaturated flow. The 2-4 mm aggregates were packed into columns and irrigated with water with different chemistry and irrigation rate. The simple geometry allows for evaluation of the effect of indigenous organic matter, chemistry of irrigation water and irrigation intensity.

Modelling of colloid release, transport and recapture
The objectives were:

- to develop a model capable of describing the leaching of colloids from aggregated soil
- to identify key parameters for leaching of in-situ mobilized colloids from aggregated soil

A model was developed for in-situ mobilization of colloids from unsaturated aggregated soil. The model describes the colloid transport by convection-dispersion in the inter-aggregate pores. Colloids are released from aggregate surfaces and air-water interfaces as a function of ionic strength at the aggregate surface and the mobile water respectively. When colloids are released from the aggregate surface they have to diffuse through a stagnant layer of water before reaching the flowing water. The ionic strength is simulated using a two-domain model with convection-dispersion in the mobile domain (inter-aggregate pores) and a mechanistic diffusion model in the immobile domain (intra-aggregate pores). The model was calibrated against the leaching experiments with separate parameter sets for the *Manured* and *Depleted soil*. A sensitivity analysis was conducted to identify key parameters for colloid leaching.

Hydrophobic sorption in relation to facilitated transport

The objectives were:

- to evaluate how the indigenous organic matter content affects the sorption of a hydrophobic organic compound to the potentially mobile colloids
- to evaluate how the degree of aggregate disruption affects the sorption properties of a hydrophobic organic compound to the potentially mobile colloids
- to evaluate how the solution chemistry affects the sorption of a hydrophobic organic compound to the potentially mobile colloids
- to evaluate how these changes affect the facilitated transport of a hydrophobic organic compound

Sorption experiments with pyrene were conducted using the bulk soil and colloids released from aggregates by chemical/mechanical break-down of aggregates, mechanical break-down of aggregates and spontaneous release on the *Manured* and *Depleted soil*. The sorption was investigated using different solution chemistries. The sorption data were fitted to Freundlich isotherms and the Freundlich parameters were evaluated. A static leaching model was calibrated against leaching experiments with pyrene from columns packed with aggregates. The model was used to evaluate how the differences in sorption properties would affect the colloid-facilitated transport of pyrene.

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2. SOIL COLLOIDS AND THE RELEASE FROM SOIL AGGREGATES

The initiating process for the colloid-facilitated transport is the release of the colloidal particle from the soil aggregate. The colloid properties, solution chemistry and the way the colloids are associated in the aggregate influence the likelihood of a colloidal particle to be released.

2.1. COLLOIDS IN SOILS

Colloidal particles are small particles (in the following referred to as colloids). The size is defined to be between 1 nm and 1 µm (e.g. Hunter, 1986). In soils, the entire clay fraction is normally considered to be colloidal, since the clay minerals behave as colloids. The motion of colloids is more dominated by Brownian motions than by gravity. When colloids are stable, the low gravitational settling will render them in suspension for longer periods. Another of the important characteristics of colloidal particles is that the specific surface is large (> 10^2 m^2/g, Kretzschmar et al., 1999). This provides the colloidal particles with a high reactivity and defines the importance of soil colloids in processes like sorption, ion exchange and water retention. Although small parts of the colloids in soils are microorganisms and viruses, soil colloids are mostly complex assemblages of clay minerals, oxides and hydroxides, and organic matter (Figure 2). The clay minerals have an overall negative charge due to isomorph substitution and ionization of functional groups on the surface of the mineral. The charge originating from isomorph substitution is regarded as a permanent charge and the charge originating from ionization is pH-dependent. Oxides and hydroxides generally have a positive charge at neutral pH, but the charge is highly pH-dependent. Coatings of oxides on layer-silicate minerals may drastically alter the charge of the colloid and hereby the stability.

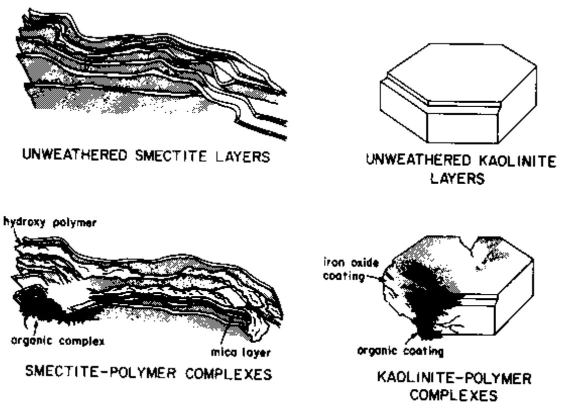


Figure 2: Natural soil colloids and their unweathered origin (from Sposito, 1989).

2.2. SOIL ORGANIC MATTER

Soil contains different kinds of organic matter but the major groups are *polysaccharides* and *humic substances*. Polysaccharides are excreted from plant roots, microorganisms and fungi to protect the living cells from the environmental stresses in the soil. The polysaccharides are produced in large amounts in the soil but are degraded fast. The stable parts of the organic matter in soil (humic substances) are remains from microbial life. Humic substances have traditionally been devided into fulvic and humic acids and humin according to the solvability in different solvents. The humic materials are large rigid biomolecules with many functional groups and an overall negative charge at neutral pH. The charge is highly pH-dependent with a higher charge at lower pH, due to protonation. The humic material is soils are normally found in association with the inorganic particles.

2.3. ELECTRICAL DOUBLE LAYER

If a charged colloid is placed in an electrolytic solution, the field around the colloid will attract ions with opposite charge (counterions) to the surface and repel the ions of the same charge (coions) away from the surface. Together the polyanionic surface charge and the swarm of counterions in the vicinity of the surface constitute the electrical double layer (Hiemenez, 1986). The swarm of counterions is referred to as the diffusive layer. When equilibrium is achieved in a suspension of colloids the electrochemical potential in the double layer will be balanced by the electrochemical potential of the bulk solution. Two different models for the distribution of ions and counterions in the vicinity of the colloid will be described: i) the Gouy-Chapmann model and ii) the Stern model.

2.3.1. GOUY-CHAPMANN MODEL

In the Gouy-Chapmann model the charge is considered evenly distributed over the surface and it is assumed that the ions are point charges and that the dielectrical constant is invariant with the position in the double layer. The Poisson-Bolzmann equation describes the variation in the electrical potential (ψ) throughout the diffuse layer surrounding a single spherical particle:

$$\frac{d^2\psi}{dx^2} = -\frac{e}{\varepsilon} z c_0 \exp\left[-\frac{ze\psi}{k_B T}\right] \qquad [2.1]$$

where e is the elementary charge, ε is the dielectrical constant of the electrolytic solution, z is the ionic valence, c_0 is the electrolyte concentration far away from the double layer, k_B is the Boltzmann constant and T is temperature.

At low electrical potentials of the double layer, the Poisson-Boltzmann equation simplifies to

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi \qquad [2.2]$$

where κ is the Debye-Hückel parameter.

$$\kappa^2 = \frac{e^2}{\varepsilon k_B T} z^2 c_0 \qquad [2.3]$$

In equilibrium the potential of the diffuse layer may then be approximated by

$$\psi = \psi_0 \exp[-\kappa x] \qquad [2.4]$$

where ψ_0 is the electrical potential of the surface of the colloid.

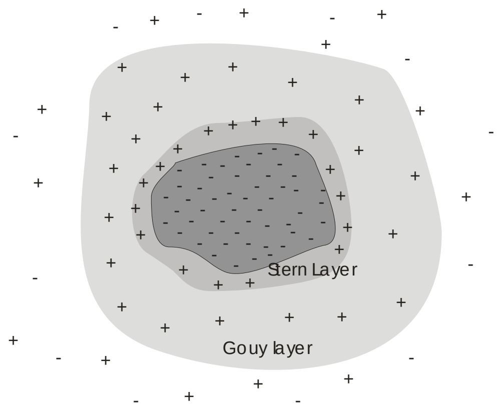
$1/\kappa$ may also be regarded as the thickness of the electrical double layer. This parameter has values ranging from one µm in pure water to one nm in concentrated electrolytic solutions (Gregory, 1989). The quantitive application of the Gouy-Chapmann model is limited since the ions are considered point charges. At moderate surface potentials it gives absurdly high values for the amount of counterions adsorbed into the diffuse layer (Sparks, 1999).

2.3.2. STERN MODEL

Stern divided the diffuse layer into two parts: a compact layer of adsorbed counterions (the Stern layer) and a more diffuse part (the Gouy layer). This model accounts for the finite size of the ions and the possibility of specific adsorption of ions. The total surface charge (σ) outbalances the sum of the charge of the Stern layer (σ_1) and the Gouy layer (σ_2)

$$\sigma = -(\sigma_1 + \sigma_2) \qquad [2.5]$$

The Stern Layer (Figure 3) is generally considered to have a thickness corresponding to the size of the hydrated counterion (δ), i.e. between 0.3 and 0.5 nm depending on the type of counterion (Gregory, 1989). There is currently no method to measure the Stern potential, but the zeta-potential has been used.



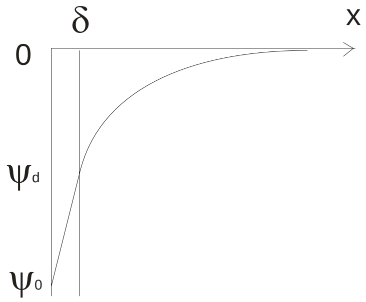


Figure 3: The Stern model for the electrical double layer

For a flat colloid (clay platelet) the charge of the Stern layer may be calculated by Sparks (1999):

$$\sigma_1 = \frac{N_i zF}{1 + \frac{N_A w}{Mc_0} \exp\left[-\frac{zF\psi_d + \phi_{sa}}{RT}\right]} \qquad [2.6]$$

where N_i is number of adsorption sites available per area for ionic species, N_A is Avogadro's number, M is the molar mass of the solvent, w is the solvent density, ϕ_{sa} is the specific adsorption potential, ψ_d is the Stern potential and d is the thickness of the Stern layer.

The Gouy layer charge may be calculated by Sparks (1999):

$$\sigma_2 = \sqrt{\frac{2c\varepsilon RT}{\pi}} \sinh\left[\frac{zF\psi_d}{2RT}\right] \qquad [2.7]$$

The double layer of colloids may be influenced by the chemistry of the solution in two ways. The extension of the diffuse layer may be affected and the effective surface potential (Stern potential) may be affected. When the electrolyte concentration is raised, the electrical double layers expand. Higher electrolyte concentration will also increase the amount of adsorbed ions in the Stern layer and the Stern potential will be decreased. If the electrolytes are indifferent, the adsorption will be governed by Eq [2.6] and the effect will be limited (Figure 4a and 4b). If the adsorbing ions are specifically adsorbing counterions, the sorption is governed by specific non-electrostatic affinity. The sorption may proceed to an extent where the sign of the Stern potential is reversed (Figure 4c).

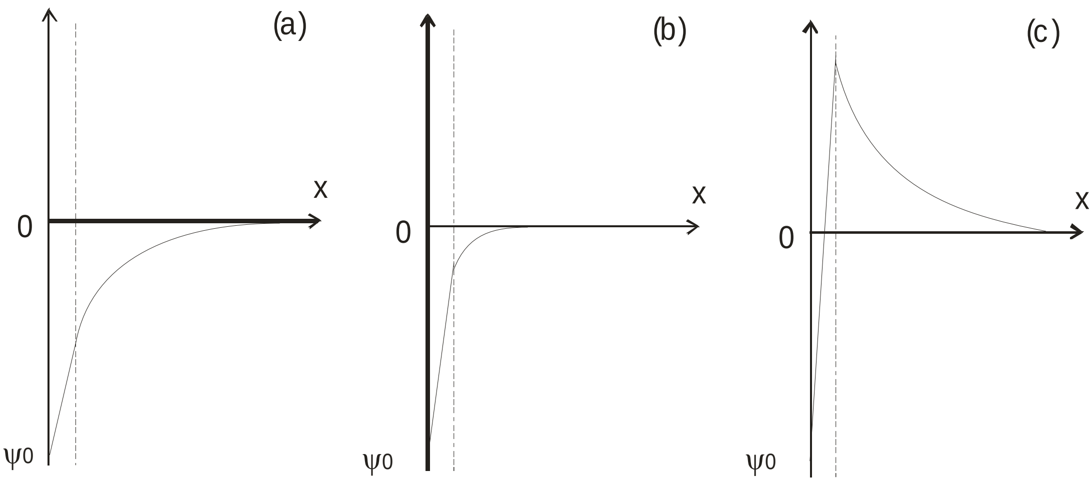


Figure 4: The electrical double layer with (a) a low concentration of indifferent electrolytes, (b) a high concentration of indifferent electrolytes, and (c) with specifically adsorbing counterions.

2.4. VAN DER WAALS INTERACTION

The Van der Waals force is an overall attractive force, acting between atoms and molecules but also between macroscopic objects, and it is the driving force of flocculation of colloids. The Van der Waals force arises from spontaneous magnetic and electric polarizations, resulting in an electromagnetic field in the bodies and the gap between them. Dipole and induced dipole interactions together with hydrogen bonding and short-range repulsion from Coulombic repulsion constitute the total Van der Waals force. The dielectical data for the interacting bodies and the material between them are important parameters in determining the magnitude of the Van der Waals force.

The traditional way to calculate the Van der Waals force is developed by Hamaker (1937). The assumption is that the intermolecular forces are pair-wise additive. The interaction energy between two particles is assumed to be the sum of all the interactions energies of the molecules in one particle with the molecules in the other particle. For two spheres radius a_1 and a_2 separated by the distance d of vacuum, the interaction energy at close approach V_A is:

$$V_A = -\frac{A_{12}}{6d}\frac{a_1 a_2}{(a_1 + a_2)} \quad [2.8]$$

where A_{12} is the Hamaker constant of the interaction between media 1 and 2 of which the spheres are composed.

For two theoretical 2:1 layer-silicate mineral, the attractive energy is (Sparks, 1999):

$$V_A = \frac{-A}{48 \cdot \pi}\left(\frac{1}{d^2} + \frac{1}{(d+\Delta)^2} - \frac{2}{(d+½\Delta)^2}\right) \quad [2.9]$$

where A is the Hamaker constant for the mineral, d is the distance between the mineral platelets, and Δ is the thickness of the unit layers.

2.5. HYDRATION EFFECTS

At very close approach other forces may affect the flocculation. Water molecules close to the surface of the ions and charged colloids tend to create a semi-crystalline structure of bound water molecules. When the colloids are approaching very closely, the bound water molecules will repel each other. If the water molecules are to break up the structure the free energy of the system must increase. The distances of closest approach will be determined by the strength of the hydration effect and the strength of the Van der Waals force. The flocculation of particles is affected when the distance between the colloids are a few molecule layers (Gregory, 1989).

2.6. COLLOID STABILITY

A colloid suspension is stable when the average size of the colloids does not increase at a significant rate to a point where gravitational settling can occur. Flocculation, coagulation, and aggregation are different terms describing the processes resulting from unstable suspensions. The term coagulation will be used as the general term for the attachment of particles to each other. Flocculation is used for describing loose structuring in an open network, often of a more temporary nature. Aggregation is used to describe the creation of more permanent compact structures.

2.6.1. COMBINED INTERACTION

The combination of the electrical potential, the Van der Waals potential and the short-range forces determine the interaction between two colloidal particles. When the electrical double layer repulsive potential is expanding to a degree where the double layers interact (low ionic strength), the sum of the electrical energy and the Van der Waals energy constitute an energy barrier towards flocculation (Figure 5a). For flocculation to occur, the colloids have to overcome the energy barrier and flocculation will be slow. If the electrical double layer repulsive energy only acts over a short distance (high ionic strength), the energy barrier will be low or completely disappear, leading to fast flocculation (Figure 5b). Short-range forces (e.g. hydration effects) limit the depth of the primary minimum. If no such short-range forces were present, the primary minimum would be infinitely deep and resuspension of coagulated colloids impossible.

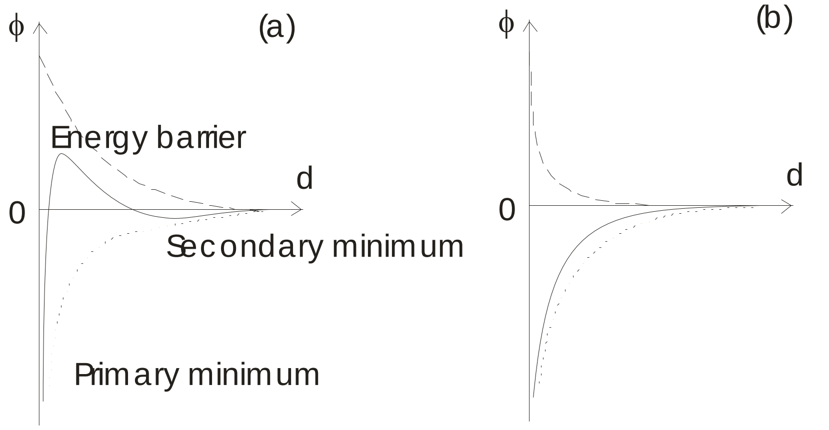


Figure 5: The interaction potential as a function of separation distance, d. (a) With slow flocculation controlled by the energy barrier and (b) with rapid flocculation. — total interaction potential energy, - - electrical interaction potential energy, and ··· Van der Waals interaction potential energy.

Leaving out the short-range forces, the interaction potential energy for two equal spheres is:

$$\phi_t = 32 \cdot \pi\, \varepsilon\, a \left(\frac{K_b T}{z\, e} \right) \gamma^2 \exp(-\kappa\, d) - \frac{Aa}{12 \cdot d} \qquad [2.10]$$

where ϕ_t is the total energy of interaction and γ is a dimensionless function of the surface potential. The *Critical Coagulation Concentration* (CCC) is the concentration of electrolyte where fast flocculation begins. At the point of fast flocculation:

$$\frac{d\phi_t}{dd} = 0 \text{ and } \phi_t = 0 \qquad \Rightarrow$$

$$CCC = Const \left(\frac{\gamma^4}{A^2 z^6} \right) \qquad [2.11]$$

CCC varies inversely with the sixth power of the counterion valence (Shulze-Hardy rule). Since soil colloids are heterogeneous, it is complicated to determine the CCC value. The flocculation progresses over a range in electrolyte concentration rather than occurring at one specific CCC.

2.6.2. SOIL ORGANIC MATTER AND COLLOID STABILITY

Organic matter in as small amounts as one percent of the soil may control the surface chemistry and thus the stability of the colloids (Bertsch and Seaman, 1999). Organic matter may influence the colloid stability in different ways. (i) Organic matter has a high content of functional groups that are negatively charged at neutral pH. This may lead to decreased surface charge of the colloids and hence to an increased colloid stability (Tipping and Higgins, 1982; Gibbs, 1983; Tiller and O'Melia, 1993; Kretzschmar et al., 1997; Buffle et al., 1998). (ii) When hydrophilic polymers are sorbed to the surface of colloids, the physical size of the polymer may restrict colloids from close approach and from primary minimum coagulation (Jekel, 1986; Heil and Sposito, 1993). This is called steric stabilization (Figure 6a). Heil and Sposito (1993) found that the colloid stability was decreased with removal of the organic matter from Illitic soil colloids without observed change in the electrophoretic mobility. This was attributed to steric stabilization. (iii) Long-chain polymers may attach to more than one colloid leading to coagulation (polymer bridging) (Figure 6b). Polymer bridging was postulated by Ruehrwein and Ward (1952) to account for the flocculation of clays with addition of polyelectrolytes. It has been hypothesized that large organic polyanions such as extracellular polysaccharides excreted from microorganisms may cement together particles in microaggregates by polymer bridging (Tisdall and Oades, 1982; Gregory, 1989; Dinel et al., 1991; Buffle, 1998).

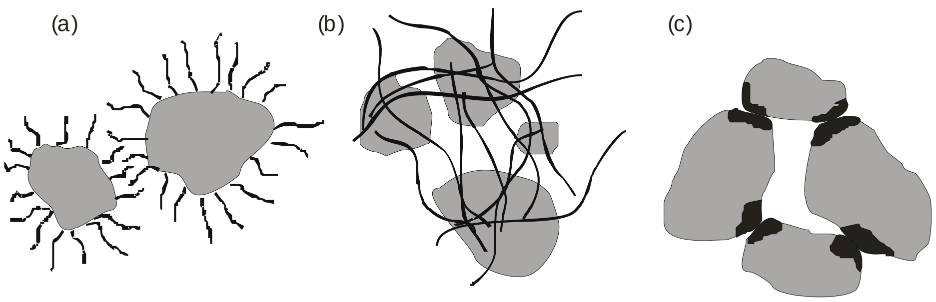


Figure 6: Stabilization of aggregates by organic matter: (a) Steric stabilization, (b) polymer bridging and (c) hydrophobic interaction

Two different binding mechanisms may attach the polyanions to the clay minerals. Polymers may be attached to positively charged areas of the clay minerals (direct polymer bridging), or may be attached to the negatively charged parts of the clay minerals by polyvalent cations (cation-polymer bridging). (iv) When part of the colloid surface is covered with hydrophobic organic matter, the colloids may coagulate by hydrophobic bonding (Figure 6(c)).

2.7. STRUCTURAL STABILITY

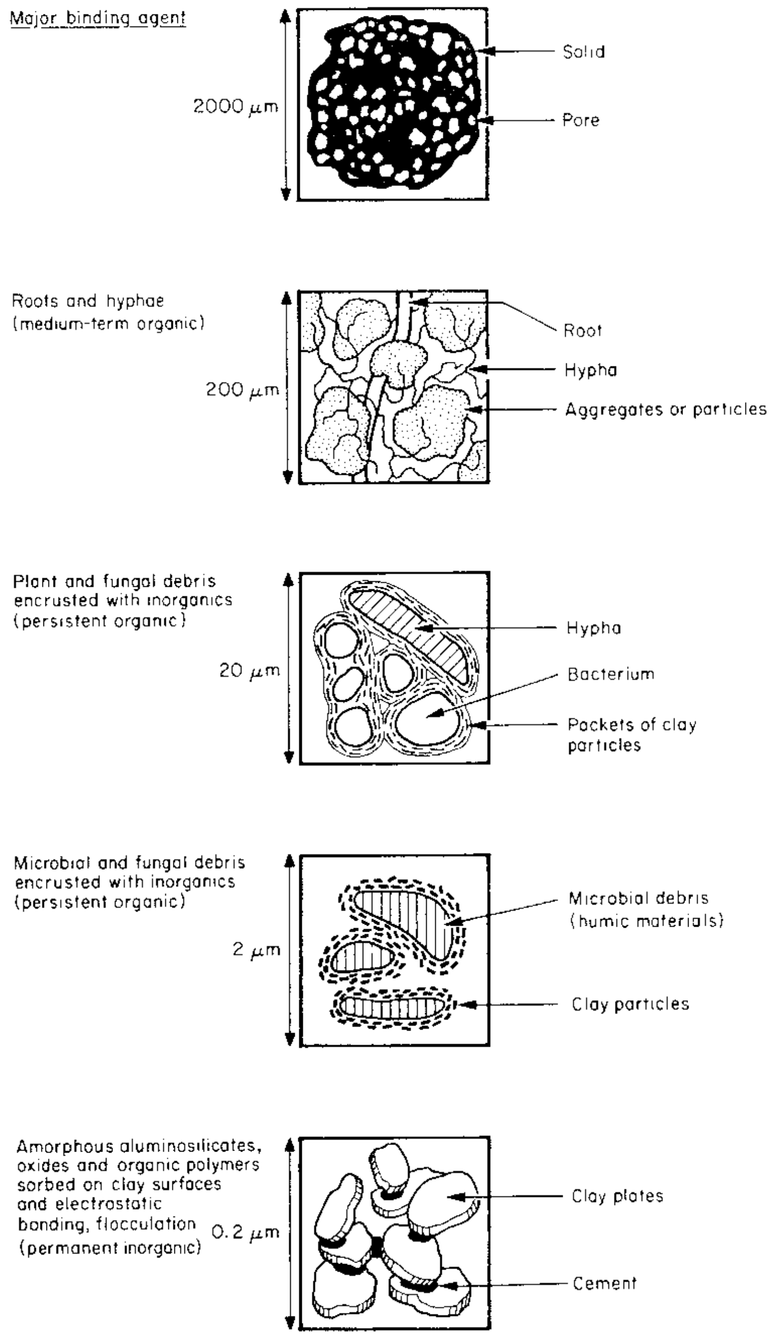


Figure 7: Model of aggregate organization and major binding agents (from Tisdall and Oades, 1982).

The structural stability or the aggregate strength of the soil has great practical importance in agriculture. Disruption of the aggregate structure leads to reduced permeability of the soil to air and water. In clay soils the amount and type of clay minerals is a major determinant for aggregate strength, especially in dry soils. Organic matter also plays a significant role in strengthening of aggregates when the soil is wet (Munkholm et al. 2002) or when it is not dominated by inorganic cementing agents (e.g. sesquioxides, clays) (Tisdall and Oades, 1982). The effect of organic matter as a binding agent has been classified into transient, temporary, and persistent (Tisdall and Oades, 1982). The transient binding agents are decomposed rapidly by microaggregates and consist mainly of polysaccharides (Figure 7). The transient binding agents are mainly mucilages produced by roots and microorganisms (Russel, 1973; Oades, 1978) and they stabilize larger aggregates. The temporal binding agents are roots and hyphae, also mainly stabilizing larger aggregates. The persistant binding agents are degraded aromatic humic material, remains of roots, hyphea, bacterial cells and mucilage. The persistant binding agents strengthen the microaggregates. Clay platelets are attracted to the surface of small particles of humic material and small aggregates may form (Tisdall and Oades, 1982).

Aggregates may be broken down due to external mechanical stress (tillage, erosive flow and raindrop impact), differential swelling and slaking. Swelling is the process where clay minerals expand as the double-layer forces between the sheets are increased. Differential swelling of the clay minerals in different parts of the aggregate may lead to disruption of the aggregate. Slaking is a process of aggregate breakdown occurring only with rapid wetting (Figure 8). When aggregates are wetted fast, the exterior of the aggregate may be saturated with water and the interior remain unsaturated with entrapped air in the centre of the aggregate. When the capillary forces drag the water inwards in the capillary pores of the aggregate, the pressure in the entrapped air increases, and may eventually break up the aggregate. Organic binding agents may increase the aggregate strength and reduce the breakdown due to external mechanical stress and differential swelling and slaking (Tisdall and Oades, 1982; Chenu et al., 2000). The resistance to slaking was increased up to four times when long-chain polymers were added (Dinel et al., 1991). Haynes and Swift (1990) suggested that increases in aggregate stability as a function of landuse may be viewed as merely a shift in the proportions of aggregates containing enough C to be stable.

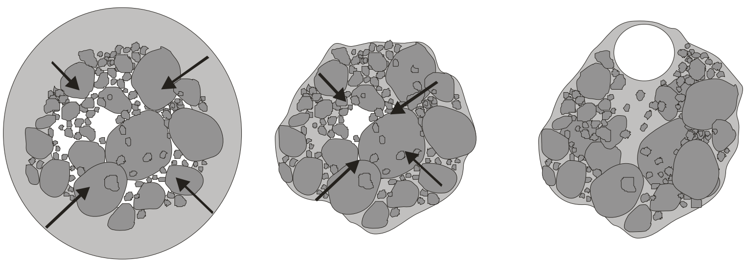


Figure 8: Slaking of a soil aggregate upon wetting.

2.8. COLLOID RELEASE FROM SOIL AGGREGATES

Colloids may be released from aggregates by different processes: chemical dispersion by double layer interaction, desorption from the air-water interface, hydrodynamic shear or raindrop impact (Figure 9).

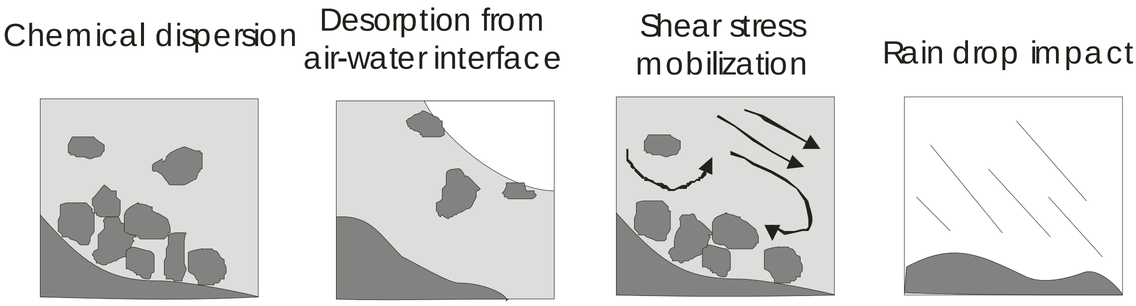


Figure 9: The different processes of release from soil aggregates.

2.8.1. CHEMICAL DISPERSION

Chemical dispersion is the process of mutual repulsion of colloids upon wetting. It is the most important process in releasing single particles from soil (Le Bissonnais, 1996). Low ionic strength and univalent counterions enhances the magnitude of the double layer and increases the electrostatic repulsion between the colloid and the surface of attachment (e.g. Kalley et al., 1987). The processes of detachment and attachment of colloids are both first-order reactions with the energy barrier towards detachment and attachment acting as activation energy (Ruckenstein and Prieve, 1976).

$$k_{\det} \propto e^{-\left(\frac{|\phi_{\max}-\phi_{\min}|}{kT}\right)} \qquad [2.12]$$

$$k_{att} \propto e^{-\left(\frac{|\phi_{\max}|}{kT}\right)} \qquad [2.13]$$

where $\phi_{\max}$ is the maximum of the colloid interaction curve, $\phi_{\min}$ is the depth of the primary minimum (se Figure 5). Both processes act at the same time and the combination of the two determines the net colloid release. If no energy barrier exists, local diffusion over the interaction boundary layer will control the overall release process (Ruckensten and Prieve, 1976; Ryan and Elimelech, 1996).

Organic matter may affect the chemical dispersion in two ways. As discussed earlier the organic matter may increase colloid stability by increasing the negative colloid charge or introducing steric stabilization (Gregory, 1989; Kretzschmar et al., 1995; Kaplan et al., 1997). This leads to higher dispersion of colloids in the soil. The increased stability suggests that the organic coated colloids will be released more readily than the non-coated colloids. It has been observed that the mobile colloid fraction in soils was enriched in organic carbon compared with the bulk soil (Kaplan et al., 1993; Laegdsmand et al., 2000) indicating that preferential leaching of organic-coated colloids with higher colloid stability occurs. Organic matter may also affect the aggregate strength. Mechanical breakdown may enhance the chemical dispersion by increasing the aggregate surface area, since spontaneous dispersion of colloids in soil, apart from the double layer interactions, is determined by the aggregate surface area (Kay and Dexter, 1990). Organic matter increases the aggregate strength by polymer bridging or hydrophobic bonding. This leads to lower aggregate breakdown and possibly to higher chemical dispersion of colloids in the soil.

2.8.2. DESORPTION FROM AIR-WATER INTERFACES

Wan and Wilson (1994) found that colloids sorbed onto the air-water interfaces and that especially hydrophobic colloids sorbed in large amounts. Adsorption of colloids in unsaturared sand columns and release upon saturation has been attributed to this process (Wan and Wilson, 1994; Ullum et al., 2002). Christ et al. (2002) found that hydrophilic colloids sorbed to the air-water–solid interface rather than the air-water interface. If the chemical conditions in the water changes, e.g. by lowered ionic strength, then the expanding double layers of the colloids associated with the air interface will lead to lowered sorption capacity of the interface (Lenhart and Saiers, 2002) and colloids will desorb. When flow changes in the soil (e.g. at irrigation start and transient flow), the moving air-water interface may also mobilize colloids (Saiers and Lenhart, 2003).

2.8.3. RELEASE BY EROSIVE FLOW AND RAIN-DROP IMPACT

Release of colloids by hydrodynamic shear is not believed to be a dominant process in pores in natural soil as the flow velocity generally is low. However, it is possible that narrow passages and ducts in the pore system may provide the conditions for shear stress mobilization. Surface erosion on slopes may also provide the conditions for shear stress mobilization.

When raindrops hit the surface, the mechanical energy stored in the raindrop may break down aggregates. The release of colloids will be determined by the stability of the aggregates, amount of mechanical energy (raindrop size and intensity) as well as the chemistry of the raindrops (Agassi et al., 1985).

2.9. RELEASE OF COLLOIDS IN BATCH SYSTEMS

The mobilization of colloids may be studied in batch systems to evaluate the potential for colloid release (Kay and Dexter, 1990). The clay content of the soil has been used as a predictor for the release of colloids by Jarvis et al. (1999), based on the relationship between clay content and the amount of water-dispersible colloids found by Brubaker et al. (1992). The release of the total clay fraction involves total chemical and mechanical dispersion of the aggregates. The water-dispersible colloids method has also been used for the prediction of the amount of releasable colloids in soil (Seta and Karathanasis, 1996). Water-dispersible colloids are normally measured by applying mechanical stress to soil/water mixtures (end-over-end rotation of a sample containing water and soil aggregates for a longer period of time). Miller and Barahudin (1986) observed that the amount of water-dispersible clay was highly correlated with the soil loss due to surface erosion. Ramsey et al. (1986) found that if the sample container was only rotated for a short period of time, the amount of colloids released was much lower. This method is in the following referred to as Spontaneous Water-dispersible Colloids (S*WDC*). It involves a low degree of mechanical breakdown to simulate release without disruption of the aggregate structure. Kay and Dexter (1990) found that the aggregate surface area and the dispersibility of the clay were major determinants for the release of S*WDC*.

2.9.1. DISPERSIBLE COLLOIDS AND COLLOID-ASSOCIATED ORGANIC MATTER

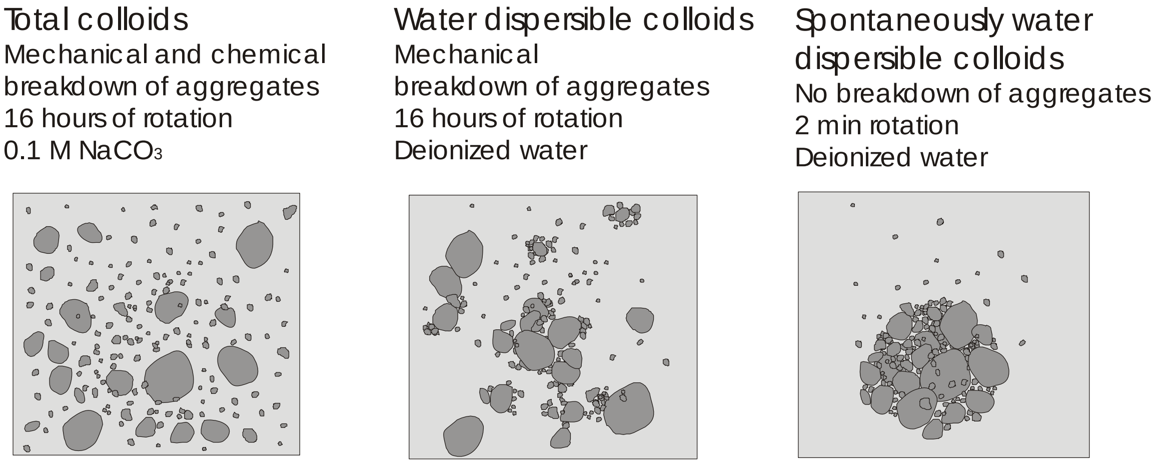


Figure 10: The three dispersion methods used.

Dispersible colloids released from soil by three different degrees of aggregate breakdown were isolated from the *Manured* and *Depleted soil* (Paper I). The dispersible colloid fractions were: Total colloids (*TC*) released by total chemical and mechanical breakdown of the aggregates, Water-dispersible colloids (*WDC*) released from soil by mechanical breakdown of aggregates, Spontaneous water-dispersible colloids (S*WDC*) released spontaneously with only little mechanical breakdown. The air-dry soil was saturated with artificial soil water and immersed in liquid (DW or 0.1 M $NaCO_3$) in a soil:liquid ratio of 1:8 (w/w) in a sample container. The mechanical stress was applied (16 hours end-over-end rotation or 10 inversions of the sample container) and the suspension was left to settle to isolate the particles < 2 µm. The settled particles from the *TC* suspensions were resuspended in 0.1 $NaCO_3$ and left to settle five times. After the isolation procedure, the colloids in the *TC* suspension were washed in DW five times to remove excess Na^+ and at last resuspended in artificial soil water. Figure 10 shows the different methods of colloid release. Please consult Paper I for further description of the experimental details.

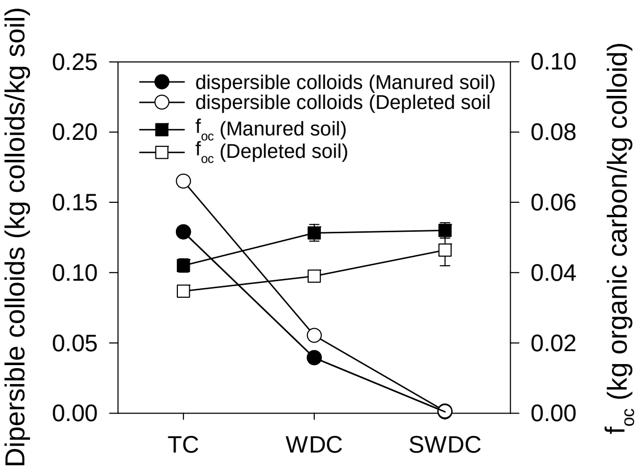


Figure 11: Amount of dispersible colloids and fraction of organic matter (f_{oc}) (Paper I).

Dispersible colloid concentrations and mass fraction organic carbon (f_{oc}) varied as a result of the different fractionation methods and soils (Figure 11). The *TC* fractionation method released the highest amount of colloids (76 and 87% of the clay fraction for the *Manured* and *Depleted soil,* respectively) with the lowest f_{oc}. The S*WDC* fractionation method released less than 1% of the clay fraction. The lower amounts of colloids generally released from the *Manured soil* compared with the *Depleted soil* were probably due to organic matter stabilization of the aggregates. The colloids from the *Manured soil* had a higher mass fraction of organic carbon relative to the *Depleted soil*.

2.9.2. COLLOID SIZE DISTRIBUTION

The release process had no significant effect on the size distribution of particles above 1 µm and neither did the soil organic matter content (not shown). Between 65 and 85% of the total number of particles existed as coarse colloids (> 1 µm). The mean size of these colloids was 10 µm but was highly variable when mechanical stress was applied to the suspensions. The coarse colloids were aggregates/flocs of colloids formed after the preparation of the suspensions since the original suspension was sedimented to a particle size < 2 µm.

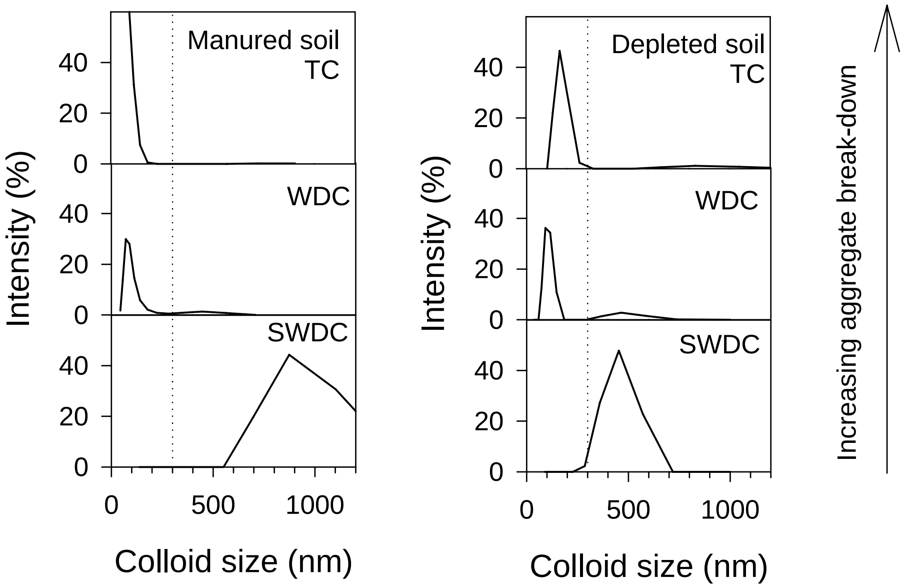


Figure 12: The particle size distribution for the colloids with a particle size below 1 µm (data from Paper I).

The colloids with a particle size below 1 µm however, showed a strong dependency of the method of release (Figure 12). The S*WDC* colloids had a mono-disperse size distribution with a peak particle size above 300 nm but the *WDC* and *TC* had two distrinct classes of colloids: one above and one below 300 nm.

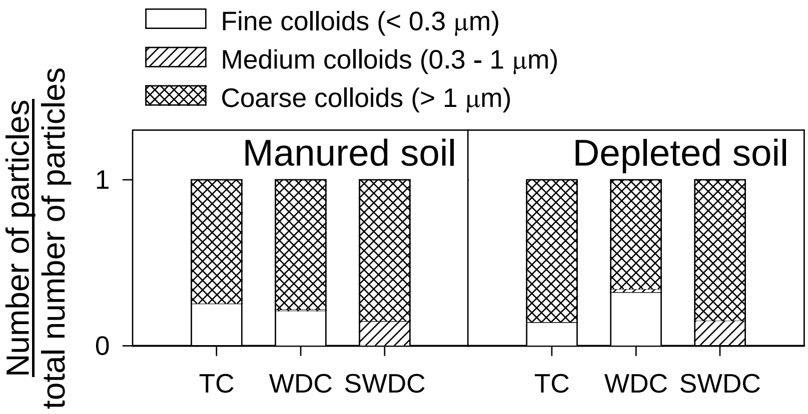


Figure 13: Distribution of colloids in three particle size classes (Paper I)

In the *TC* suspensions, almost all particles were large or fine and the amount of medium size colloids was only 0.1 and 0.3% for *Manured* and *Depleted soil* respectively (Figure 13). The chemical dispersion in the *TC* suspensions released large amounts of fine colloids (<0.3 µm) and almost no medium colloids (0.3-1 µm). The *WDC* suspension of the *Manured soil* contained 0.7% of medium-size colloids and 21.1% fine colloids. The *WDC* suspension of the *Depleted soil* contained 2.0 % medium-size colloids and 32.2 % fine colloids. The mechanical stress employed in the *WDC* suspensions also released large amounts of fine colloids in both soils and small amounts of medium sized colloids. The opposite was the case for the SWDC suspensions. In the *Manured* and *Depleted soil* respectively 14.8 and 15.3 % of the colloids were medium colloids and no fine colloids could be measured.

2.9.3. ORGANIC MATTER ASSOCIATED WITH THE DIFFERENT COLLOID SIZE CLASSES

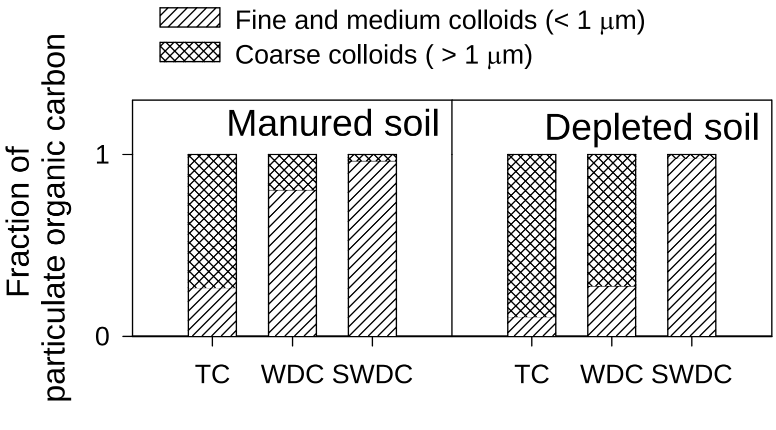


Figure 14: Organic matter associated with the colloids below and above one micrometer (Paper I)

In suspensions from the *Manured soil* a larger fraction of the organic matter was generally associated with the fine and medium-size colloids (< 1 µm) compared with the *Depleted soil* (Figure 14). The organic matter was distributed differently among the three types of suspensions. The organic matter associated with the colloids in *TC* suspensions was preferentially associated with the larger colloids. The organic matter associated with the colloids of the *WDC* suspension on

the *Manured soil* was predominantly associated with the medium and fine colloids (< 1 μm). On the *WDC* suspension from the *Depleted soil* more was associated with the large colloids.
In the S*WDC* suspensions the organic matter was preferentially associated with the fine and medium-size colloids (< 1 μm). Since no fine colloids were present in the S*WDC* suspensions the organic matter must have been associated solely with the medium-size colloids.

In the *TC* and WDC suspensions there was a distinct class of colloids smaller than 300 nm and a large part of the organic matter was associated with particles > 1 μm. The S*WDC* suspensions contained no fine colloids (0.03 – 0.3 μm) and almost all colloid-associated carbon was present in the < 1 μm colloids class. It seems that the chemical and mechanical stress applied in the preparation of WDC and TC suspensions induced break-down of medium colloids under release of organic matter and fine colloids. This indicates that the medium size colloids are in fact micro-aggregates and that the cementing agent is organic matter. This supports the theory of aggregate hierarchy by Tisdall and Oades (1982) suggesting that the micro-aggregates (< 2 μm) of the soil consisted of a core of humic material surrounded by clay platelets (Figure 7).

2.10. Conclusions

2.10.1. Indigenous organic matter

A higher content of organic matter reduced the release of colloids by three different batch techniques. Fewer colloids were released from the *Manured soil* with chemical/mechanical and mechanical breakdown of aggregates as well as with spontaneous release compared with *Depleted soil*. The amount of organic matter associated with released colloids was higher for the *Manured soil* compared with the *Depleted soil*. Since the *Manured soil* released fewer colloids than the *Depleted soil*, it seems that the structural stability controlled the release of colloids from aggregates by all three batch techniques.

2.10.2. Release process

More colloids were released from soil aggregates with a higher degree of aggregate breakdown. If the colloids were released by chemical and mechanical breakdown of aggregates, both coarse (> 1μm), medium (between 0.3 μm and 1μm) and fine (< 0.3 μm) size colloids were found. If the colloids were released spontaneously, only coarse and medium size colloids were found. The amount of organic matter associated with the total population of released colloids decreased with an increasing degree of aggregate breakdown. The stronger the disruption of the aggregates, the more of the organic matter was associated with the coarse colloids (> 1 μm).

It seems that the medium size colloids were converted to fine colloids by both mechanical and chemical stresses. The breakdown of medium size colloids were accompanied by removal of organic matter from the colloids. This indicates that the medium size colloids were predominantly micro-aggregates and that the cementing agent was organic matter.

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3. LEACHING OF COLLOIDS FROM SOIL

Once colloids have been mobilized from the aggregates, transport to drain, surface waters and groundwater is possible. The colloids may be transported along with the water of the soil pores until the colloids are recaptured or until the flow of water in the pores stops. The presence of surface-derived colloids in groundwater sediments indicates that the colloids may be transported through the soil, but the formation of clay-rich horizons in the soil and clay skins on macropore walls is physical evidence that colloids are recaptured during the transport through the soil pores.

3.1. TRANSPORT AND RECAPTURE OF COLLOIDS IN SOIL PORES

The transport of colloids in natural soil pores is driven by convection and dispersion in the larger pores and diffusion in the small pores. Diffusion of colloids is strongly retarded compared with the diffusion of solutes, due to a lower diffusion coefficient. Early breakthrough of colloids when applied to soil columns has been observed (e.g. Jacobsen et al. 1997; Grolimund et al, 1998; McCarthy et al., 2002). This may be attributed to size exclusion or retarded diffusion. Colloids are restricted to movement in pores larger than their size (size exclusion), but also repulsion between the negatively charged soil matrix in the smaller soil pores and the negatively charged colloids prevents the colloids from entering small pores (anion exclusion). Colloids and large organic molecules are transported slowly from the mobile flow domain to the immobile, due to a low diffusion coefficient. All of these three processes lead to a lower exchange with the immobile or slowly mobile water and to faster breakthrough of colloids compared with conservative tracer.

Colloids may be removed from solution by deposition onto the stationary soil particles, pore straining, film straining, and by adsorption to the air-water interface (e.g. Seta and Karathanasis, 1997; Grolimund et al., 1998; Grolimund et al. 2001, Saiers, 2002) (Figure 15):

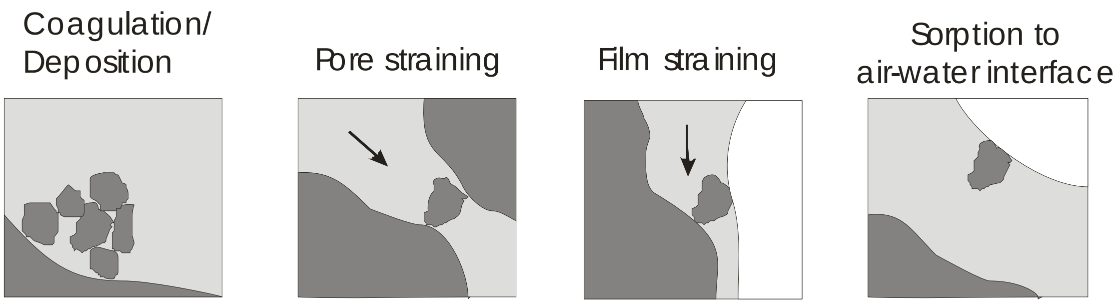

Figure 15: The four major capture processes of colloids in a natural soil media.

3.1.1. COAGULATION AND DEPOSITION ONTO SOIL SURFACES

Colloids may coagulate and form larger flocs that may sediment or be strained in the soil. Colloids may also be deposited directly on the stationary soil surface. Coagulation and deposition depend on the chemistry of the soil water and is a dominating process only when chemical conditions are favorable for flocculation (double layers are condensed). When colloids are deposited on stationary soil particles, the net deposition rate may be calculated by Eq [2.12] and [2.13]. If no energy barrier towards deposition is present, the diffusion of the colloids over the interaction boundary layer will control the deposition (Ruckenstein and Prieve, 1976).

3.1.2. STRAINING PROCESSES

Pore straining is the process of physical capture of colloids entering small pores. Preferential flow will reduce the straining since colloids are transported fast though the soil, bypassing most of the smaller pores. Film straining is a process of capture due to a low water film thickness and discontinuity of the water phase. The process of recapture by film straining may occur under transport in unsaturated soil. If conditions are favorable for deposition, the likelihood of colloids being strained by either pore straining or film straining in the soil is higher since both pore and film straining depend on the particle size.

3.1.3. ADSORPTION ONTO AIR-WATER INTERFACES

Adsorption onto the air-water interface has been described by Wan and Wilson, 1994. Especially hydrophobic colloids (e.g. colloids with a high degree of organic coating) are subject to this kind of capture (Wan and Wilson, 1994). Wan and Tokunaga (2002) found that kaolinite colloids showed high affinity for the air-water interface. The sorption capacity was pH- and ionic strength dependent. Illite colloids showed the same pH and ionic strength dependence but a lower affinity. Na-Montmorillonit and Bentonite were not sorbed onto the air-water interface (Wan and Tokunaga, 2002).

3.2. LEACHING OF COLLOIDS FROM AGGREGATED SOIL

In-situ release and leaching of colloids from naturally structured topsoils have been investigated by Jacobsen et al. (1997), Jarvis et al. (1999), Laegdsmand et al. (2000), Villholth at al. (2000), Schelde et al. (2002), and Kjaergaard et al. (2004) but the relative importance of the processes described above is not well-established. It was demonstrated that leaching from structured soil was controlled by a time-dependent process (Jacobsen et al., 1997; Laegdsmand et al., 2000; Schelde et al., 2002) most likely a diffusion limitation of some of the processes involved in colloid mobilization, viz colloid diffusion or ion diffusion out of the soil matrix. Kjaergaard et al. (2004) found that the mobilization was affected by clay content, initial water content and preferential flow. The leaching of colloids from structured soil was affected by ionic strength of the pore water when high ionic strength pore water was exchanged with low ionic strength irrigation water (Laegdsmand et al., 2000; Kjaergaard et al., 2004). Laegdsmand et al. (2000) observed that the steady-state flux of colloids at different pore water velocities was controlled both by the velocity and by the area of contact between the pore wall and the flowing water.

When dealing with structured soil, there is a tendency that the processes involved in colloid leaching are hidden by a high variability of the soil structure. Also, the effect of preferential flow on colloid leaching in structured soils becomes indistinguishable from the effect of ionic strength on colloid release, as the ionic strength of the effluent is determined by the exchange of infiltrating water with resident water. When there is high degree of preferential flow, low-ionic strength infiltrating water will bypass most of the soil and the effluent will have low ionic strength. It will then be difficult to determine which processes are involved in colloid leaching.

As discussed in the previous chapter the colloid stability is influenced by the organic matter content. A lower stability also increases the flocculation and hereby the capture of colloids in the soil. Kretzschmar et al. (1995) observed that the recapture was increased with the removal of natural organic coatings on colloids, when measuring the transport of colloids through intact soil.

I conducted leaching experiments on unsaturated columns packed with natural soil aggregates. (Paper II). The idea was to create a hydrologically simple but chemically realistic soil system for the study of colloid leaching from the source layer in the soil. The air-dry aggregates were packed in columns and slowly saturated (one week) with artificial soil water, incubated for a week and then leaching experiments were conducted. The lower boundary condition for the experiments was -10 kPa. Conservative tracer experiments were also conducted with the same boundary conditions as the leaching experiments. Figure 16 shows the experimental setup. Please consult Paper II for further details regarding the experiments.

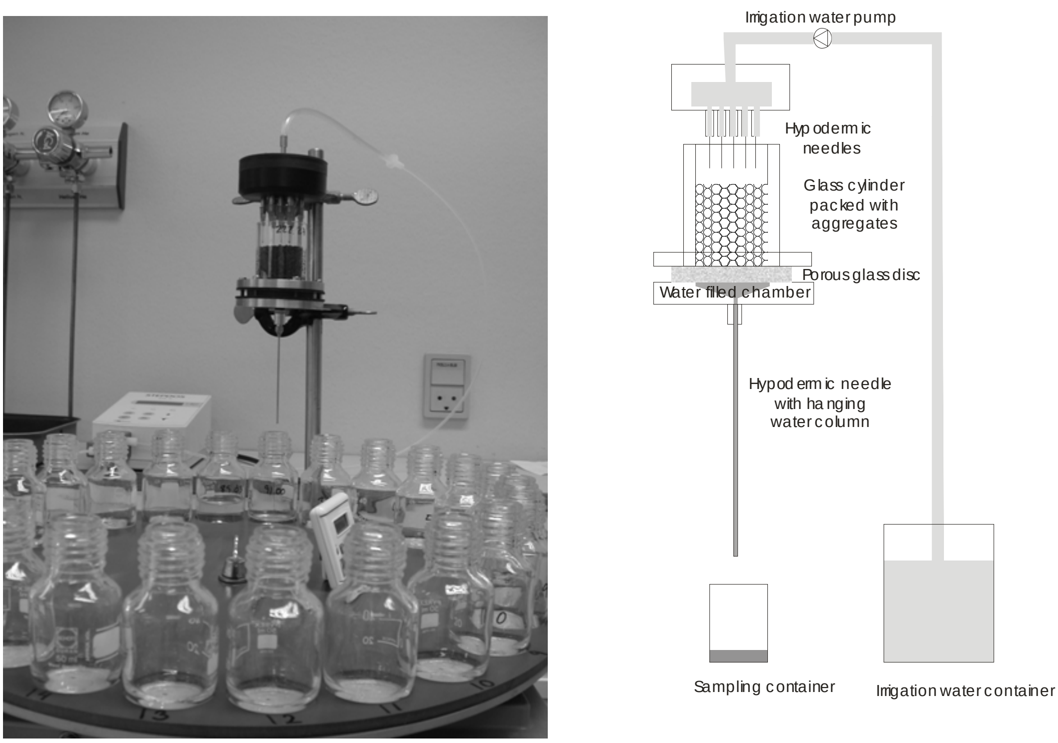

Figure 16: Experimental set-up for the leaching experiments (Paper II)

3.2.1. CHEMICALLY INDUCED CHANGES OF THE FLOWSYSTEM

The irrigation water affected the flow system by swelling and shrinking the clay minerals (Paper II). The active flow volume (V/V_0 at $C/C_0 = 0.5$) was changed by the irrigation (Figure 17). With very low ionic strength the active flowvolume was reduced, due to swelling of clay minerals and in turn diminished soil pores. Also monovalent cations had this effect but to a lesser extent. Divalent ions lead to a higher active flowvolume due to shrinkage of clay minerals and opening of soil pores. The flow system was more affected by the chemistry on the *Depleted soil* compared to the *Manured soil*. This was the result of the higher organic matter content. A higher organic matter content increases the aggregate strength and reduces the wettability of the aggregates (Sullivan, 1990 and Chenu et al., 2000)

Table 1: Active flow volume (V/V0 at $C/C_0 = 0.5$) calculated from tracer BTC in the experiments with different irrigation chemistry (Paper II)

Soil type	0.001 M $CaCl_2$	0.01 M $CaCl_2$	0.003 M KCl	0.03 M KCl	DW
Manured soil	0.72	0.77	0.71	0.67	0.72
Depleted soil	0.84	0.86	0.80	0.68	0.56

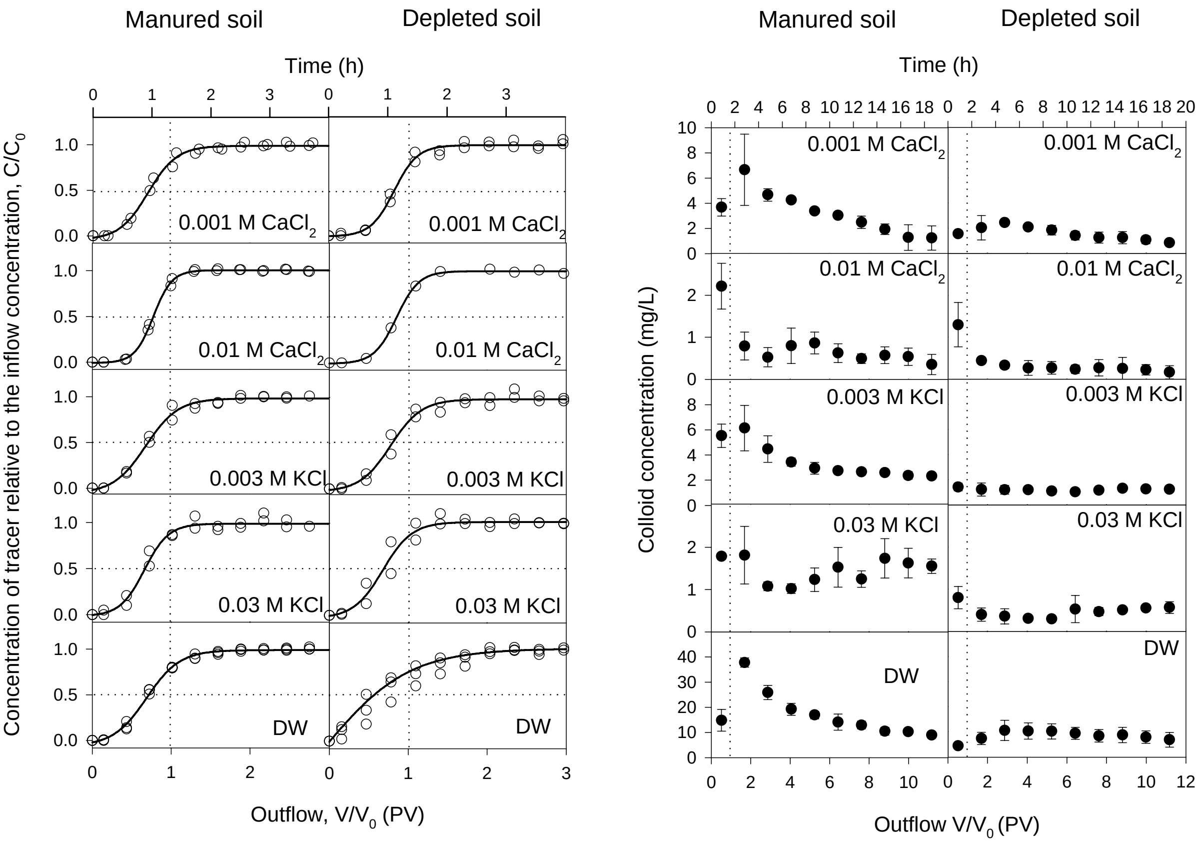

Figure 17: Conservative tracer BTC and concentration of colloids of the experiments with different irrigation intensity and two different soils (Paper II).

3.2.2. LEACHING OF COLLOIDS AS AFFECTED BY INDIGENOUS ORGANIC MATTER

Figure 17 shows the leaching of colloids from the columns packed with aggregates from the two soils, when irrigating with three levels of ionic strength and two different cations. The sources of colloids were not exhausted during the experimental period, even when irrigating with high ionic strength water. The leaching concentration decreased towards a non-zero value. The level of colloid concentration was generally low compared to experiments with field moist soil. This may be due to the wetting history of the aggregates prior to the experiments. (Kay and Dexter, 1990; Nelson et al., 1998). The leaching was significantly higher from the *Manured soil* compared to the *Depleted soil* at all times and chemical treatments (Figure 18). This indicated that the structural stability did not control the leaching of colloids. The colloid stability was probably more important for the leaching of colloids.

3.2.3. Leaching of colloids as affected by solution chemistry

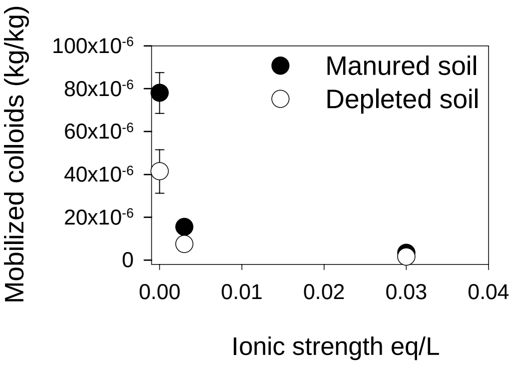

Figure 18: The accumulated mass of colloids leached from repacked soil columns after 20 hours of irrigation with three levels of ionic strength (Deionized water and $CaCl_2$) (Paper II).

Leaching of colloids was highly dependent on the ionic strength of the irrigation water (Paper II). As we would expect colloid leaching increased with decreasing ionic strength of the irrigation water in a non-linear way (Figure 18). If the colloids in the soil had been homogenous, the leaching would have been high with low ionic strength and an abrupt decrease to zero when the CCC value was exceeded. The natural soil colloids are highly heterogeneous and the different colloids have different CCC values. The shape of the response curve to ionic strength probably reflected the distribution of the indigenous colloid population between classes of different stability.

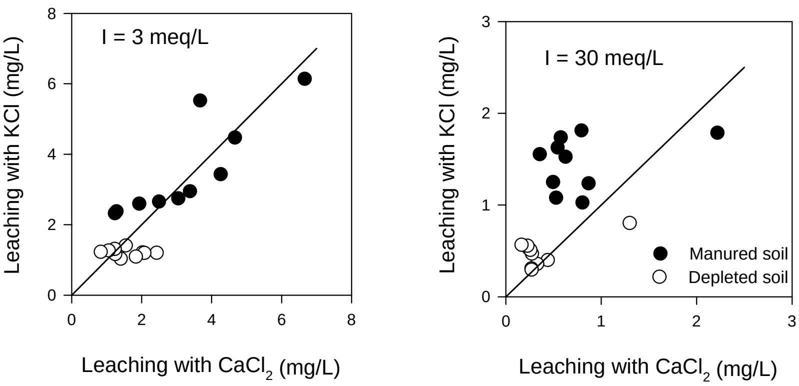

Figure 19: Colloid leaching from aggregate columns with two levels of ionic strength (Paper II).

According to the Schultze-Hardy rule, we would expect that the leaching was higher when irrigation with monovalent K^+ compared to divalent Ca^{2+}. This was not significant with low ionic strength (Figure 19). At high ionic strength however the leaching was clearly enhanced when irrigating with K^+ compared to Ca^{2+}. This was probably as a result of the diffusion retarded replacement of divalent ions with monovalent ions at the surface of the colloids. This led to slowly increasing repulsive forces between colloids associated in the aggregates and consequently to higher leaching.

The leaching of dissolved organic matter was also investigated. The leaching was higher from the Manured soil and was not significantly affected by solution chemistry. The leaching of DOM was slightly higher with deionized water.

3.2.4. LEACHING OF COLLOIDS AS AFFECTED BY IRRIGATION INTENSITY

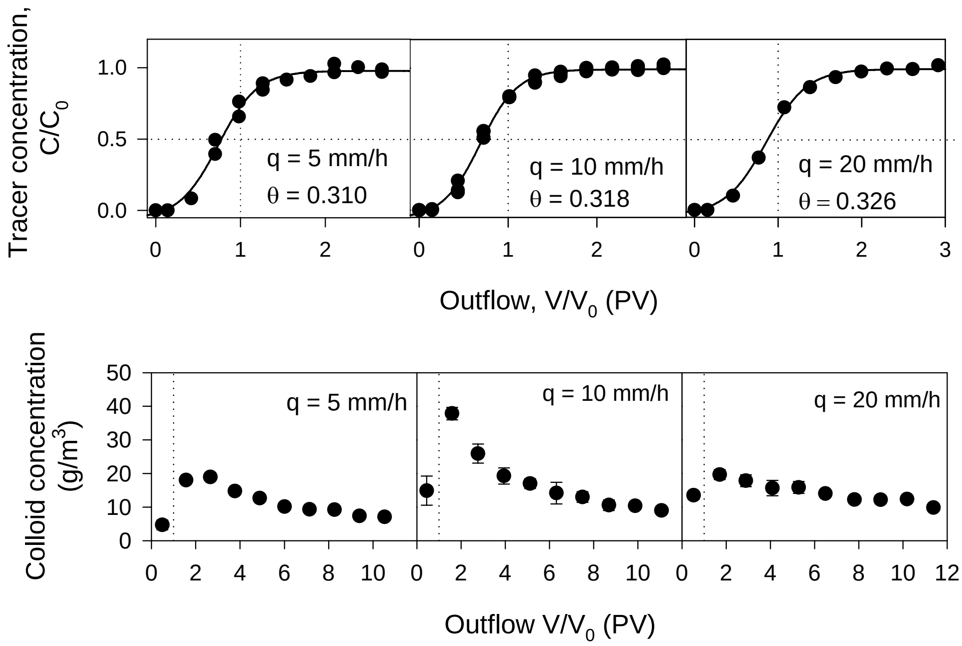

Figure 20: Colloid concentration in effluent and mass flux from columns packed with aggregates from the *Manured soil*

The water content of the experiments was slightly different for the three irrigation intensities. The tracer experiments showed that the level of active water content (V/V_0 at $C/C_0 = 0.5$) was higher with 20 mm/h and lowest with 10 mm/h (Table 2). This reflect that the more pendular rings were connected with 20 mm/h. The slightly higher flow volume at 5 compared to 10 mm/h shows a higher percentage of active water and a higher diffusive exchange due to a longer time of reaction.

Table 2: Active flow volume (V/V_0 at $C/C_0 = 0.5$) calculated from tracer BTC in the experiments with different irrigation intensity

	5 mm/h	10 mm/h	20 mm/h
Manured soil	0.74	0.72	0.86

At 1.5 PV there was a peak in colloid concentration regardless of irrigation intensity (Figure 20). The peak may have been formed by sources of colloids close to the flowing water (e.g. colloids sorbed onto the air-water interfaces). Towards the end of the experiment the colloid concentration approached a constant value (steady-state concentration).

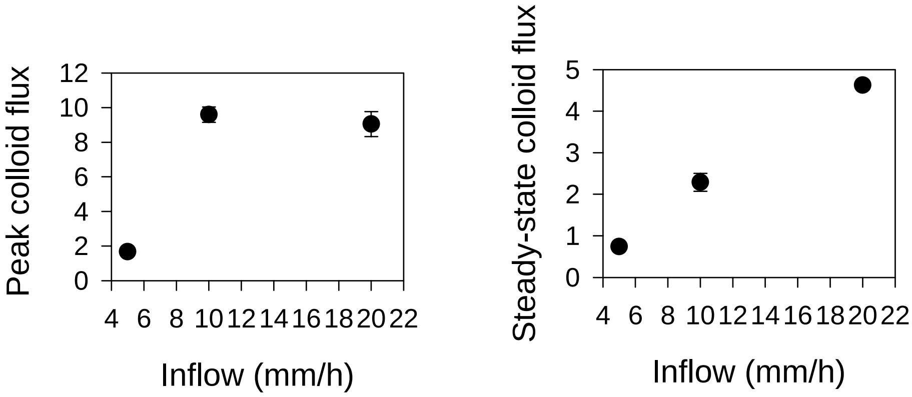

Figure 21: The flux of colloids at three irrigation intensities after 1.5 PV (peak flux) and 10 PV (steady-state flux).

The peak colloid flux was low for 5 mm/h and higher for 10 and 20 mm/h (Figure 21). The source for these colloids may not be deduced solely from the leaching curves. In the next chapter this problem will be investigated further. The steady-state fluxes were increasing with increasing irrigation intensity. The experimentally measured EC was low but constant in the late parts of the experiments where the steady-state leaching is found. Hence, the dispersion of colloids is not expected to be the limiting process for the leaching. The steady-state leaching is supposed to be controlled by the diffusion of colloids from the aggregate surfaces to the flowing water. The higher flow velocity found with higher irrigation intensity, reduced the hydraulic boundary layers surrounding the aggregates. This increased the diffusive exchange of colloids from the aggregates to the flowing water in the pores. The increased active flowvolume with 20 mm/h increased the connectivity of the pendular rings. This will also increase the release of colloids due to a higher area of contact.

3.2.5. COMPARISION OF THE BATCH METHODS AND THE LEACHING METHOD

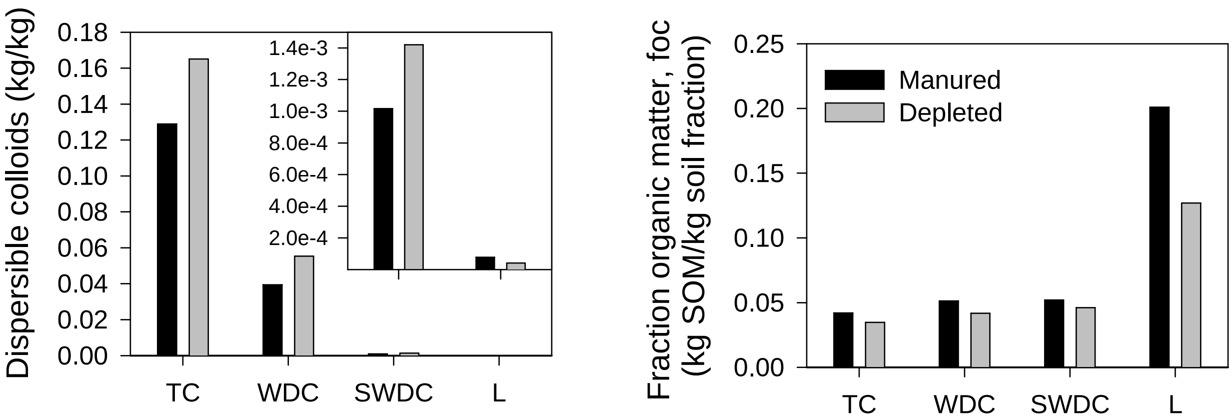

Figure 22: Comparison of the three batch methods of release with the amount of leached colloids after 20 hours of leaching with 10 mm/h DW.

The batch methods of release of colloids (*TC*, *WDC* and S*WDC*) (Paper I) were compared with the amount of colloids leached during 20 hours of irrigation with DW at 10 mm/h (Paper II). The accumulated amount of colloids leached during 20 hours of leaching with DW was 0.2 and 0.07 per cent of the total amount of *WDC* in suspension of the *Manured soil* and *Depleted soil*, respectively, and 8 and 3 per cent of the total amount of S*WDC* suspension. The mass of colloids released from the 2-4 mm aggregates in the leaching experiments was restricted by diffusion over the hydraulic boundary layer. The diffusion process favors the release of smaller colloids since the diffusion coefficient is inversely related to the radius of the colloid (Stokes-Einstein relation). The diffusion was probably less limiting in the dispersion experiments since the different methods involved rotation and consequently fast movement of the soil aggregates through the liquid. Mechanical break-down of the aggregates occurred during the batch experiments but not during leaching. Recapture of colloids may also affect the amount of colloids leached from the aggregates during column experiments. The leaching of colloids from columns packed with aggregates was larger from the *Manured soil*, but with all three kinds of batch dispersion methods the *Depleted soil* had the highest release of colloids (Figure 22). This difference illustrates the different effects of organic matter on the release of colloids in batch and the *in-situ* colloid release. The three different batch techniques involve some degree of mechanical breakdown of the aggregates. The organic matter *Depleted soil* had a lower resistance towards this breakdown and more aggregate breakdown occurred compared to the *Manured soil* leading to a higher release of colloids with the batch technique. With the leaching technique the colloid stability seemed to have a larger effect on the colloid release than the structural stability. The colloids in the *Manured soil* had a larger content of organic matter and hereby a higher stability leading to increased leaching.

3.3. CONCLUSIONS

The amount of colloids that could be leached from unsaturated columns packed with aggregates was orders of magnitude lower than the amount of dispersible colloids released in batch experiments. This could be due to diffusion limitation of the release of colloids from aggregates imbedded in a media and no mechanical breakdown of the aggregates during leaching.

3.3.1. INDIGENOUS ORGANIC MATTER

Colloid leaching was higher from columns packed with 2-4 mm aggregates from the *Manured soil* compared to the *Depleted soil*. When colloid leaching was higher from the soil with the higher organic matter content, the structural stability did not control the leaching. It is however likely that the colloid stability controlled the leaching.

The organic matter fraction (f_{oc}) of the leached colloids was around three times higher than the colloids released by batch methods. The higher f_{oc} of the leached colloids indicated that colloids with higher degree of organic coating were leached preferentially from the soil. This again indicate that the colloid stability controlled the leaching.

3.3.2. SOLUTION CHEMISTRY

Colloid leaching was strongly affected by ionic strength. Decreasing ionic strength increased the leaching in a non-linear way. The response of the colloid leaching to different ionic strength probably relied on the distribution of colloids in classes of different stability.

Colloid leaching was also affected by the valence of the dominating cation, but only after some time and only with high concentration of the ion. When irrigating with KCl more colloids were released compared to when irrigating with $CaCl_2$.

3.3.3. IRRIGATION INTENSITY

Steady-state colloid flux was increasing with increasing irrigation intensity as a result of an increasing area of contact between flowing water and aggregate surfaces and a lower thickness of the hydraulic boundary layer.

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4. MODELING OF COLLOID LEACHING

In-situ colloid release and transport through soil are affected by many different processes that depend on the physical and chemical conditions of the colloidal, soil, water and air phases. Due to the complexity of the processes, comprehensive mathematical models are usefull tools when deducing the causal relations. The transport of solute and suspended matter in homogenous porous media is controlled by convection and dispersion. In a one-dimensional form it may be expressed as:

$$\frac{\partial(\theta RC)}{\partial z} = \frac{\partial\left(\theta D\frac{\partial C}{\partial z} - qC\right)}{\partial z} - \Gamma \qquad [4.1]$$

where θ is the water content, R is the retention, C is the concentration, D is the dispersion, q is the Darcy flow and Γ is the sink term.

Models based on the simple convection dispersion approach (usually referred to as Local Equilibrium Assumption (LEA) models) may successfully describe the flow in a homogenous media but not the flow in structured soil. The physical structures (aggregates) found in soils leads to physical non-equilibrium between the intra-aggregate water and the inter-aggregate water (Nielsen et al., 1986). This physical non-equilibrium leads to early breakthrough of solutes and long tailing. To account for the non-equilibrium, the models have to contain more than one domain (usually two). Models of solute transport containing a mobile and an immobile water domain have been introduced by Deans (1963), Coat and Smith (1964), Skopp and Warrick (1974) and van Genuchten and Wierenga (1976). The coupling between the mobile and the immobile domain is usually simulated by first-order kinetics. For a more mechanistic simulation the diffusion within the aggregates may be simulated explicitly for simple aggregate shapes. Rasmussen and Neretnieks (1980) and van Genuchten (1985) proposed such mechanistic models for spherical aggregates. The mechanistic diffusion model is often left out due to the complicated nature of the calculations (Brusseau and Rao, 1990).

Special problems arise when simulating the transport of colloids instead of solutes. Colloids are restricted to movement in the larger pores in the soil, due to their size. This particular characteristic of colloids needs a special treatment in the model, since the entire wetted part of the soil will not be accessible for the colloids. Furthermore, the release of colloids is an activated process and is strongly dependent on the chemistry of the water in the soil.

Models for colloid transport in saturated flow and unsaturated flow have been proposed. The saturated flow is mainly found in groundwater systems, where colloid release and transport may be modeled by two phases: soil and water. The unsaturated system requires a description of the constraining properties of the air phase as well. For the release of colloids, two different types of sources may be considered: A limited and an unlimited source. The limited source is relevant in natural systems with few colloids (e.g. groundwater systems) and in artificial systems (e.g. colloids deposited on sand grains). The unlimited source is found in soil systems (especially clay soils) where the aggregates consist of releasable colloids embedded in aggregates.

4.1. MODELING APPROACHES WITH SATURATED FLOW

In saturated flow the models have to contain a description of the transport of colloids in the porous media and a function for flocculation and pore straining of the colloids.

4.1.1. SATURATED HOMOGENEOUS MEDIA

The transport of colloids in saturated homogeneous media may be described by LEA models based only on the convection dispersion equation. Bradford et al. (2002) simulated the transport of colloids in saturated porous media using a modified version of Hydrus 1D. Colloid attachment and detachment was simulated using first-order kinetics. Straining was simulated using irreversible first-order kinetics with a depth variable rate constant. Exclusion of colloids from the smallest pores was simulated by a colloid-accessible water content smaller than the true water content of the media. Bradford et al. (2002) found that the distribution of colloids with depth was not adequately described by the first-order attachment/detachment model. Grolimund and Borcovec (2001) simulated the release of colloids by advancing chromatographic fronts. They found that the non-exponential decay observed in experimental studies could not be described by one single population of colloids, but had to involve different classes of colloids.

4.1.2. SATURATED HETEROGENEOUS MEDIA

Abdel-Salem and Chrysikopoulos (1995) simulated contaminant transport in the presence of colloids in a saturated, fractured media. The deposition was simulated by first-order kinetics. A key parameter for the colloid-facilitated transport was found to be the fracture surface capacity for colloids. Sun et al. (2001) developed a two-dimensional model to simulate transport of colloids in a physically and geochemically heterogeneous, porous media. The surface of the media was divided into surface favorable and unfavorable for deposition. They found that both physically and geochemically layered heterogeneities created preferential transport of colloids. If the heterogeneities were randomly distributed they found that the physical heterogeneities had a large effect on colloid transport behavior. The colloid transport in a media with geochemical heterogeneities was only slightly affected compared with leaching in the homogenous case. This means that the deposition of colloids in porous media containing random geochemical heterogeneities may be modeled assuming mean properties of the media.

4.2. MODELING APPROACHES WITH UNSATURATED FLOW

In unsaturated flow, the model in addition had to include a description of the interaction with the air-water interface and with low water content a description of film straining.

4.2.1. UNSATURATED HOMOGENEOUS MEDIA

Corapcioglu and Choi (1996) and later Lenhart and Saiers (2002) simulated the interactions with the air-water interface as pseudo second-order kinetics, relying on both colloid concentration in the water phase and the mass deficit of sorbed colloids on the air-water interface. Wan and Tokanuga (1997) and later Lenhart and Saiers (2002) simulated the film straining in steady flow by first-order kinetics depending on the pendular ring discontinuity, film thickness and flow rate. Saiers and Lenhart (2003) simulated colloid scavenging under transient flow conditions using a first-order reaction to simulate the film straining of colloids from the flowing water. The immobilized colloid population was divided into compartments with individual release response to variations in the water content.

4.2.2. UNSATURATED AGGREGATED SOIL

Schelde et al. (2002) simulated the leaching from intact soil cores by an equivalent macropore approach. The colloids were released from the immediate surroundings (crust) of a single macropore. The colloids diffused from the crust through a hydraulic boundary layer into the flowing water of the macropore. The model simulated the seemingly unlimited source of colloids leached from structured soil cores, as well as the dynamics of leaching after a pause in the irrigation without further calibration. However, the calibrated diffusion coefficients of the crust were higher than for the hydraulic boundary layer.

4.2.3. FIELD SIMULATIONS

Jarvis et al. (1999) and Villholth et al. (2000) simulated leaching of colloids to tile drains by natural rain and simulated rain from two field locations. The model used was an extended version of the model MACRO (Jarvis et al., 1999). Mechanical impact by raindrops was supposed to be the initiating process. Colloids were released from the surface proportional to the kinetic energy in the rain, the rain intensity and the dispersion potential of the soil. The dispersion potential was calculated as a source that was renewed slowly. The maximum dispersion potential was correlated to the clay content. Straining was simulated proportional to the flux of particles. The model simulated the timing and magnitude of the peak in tile drain concentration following a rain event, but the tailing after rain events was not reproduced by the model. This may be due to mobilization of colloids in the soil by chemical dispersion.

4.3. NEW MODEL OF COLLOID LEACHING

When the topsoil system is simulated, four main characteristics are to be considered. The four characteristics also discussed in the introduction are: The topsoil is dominated by preferential flow, flow is unsaturated, the chemistry is changing dynamically with infiltration of water, and the source of colloids is unlimited in clay soils (for all practical time scales). All of these processes have not been simulated simultaneously before.

4.3.1. MODEL CONCEPTS

A model, describing the release, transport, and recapture of colloids in an unsaturated aggregated media under stationary flow, was developed (Paper III). The model consists of intra-aggregate water, stagnant water in the inter-aggregate pores and mobile water in the inter-aggregate pores. In the intra-aggregate water and the stagnant water the diffusion is the only transport process. The intra-aggregate water is inaccessible to colloids. Three processes control the release and recapture of colloids: (i) colloids may be released from the surface of the aggregates and diffuse through the stagnant water film to reach the mobile water, (ii) colloids may sorb/desorb at the air-water interface, and (iii) colloids may flocculate and become captured in the soil (Figure 23).

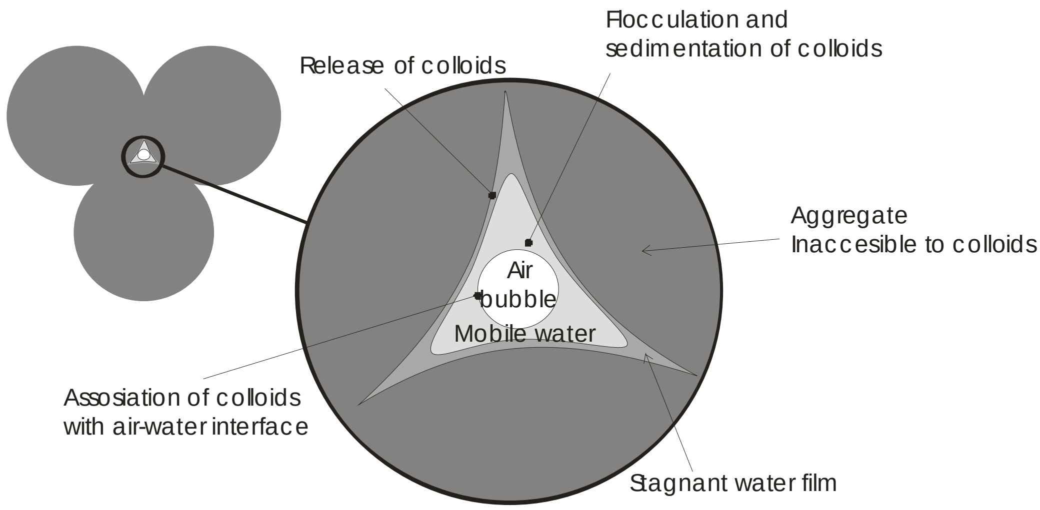

Figure 23: The colloid-related processes of the model (Paper III)

The ionic strength of the pore water was simulated by a mechanistic diffusion model inside the aggregates, followed by diffusion in a stagnant layer of water surrounding the aggregate and convection-dispersion in the mobile water. The ions contributing to the ionic strength was released from the soil within the aggregates by first-order kinetics (Paper III).

4.3.2. COLLOID DYNAMICS

The transport of colloids in the inter-aggregate pores was simulated by convection-dispersion:

$$\frac{\partial C_{coll}}{\partial t} = D_{coll}\frac{\partial^2 C_{coll}}{\partial z^2} - v\frac{\partial C_{coll}}{\partial z} - \Gamma^* \qquad [4.2]$$

where t is time, C_{coll} is the colloid concentration in the interaggregate pores, z is the distance from the top of the soil, D_{coll} is the dispersion coefficient, v is the porewater velocity, Γ^* is the normalized sink term accounting for transport of colloids through a layer of stagnant water surrounding the aggregates, the sorption/desorption to the air-water interface and the flocculation and straining of flocs.

It was assumed that the colloids were excluded from the intra-aggregate pores. *Release from aggregate surfaces* was simulated by an equilibrium concentration of colloids varying with ionic strength at the surface of the aggregate:

$$C_{coll,agg,eq} = \begin{cases} C_{coll,agg,\max} e^{-bI_{agg}}; & for\ I_{agg} < I_{agg,crit} \\ C_{coll,agg,\max} e^{-bI_{agg,crit}}; & for\ I_{agg} \geq I_{agg,crit} \end{cases} \qquad [4.3]$$

where $C_{coll,agg,eq}$ is the colloid concentration at the aggregate surface, $C_{coll,agg,max}$ is the colloid concentration at zero ionic strength, b is a constant, I_{agg} is the ionic strength at the aggregate surface, and $I_{agg,crit}$ is the critical ionic strength. When I_{agg} exceeds $I_{agg,crit}$ the concentration of colloids at the aggregate surface is constant.

The first order heterogeneous release/attachment model normally used in colloid transport studies was not used in the present model. It demands a high number of parameters and will not anyway be able to describe the natural population of colloids. Grolimund and Borcovec (1999) found that the non-exponential leaching behavior of natural colloids could not be simulated with the first order model without having different populations of colloids with different colloid stability. Furthermore, I assumed that the release of colloids from the aggregates was a fast process compared to the diffusion from the aggregate surface to the flowing water. This is a reasonable assumption when the energy barrier against release has disappered (Ruckenstein, and Prieve, 1976; Ryan and Elimelech, 1996). Grolimund and Borcovec (1999) found that the distribution of activation energies (height of the energy barrier) in natural colloids could be described by an exponentially decreasing function of the activation energy. This means that the colloids released always will be dominated by colloids released fast. The number of colloids released over an energy barrier will be minimal. This justify the use of diffusion to control the release.

The transport of colloids from the aggregate surface to the mobile water was limited by *diffusion in the stagnant layer of water*. The flux of diffusing colloids through the stagnant water was calculated by:

$$J_{coll,agg} = \frac{4\pi a^2 D_{coll(w)}}{*\delta f}\left(C_{coll,agg,eq} - C_{coll(m)}\right) \qquad [4.4]$$

where a is the aggregate radius, $D_{coll(w)}$ is the diffusion coefficient of the colloids in water, $C_{coll(m)}$ is the colloid concentration in the mobile water, and $*\delta f$ is the equivalent thickness of the stagnant water layer, assuming that the diffusion progresses over the entire surface of the aggregates.

Sorption and desorption to the air-water interface was simulated using first-order kinetics depending on the mass deficit of the air-water interface, with a invariable rate constant and the sorption capacity proportional to the ionic strength:

$$\frac{\partial M_{aw}}{\partial t} = k_{aw}\left(M_{eq,aw} - M_{aw}\right) \qquad [4.5]$$

$$M_{eq,aw} = \begin{cases} M_{\min,aw}; & for\, I_m < I_{\min,aw} \\ \dfrac{M_{\max,aw} - M_{\min,aw}}{I_{\max,aw} - I_{\min,aw}}(I_m - I_{\max,aw}) + M_{\max,aw}; & for\, I_{\min,aw} \le I_m \le I_{\min,aw} \\ M_{\max,aw}; & for\, I_m > I_{\max,aw} \end{cases}$$

where M_{aw} is the amount of colloids sorbed to the air-water interface, k_{aw} is the rate coefficient for release and sorption to the air-water interface, and $M_{eq,aw}$ is the equilibrium sorption capacity.

Flocculation and straining of flocs was simulated using irreversible first-order kinetics depending on the ionic strength of the mobile water.

$$\left[\frac{\partial C_{coll}}{\partial t}\right]_{str} = k_{str} C_{coll(m)} \qquad [4.6]$$

where k_{str} is the rate constant for the straining. Below the critical ionic strength ($I_{str,crit}$) straining was zero.

Please consult Paper III for a more thorough description of the model, the numerical approximations used and the initial and boundary conditions.

4.3.3. MODEL CALIBRATION

The model was calibrated using the colloid leaching experiments with three levels of ionic strength described in Paper II. Only the leaching experiments with $CaCl_2$ were used. The hydraulic parameters of the model were calibrated using the conservative tracer experiments (Paper III). The calibrated hydraulic parameters are shown in Table 3. The change in conservative tracer BTC could be simulated mainly by changing the hydrodynamic dispersion coefficient (D_h).

Table 3: Hydraulic parameters calibrated against conservative tracer breakthrough. I is the ionic strength of the irrigation water, θ is the measured water content, θ_m is the calibrated mobile water content, D_h is the hydrodynamic dispersion coefficient, and *δf is the equivalent thickness of the stagnant water surrounding the aggregate (Paper III).

Parameter	Manured soil			Depleted soil		
I [eq/m^3]	10^{-4}	3	30	10^{-4}	3	30
θ	0.318	0.318	0.318	0.288	0.288	0.288
θ_m	0.17	0.17	0.18	0.17	0.17	0.17
D_h	0.03	0.02	0.002	0.08	0.006	0.004
δf [m]	0.0009	0.0009	0.0009	0.0006	0.0006	0.0006

The release of ions of from soil inside the aggregates was calibrated towards the electrical conductivity (EC) of the effluent from the experiments (Paper III). The calibration criterion was that a single linear relation could be achieved between EC after 6 PV and the simulated ionic strength after 6 PV for all three irrigation chemistries (I_{irr} = 10^{-4}, 3 and 30 eq/m^3).

Table 4: Parameters calibrated against effluent C_{coll} of the chemistry experiments. (-) means that the same value was used for the two soils (Paper III).

Parameter	Manured soil	Depleted soil
$I_{agg,crit}$ [eq/m^3]	8	-
$C_{coll,agg,max}$ [g/m^3]	1200	-
b	0.37	0.60
$M_{max,aw}$ [g/m^3 bulk soil]	60	16
$M_{min,aw}$ [g/m^3 bulk soil]	1.6	-
$I_{max,aw}$ [eq/m^3]	7	-
$I_{min,aw}$ [eq/m^3]	4	-
k_{aw} [s^{-1}]	6 10^{-5}	5 10^{-5}
$I_{str,crit}$ [eq/m^3]	3	-
k_{str} [s^{-1}]	1.3 10^{-3}	-

The colloid parameters were calibrated against the effluent colloid concentration of the three experiments with different irrigation ionic strength (Paper III). The calibrated parameter set was different for the two soils (Table 4). The exponent (b) determining how the concentration of colloids at the aggregate surface decreases with ionic strength was higher on the *Depleted soil*. The potential amount of colloids sorbed to the air-water interface at high ionic strength ($C_{coll,agg,max}$) was lower on *Depleted soil*. The rate coefficient of the sorption/desorption at the air-water interface (k_{aw}) was also slightly lower on the *Manured soil*.

Figure 24 shows the differences between the parameters $C_{coll,agg,eq}$ and $M_{coll,aw,eq}$ for the two soils as a function of the ionic strength. The *Depleted soil* had a faster decline in colloid concentration at the aggregate surface ($C_{coll,agg,eq}$) with increasing ionic strength and the steady colloid concentration at high ionic strength was lower on this soil. This indicates that the colloids from the *Depleted soil* were more unstable than the colloids from the *Manured soil* as would also be expected due to the lower organic matter content. The air-water interface had a lower sorption capacity for colloids

($M_{coll,aw,eq}$) at high ionic strength on the *Depleted soil*. This may be the result of a difference in surface properties of the colloids from the two soils. The air-water interface area may also be lower in the *Depleted soil*.

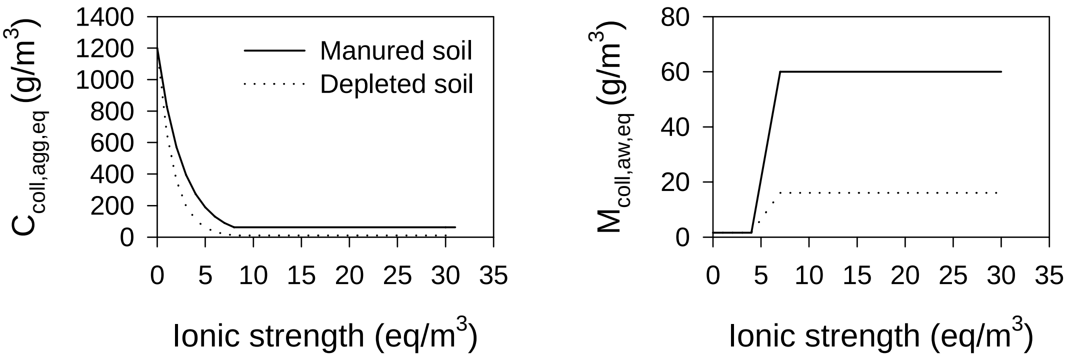

Figure 24: The variation of the parameters $C_{coll,agg,eq}$ and $M_{coll,aw,eq}$ with ionic strength on the two soils

4.3.4. SIMULATIONS OF THREE LEVELS OF IRRIGATION IONIC STRENGTH

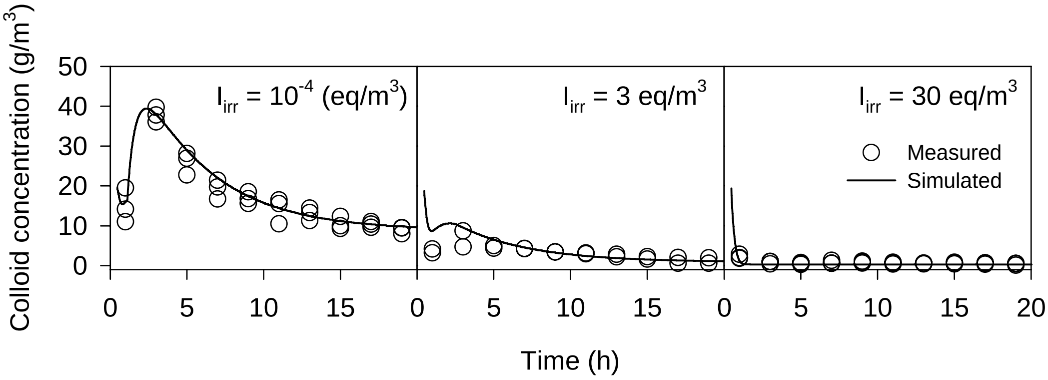

Figure 25: The simulated and measured colloid concentrations from columns packed with aggregates from *Manured soil* when irrigating with solutions with three different chemistries.

Figure 25 and Figure 26 show the simulations of the three levels of ionic strength using the calibrated parameterset of the two soils. There was a good aggrement between the measured an simulated leaching of colloids when using the calibrated parameterset. The initial colloid concentration was not simulated correctly, probably as a result of non-steady-state in the initial parts of the experiments.

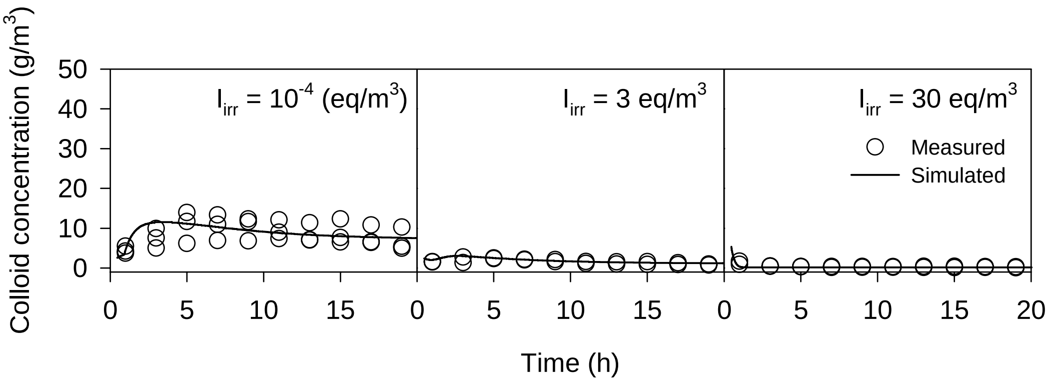

Figure 26: The simulated and measured colloid concentrations from columns packed with aggregates from *Depleted soil* when irrigating with solutions with three different chemistries.

4.3.5. DOMINATING PROCESSES

At low ionic strength ($I_{irr} = 10^{-4}$ eq/m^3) on *Manured soil* the initial peak in the concentration resulted from release from the air-water interface, since the removal of the air-water interface from the modeling removed the peak (Figure 27). The straining only had effect on leaching at the beginning of the experiment when the ionic strength was low. At medium ionic strength ($I_{irr} = 3$ eq/m^3) the initial peak also resulted from desorption from the air-water interface, but the concentration was reduced by the flocculation and straining process. The dominating process affecting leaching when irrigating with high ionic strength irrigation water ($I_{irr} = 30$ eq/m^3) was the release from the aggregate surface. When the flocculation and straining was removed, the concentration in the beginning of the simulation was higher and if the air-water interface was removed, the concentration at the beginning was slightly lower.

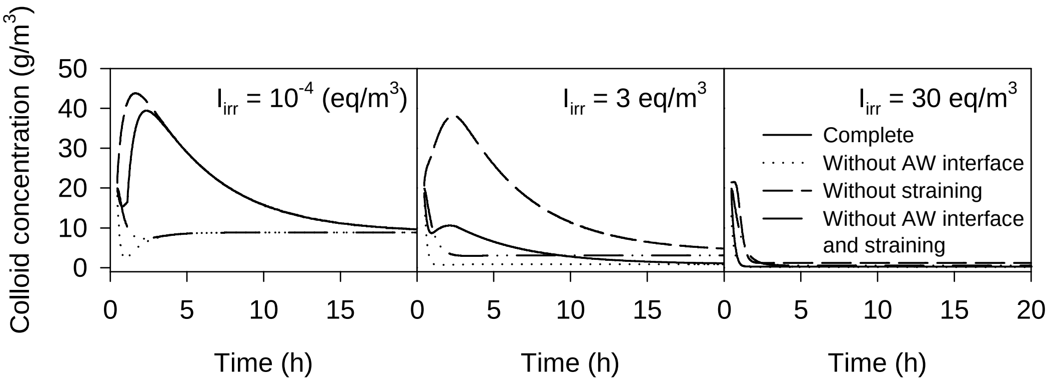

Figure 27: Simulations of the three different chemical treatments on the *Manured soil*. "*Complete*" means that the simulation included all three processes, "*Without aw interface*" means that the air-water interface sorption and desorption was not included in the model, "*Without straining*" means that the model did not include straining, "*Without aw interface and straining*" means that both the air-water interface sorption and desorption and the straining process were excluded from the model.

4.3.6. SENSITIVITY OF THE MODEL TO KEY PARAMETERS

Table 5 show the sensitivity of the effluent colloid concentration to changes in selected parameters. The sensitivity of the selected parameters was evaluated using the standard parameter set from the *Manured soil* and medium irrigation intensity (10 mm/h) and irrigation water with low ionic strength ($I_{irr} = 10^{-4}$ eq/m^3).

Hydraulic parameters for the mobile domain
If D_h was reduced from 0.03 to 0.005 the steady-state leaching was increased with 73% and if it was increased to 0.045 the leaching was reduced with 31%. When D_h was reduced, the velocity distribution narrowed and the colloid concentration in the effluent increased due to reduced residence time. The mobile water content mainly affected the initial leaching of colloids. When θ_m was changed from 0.17 to 0.13 the peak concentration was increased by 12% and when θ_m was increased to 0.25, the peak concentration was reduced by 9%.

Ion parameters
The rate of ion release is also of minor importance to the effluent concentration. Reducing the release rate to zero increased the steady-state colloid leaching by 20%. The ion diffusion coefficient has some influence on the colloid leaching in the initial parts of the experiments. If the ion diffusion coefficient was increased, the ions were transported faster out to the pore water leading to higher concentration of ions in the mobile water in the early stages of the simulation. This led to a delay in desorption from the air-water interface. If D_{ion} was reduced one order of magnitude the initial peak is only increased by 5% and if it was increased one order of magnitude the initial peak decreased with 45%.

Colloid release from aggregate surface
The maximal colloid concentration at the aggregate surface ($C_{col,agg,max}$) has a straightforward effect on steady-state colloid leaching. If $C_{col,agg,max}$ doubled, the steady-state colloid leaching doubled and if $C_{col,agg,max}$ was reduced to zero, the steady-state colloid leaching approached zero. The exponent determining the dependency of colloid concentration at the aggregate surface on ionic strength (b) had a large effect on the initial colloid concentration in the mobile water when the ionic strength of the pore water was high. In the later stages of the simulation when the ionic strength was low, the exponent had less influence on the amount of colloids leached. A doubling of b reduced the steady-state leaching with 15% and a reduction of b to zero increases the steady-state leching with 19 %.

Diffusion in stagnant water
If $*\delta f$ was reduced from 0.0009 m to 0.0006 m the steady-state leaching was increased by 600% and if it was increased to 0.0017 it was reduced with 43%. If $*\delta f$ was low, the diffusion distance from the aggregate surface to the flowing water was small and more colloids could be transported from the immobile domain to the mobile domain. With very low $*\delta f$, the initial leaching of colloids were reduced as the diffusive exchange of ions from the immobile domain to the mobile domain increased, leading to a higher ionic strength of the mobile water and thus a reduced release of colloids from the air-water interface. Colloid leaching was highly affected by the colloid diffusion coefficient. A larger colloid diffusion coefficient (smaller size of colloids) leads to a higher flux through the stagnant water film around the aggregates and to higher level of leaching. Doubling of the diffusion coefficient for colloids leads to a doubling in steady-state leaching.

Air-water interface
The sorption capacity of the air-water interface ($M_{aw,max}$) had a large effect on colloid leaching during the first 10 hours. Doubling of the $M_{aw,max}$ increased the initial peak with 88 % and reducing it to a third reduced the initial peak with 55 %. The rate of release from the air-water interface (k_{aw}) also has high effect on the initial leaching. Lowering of k_{aw} led to a slower release from the air-

water interface and subsequent to a longer period of release from the air-water interface. When k_{aw} is doubled the initial peak is increased with 70 % and if it is reduced to a third the initial peak is reduced with 52 %. The air-water interface had a large influence on the leaching due to the closeness to the flowing water (low diffusion distance). The aggregate surface may have a larger pool of colloids but leaching was hindered by a stagnant water layer.

Generally, the model was most sensitive to the parameters determining the air-water interfaces and the parameters determining the diffusion of colloids through the stagnant water film.

4.3.7. SEMI-VALIDATION

A semi-validation was conducted using data from leaching experiments with two additional levels of irrigation intensity on *Manured soil* (from Paper II). The hydraulic part of the model was initially calibrated towards the tracer experiments (Paper III). Both the total water content (θ) and the mobile water content (θ_m) of the experiments increased with increasing irrigation intensity (Table 6). This leads to a different surface area of the air-water interface and different area of contact between the flowing water and the air-water interfaces. The hydrodynamic dispersion was higher with 20 mm/h, probably as a result of an increased connectivity of the pendular rings. The equivalent thickness of the stagnant water film decreased with increasing irrigation intensity, due to a higher flow velocity and consequently a lower hydraulic boundary layer thickness.

Table 5: The sensitivity the colloid concentration to changes in selected parameters (data from Paper III).

Parameter	value	Interval of change	Interval of response	Response concentration	sensitivity
Hydrological parameters					
Hydrodynamic dispersion coefficient (D_h)	0.03	[0.005;0.045]	[+73%;-31%]	steady-state	sensitive
Mobile water content (θ_m)	0.17	[0.13;0.25]	[+12%;-9%]	peak	slightly sensitive
Ion parameters					
Rate coefficient for ions (k_{ion})	0.0008 s^{-1}	[0;0.0016]	[+20%;-14%]	steady-state	slightly sensitive
Ion diffusion coefficient ($D_{ion,w}$)	$2 \cdot 10^{-9}$	[$2 \cdot 10^{-10}$;$2 \cdot 10^{-8}$]	[5% ;-45%]	peak	slightly sensitive
Aggregate release parameters					
Maximum colloid concentration at the colloid surface ($C_{coll,agg,max}$)	1200	[0;2400]	[-100%;100%]	steady-state	sensitive
Aggregate surface concentration dependency of ionic strength (b)	0.37	[0;3.7]	[19%;-15%]	steady-state	slightly sensitive
Diffusion parameters					
Equivalent film thickness (*δf)	0.0009	[0.0001;0.0017]	[+600%;-43%]	steady-state	very sensitive
Colloid diffusion coefficient ($D_{coll,w}$)	10^{-12}	[10^{-13};$5 \cdot 10^{-12}$]	[-90% ;500%]	steady-state	very sensitive
Air-water interface parameters					
Maximum sorption capacity of the air-water interface ($M_{aw,max}$)	60	[20;120]	[-55%;88%]	peak	very sensitive

rate constant for air-water interface (k_{aw})	$6 \cdot 10^{-4}$	[$2 \cdot 10^{-4}$; $12 \cdot 10^{-4}$]	[-52%;70%]	peak	sensitive

Table 6: Measured and calibrated hydraulic parameters for the experiments with different irrigation intensity. q is the irrigation intensity, θ is the measured water content, θ_m is the calibrated mobile water content, D_h is the hydrodynamic dispersion coefficient, and *δf is the equivalent thickness of the stagnant water surrounding the aggregate (Paper III).

Parameter			
q [mm/h]	5	10	20
θ	0.310	0.318	0.326
θ_m	0.16	0.17	0.26
D_h	0.03	0.03	0.009
δf [m]	0.0016	0.0009	0.0007

The calibrated parameter set from the *Manured soil* was used to simulate leaching of colloids at 5 and 20 mm/h irrigation intensity. The simulated leaching was then compared to the measured leaching from columns with aggregates irrigated with 5 and 20 mm/h. Since the water content was changing when irrigating with higher or lower intensity (Table 6) the characteristics of the air-water interface was also expected to change. Since the mobile water content changes it is also expected that the contact between the flowing water and the air-water interfaces changes. Hence, we would not expect to get a perfect agreement between simulated and measured leaching since the dynamic change in the air-water interface was not simulated by the model. The simulated leaching with 5 mm/h gave a poor agreement with the measured in the initial stages of the experiments (Figure 28).

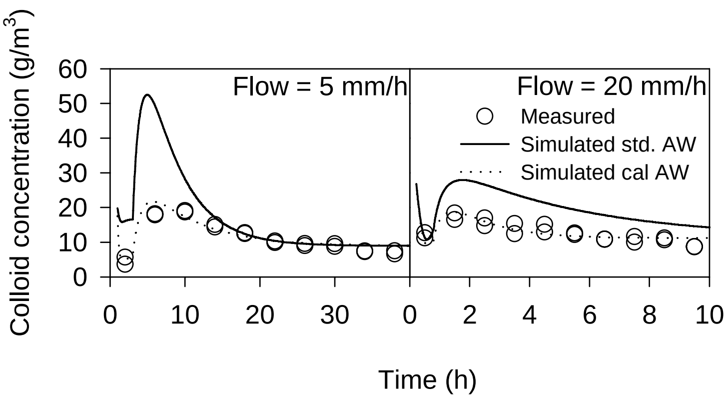

Figure 28: The simulated and measured colloid concentrations from columns packed with aggregates from *Manured soil* when irrigating with 5 mm/h and 20 mm/h (Paper III).

In the experiments with 20 mm/h the simulated colloid concentration was higher than the measured in the entire experimental period. However, Figure 27 showed that the release of colloids from the air-water interface controlled the initial peak on the leaching curve but that the steady-state leaching was unaffected. The simulated leaching approached 9.0 and 11.2 g/m^3 if leaching was prolonged for 5 and 20 mm/h respectively. These values are very close to the measured concentration at the end of the experiments. This indicates that the release of colloids from the surface of the aggregates and diffusion though the stagnant water was simulated correct. After calibration of the air-water parameters a good agreement between simulated and measured leaching was achieved in the entire simulations with both irrigation intensities.

Figure 29 shows the calibrated air-water interface parameters from the irrigation intensity experiments. The calibrated maximal capacity of the air-water interface ($M_{aw,max}$) was lower for both 5 and 20 mm/h. At the 20 mm/h this is presumably the result of a smaller area air-water interface, due to higher water content. The apparently lower sorption capacity of the air-water interface at low irrigation intensity may be a result of a smaller area of contact between the flowing water and the air-water interface. The tracer experiments also indicated that the mobile water content was lower in the low irrigation intensity experiments. The rate coefficient of sorption on and desorption from the air-water interface (k_{aw}) increased with increasing irrigation intensity. The air-water interface in the experiments is supposed to surround stagnant air bubbles. A thin hydraulic boundary layer will limit the transport by diffusion around these bubbles. With lower water velocity the hydraulic boundary layer will be thicker, leading to slow diffusion (low k_{aw}), and with higher velocity it will be thinner, leading to fast diffusion (high k_{aw}).

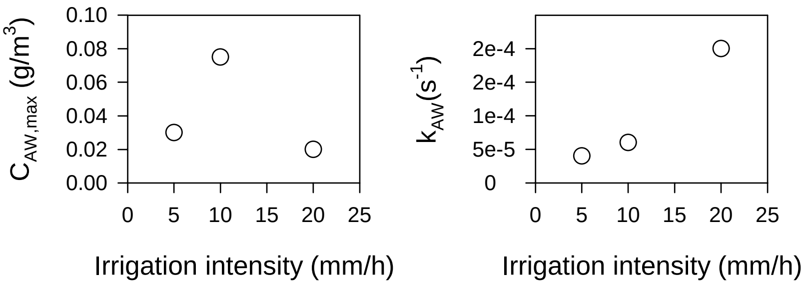

Figure 29: Calibrated parameters of the three different irrigation intensities (Paper III).

4.4. CONCLUSIONS

Colloid leaching from columns packed with soil aggregates irrigated with different ionic strength irrigation water could be simulated with one calibrated parameter set on each soil. The initial peak observed in the effluent colloid concentration from *Manured soil* and to a lesser extent from the *Depleted soil* may be explained by desorption of colloids from the air-water interface. The simulations of colloid leaching were sensitive to equivalent film thickness, the maximal colloid concentration at the aggregate surface, colloid diffusion coefficient, the sorption capacity of the air-water interface as well as the sorption/desorption rate of the colloids to the air-water interface. The parameters describing the sorption and desorption of colloids to the air-water interface and the diffusion through the stagnant water was found to be the most important key-parameters for the leaching with low ionic strength water. The model was able to simulate the diffusion-limited steady-state leaching with two additional levels of irrigation intensity.

4.4.1. INDIGENOUS ORGANIC MATTER

The difference in organic matter of the two soils affected the parameters for the dependence of colloid release from aggregates on ionic strength (b), the maximal sorption capacity of the air-water interface, and the rate coefficient of the air-water interface. Lower organic matter content lowered the amount of colloids released at high ionic strength, reduced the sorption capacity of the air-water interface, and reduced the rate of release from air-water interfaces.

4.4.2. SOLUTION CHEMISTRY

The equilibrium concentration at the aggregate surface was successfully described by an exponentially decreasing function of ionic strength upto a certain critical ionic strength. The calibrated parameter for the concentration at the aggregate surface showed that an increase in ionic strength at the aggregate surface from 0 to 7 eq/m^3, reduced the equilibrium concentration more than an order of magnitude. The highest response of the equilibrium concentration to ionic strength was found in the *Depleted* soil. At very low ionic strength the equilibrium concentration was 1200 g/m^3.

The sorption capacity of the air-water interface for colloids was successfully described by a piecewise linear function of ionic strength. The calibrated sorption capacity of the air-water interface increased with 58 g/m^3 when the ionic strength increased from 4-7 eq/m^3. The highest response of the sorption capacity to changes in ionic strength was found in *Manured soil*.

The straining could be simulated by first order kinetics only taking place above a certain critical ionic strength (3 eq/m^3).

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5. HYDROPHOBIC SORPTION AND FACILITATED TRANSPORT

The sorption of hydrophobic organic compounds (HOC) to soils and soil components has been studied by many authors and has been reviewed by e.g. Pignatello (1998) and Huang et al. (2003). The purpose of these studies has been to evaluate: (i) the probability of the chemical to be sorbed into the immobile parts of the soil, leaving the chemical unavailable for leaching and biodegradation, (ii) and to determine how fast the chemical may be released to pore water if the concentration decreased due to leaching and degradation. The purpose of this chapter is to investigate the processes of sorption in relation to colloid-facilitated transport.

5.1. HYDROPHOBIC SORPTION

The amount of HOC sorbed to soil material depends mainly on the organic matter content of the soil material (f_{oc}) (Means et al., 1980). The quality of the organic matter is a secondary determinant for the amount of HOC sorbed to the soil material (Chiou et al., 1998; Gauthier et al., 1987; Xing and Pignatello, 1997). Bed sediment and soil organic matter has been shown to have different sorption capacities (Kile et al., 1995). HOC may have a higher affinity for certain particle size fractions. Wilcke et al. (1996) and Müller et al. (2000) found that PAH had a higher affinity for the silt fraction of the soil. This was explained by a higher relative concentration of aromatic organic compounds in this fraction.

5.1.1. STRUCTURE OF ORGANIC MATTER AND HYDROPHOBIC SORPTION

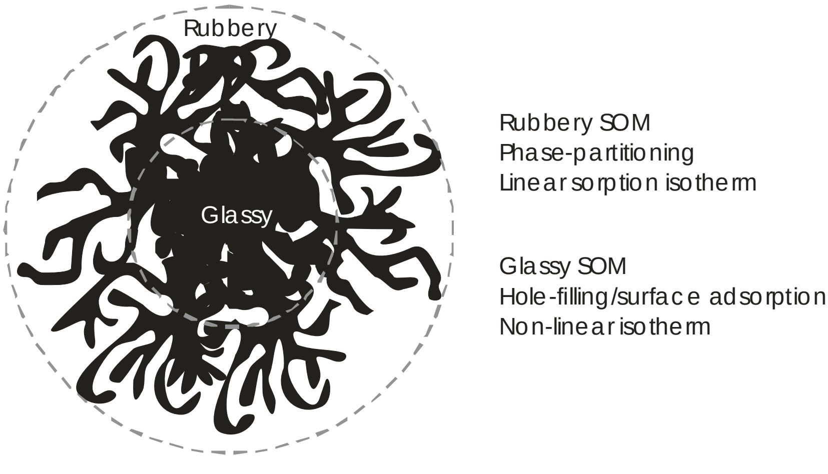

Figure 30: Structure of SOM: Interior is glassy and exterior is rubbery.

Soil organic matter (SOM) consists mainly of humic materials that may be sorbed onto the mineral phase. These humic materials may have a more or less pronounced flexible structure seem to be more condensed towards the centre, and have a diffuse outer boundary (Hayes et al., 1989) (Figure 30). The expanded and condensed parts of SOM may be described as rubbery and glassy polymer, respectively (Xing and Pignatello, 1997; Leboeuf and Weber, 1997). Sorption in the rubbery part of SOM is considered to be a phase-partitioning process by solid phase dissolution. In the glassy part of SOM the sorption process is surface adsorption by hole-filling (sorption in nano-voids in the rigid SOM structure). Xing and Pignatello (1996) found an inverse relationship between the nanovoid volume and the Freundlich sorption isotherm exponent (N). This means that glassy SOM tends to exhibit non-linear sorption of HOC and rubbery SOM a more linear HOC sorption.

5.1.2. SOLUTION CHEMISTRY AND HYDROPHOBIC SORPTION

High ionic strength may condensate SOM due to a decrease in the double-layer interactions (Ghosh and Schnitzer, 1980). The binding of HOC to dissolved humic materials decreases with increasing ionic strength (Schlautman and Morgan, 1993; Jones and Tiller, 1999) due to this condensation. The presence of di- or polyvalent cations may also condensate SOM due to cross-linking (Pignatello, 1998; Murphy et al., 1994). Divalent cations have been observed to both increase and decrease the sorption of HOC compared to univalent ions. Murphy et al. (1994) and Jones and Tiller (1999) found that the sorption of HOC decreased with divalent cations, and Schlautman and Morgan (1993) that it increased. The experiments of Schlautman and Morgan (1993) were conducted on river humic material and they may not be representative of the humic material in soils. Murphy et al. (1994), Jones and Tiller (1999) and Laor et al. (1998) found that the configuration of humic acids was altered and the sorption capacity was generally lowered when sorbed onto a mineral surface. Different minerals have different effects on the HOC sorption characteristics of the sorbed humic acids. The HOC sorption capacity of the sorbed humic materials also decreased with higher ionic strength and divalent cations (Murphy et al., 1994; Jones and Tiller, 1999). The water phase chemistry may also affect the sorption by changing the solubility of the HOC due to changed polarity of the water phase (Schwarzenbach et al., 1993).

5.2. SORPTION OF PYRENE TO COLLOIDS

Sorption of hydrophobic organic compounds (HOC) to soil colloidal material is an important process when considering colloid-facilitated transport. Colloids released from soil will generally contain the same minerals and type of organic matter as the clay fraction of the soil, but the quantitative proportions of the different mineral and organic phases may vary (Kaplan et al., 1997; Kretzschmar et al., 1999). This may lead to different sorption affinity of HOC to the mobile colloids. These differences may relate to the condition under which the colloids are released from soil. Natural soil colloids are released from soil either by *in-situ* mobilization from soil aggregates, raindrop impact, or surface erosive flow. *In-situ* mobilization from soil aggregates results from moderate chemical dispersion due to a lowering of the ionic strength by the exchange of soil water with rainwater. The release of colloids from the soil by raindrop impact or due to erosive flow results from a combination of mild chemical dispersion by low ionic strength rainwater and mechanical stress. Strong chemical dispersion, by monovalent cations and high pH, is not found in agricultural soils. When investigating the sorption properties of the fine fraction of the soil, the normal procedure is to disperse the soil by a strong dispersing agent, isolate the clay fraction and conduct sorption experiments on this fraction. But the sorption properties of the chemically dispersed clay fraction may vary from the sorption properties of the mobile colloids released by mild chemical dispersion or mechanical stress. Preferential leaching of colloids with high stability occurs from soil (Kretzschmar et al., 1995; Kaplan et al., 1997). These colloids may have a different mineral composition than the total clay fraction or may have gained their stability from organic coatings (Kretzschmar et al., 1995; Kaplan et al., 1997) or by an expanded Stern layer due to specific adsorption of monovalent cations (e.g. Singh and Uehara, 1999). The preferential leaching of certain colloid types may lead to sorption characteristics of the mobile colloids differing from those of bulk soil and the clay fraction. This key aspect of HOC sorption to colloids and, thus, colloid-facilitated transport has not been investigated in the past.

5.2.1. ISOTHERMS FOR DIFFERENT COLLOID FRACTIONS

Sorption experiments with pyrene were conducted on bulk soil and the three different fractions of the colloidal material (Paper I): Total colloids (*TC*, colloids released by total breakdown of aggregates), Water-dispersible colloids (*WDC*, colloids released by mechanical breakdown of aggregates) and Spontanous water-dispersible colloids (S*WDC*, spontaneously released colloids with low mechanical disruption of aggregates). The *TC* colloids represent the total population of colloidal particles in the soil. The *WDC* colloids represent the colloids released by surface erosive flow (Miller and Baharuddin, 1986) and the S*WDC* fraction is supposed to represent the colloids released by *in-situ* mobilization when rainwater hits the surface and infiltrates the soil. Both *Manured* and *Depleted soil* were used in the experiments. Batch sorption experiments were conducted with three levels of ionic strength (10^{-7} eq/m^3, 3 eq/m^3 and 30 eq/m^3) and two different electrolytes (KCl and $CaCl_2$) (Paper I). The experimental data were fitted to Freundlich isotherms Eq [5.1] and organic matter normalized Freundlich isotherms Eq [5.2].

$$S = K_{f,a} \cdot C^{N_a} \qquad [5.1]$$

where S is the amount of pyrene sorbed relative to dry matter [mg pyrene/kg soil], $K_{f,a}$ is the adsorption Freundlich coefficient, C is the dissolved concentration, and N_a is the Freundlich exponent.

$$S_{oc} = K_{f,a,oc} \cdot C^{N_a} \qquad [5.2]$$

where S_{oc} is the amount of pyrene sorbed relative to organic matter [mg pyrene/kg OC], and $K_{f,a,oc}$ was the organic normalized Freundlich coefficient. Parameters of the organic normalized Freundlich isotherm will be used for simulation of the facilitated transport of pyrene.

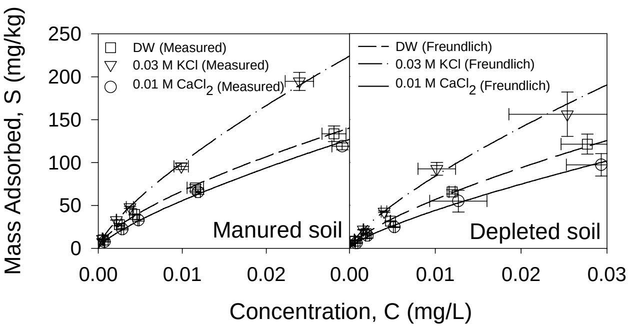

Figure 31: Examples of freundlich fit (*WDC* suspensions with three different electrolytes) (Paper I).

The data of all sorption experiments were described well by Freundlich isotherms. Figure 31 shows examples of the fitted Freundlich isotherms.

The estimated $K_{f,a}$ values was used to calculate distribution coefficients normalized towards organic matter (calculated at 0.01 g/m^3) ($K_{oc,0.01}$) (Paper I) to be able to compare the organic matter sorption capacity of the different types of colloids.

5.2.2. SORPTION CAPACITY

Karickhoff et al. (1979) found a linear relation between the octhanol-water partitioning coefficient (K_{ow}) and the organic matter normalized distribution coefficient (K_{oc}) for HOC sorption in soils.

$$K_{oc} = 0.63 \cdot K_{ow} \qquad [5.3]$$

In Figure 32 ratio between K_{oc} and K_{ow} is shown for all the different isotherms. The ratio of K_{oc} and K_{ow} was app. 0.63 for the two bulk soils investigated when the solution was 0.01 M $CaCl_2$. The colloid suspensions generally exhibited a higher ratio, varying between 0.62 – 1.3 (Figure 32). This indicates that the colloid suspensions were enriched in hydrophobic organic matter compared to the bulk soil, except for the S*WDC* suspensions. The *TC* colloids had the highest K_{oc}/K_{ow} ratio indicating that these colloids, having been released during total breakdown of microaggregates, had more hydrophobic organic matter compared with the more loosely attached S*WDC* colloids. Addition of KCl also increased the K_{oc}/K_{ow} ratios. This is consistent with a reconfiguration of the organic matter into a more open structure, due to the exchange of some of the cross-linking di- and polyvalent ions in the organic material with monovalent K^+ (Pignatello, 1998), thus exposing more of the organic matter interior to the solution. The sorption capacity of colloid associated SOM increased with increasing ionic strength when K^+ was present. This finding is apparently contradictory to that of Murphy et al. (1994). They found decreasing HOC sorption capacity with increasing ionic strength of monovalent cations in mineral-bound humic acids. Fulvic and humic acids were also found to condense with increasing ionic strength of monovalent ions (Ghosh and Schnitzer, 1980; Murphy et al., 1994). The colloid-associated SOM had an apparently different response to the ionic strength of monovalent cations than mineral-bound humic acids. However, the colloids used in the experiments were retrieved from agricultural soils with Ca^{2+} dominating the exchange complex; the effect of K^+ may be a result of ion exchange of Ca^{2+} with K^+. When the ionic strength of KCl is increased, an increasing amount of Ca^{2+} will be exchanged with K^+ and sorption will increase. When Ca^{2+} was the dominating cation in the solution, the ionic strength had little or no effect on sorption. This was also observed by Murphy et al. (1994) for mineral-bound humic acids.

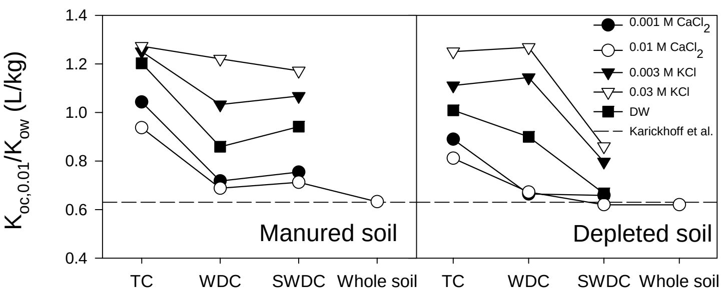

Figure 32: Ratio between organic matter normalized distribution coefficient ($K_{oc,0.01}$) and octanol-water distribution coefficient (K_{OW}) for the different suspensions and solution chemistries (Paper I).

5.2.3. NON-LINEARITY

For the two bulk soils, N_a was around 0.9 but for the colloid suspensions it was smaller, ranging between 0.65-0.82 (Table 6). *TC* suspensions exhibited more non-linear isotherms than bulk soil on both soils. Following Pignatello (1998), this is consistent with hole-filling due to a glassy structure of SOM. Hence, the SOM associated with the *TC* suspensions had a more glassy structure than the SOM in bulk soil. In *TC* suspensions the microaggregates were dispersed and only the resistant organic matter remained on the colloids. In the *Manured soil*, the N_a values were significantly lower for the *TC* suspensions compared with S*WDC* suspensions, regardless of the chemistry (Figure 33). For the *Depleted soil* the isotherms had more similar non-linearity (only significantly different between *TC* and S*WDC* suspensions in 0.03 M KCl and DW). The S*WDC* isotherms of the

Depleted soil were more non-linear than the *Manured soil*, suggesting that the easily detachable colloids from the *Depleted soil* contain glassier SOM than the easily detachable colloids from the *Manured soil*.

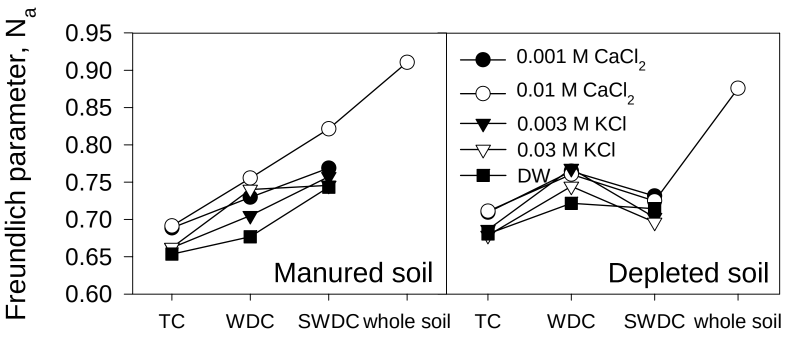

Figure 33: Freundlich exponent (N_a) for the different suspensions and solution chemistries

5.3. SIMULATION OF FACILITATED TRANSPORT OF PYRENE

In a soil system with both dissolved organic matter (DOM) and colloids, three types of mobile pyrene will be present: dissolved, DOM-sorbed and colloid-sorbed (Figure 34). The colloid-bound pyrene is exclusively sorbed to the organic matter associated with the colloids or to organic macromolecules or microorganisms. The proportions of the different types of pyrene will be determined by the amount and properties of the DOM and colloid-associated organic matter.

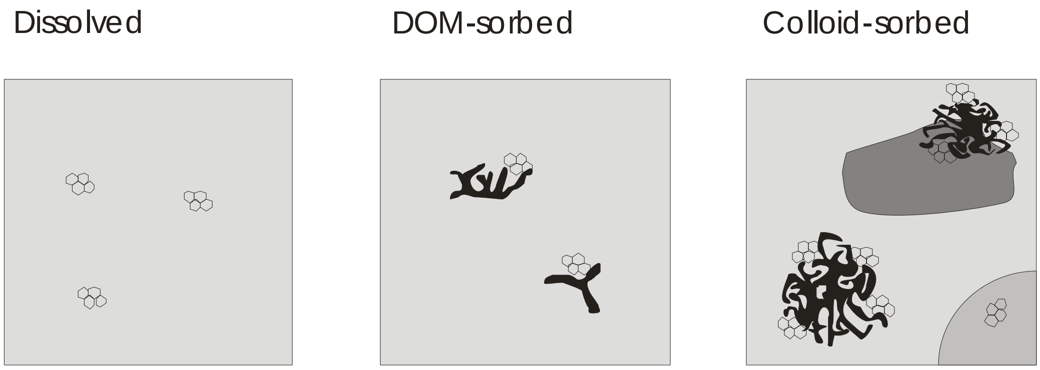

Figure 34: Three different types of mobile pyrene

The leaching of pyrene from an aggregated soil system was measured in leaching experiments. Soil aggregates were spiked with pyrene, packed in columns and incubated for one week at 2 °C. Columns were then irrigated with DW at a rate of 10 mm/h and a lower boundary condition of 10 kPa. A static leaching model was used to simulate the facilitated transport of pyrene in the leaching experiments. The amount of pyrene sorbed to the colloids was estimated according to Eq [5.2]. No transfer of pyrene between pools (dissolved, DOM-sorbed and colloid-sorbed) was assumed during the leaching process.

$$C_{tot}(t) = \left[C / C_{ini}\right]_{sim}(t)\, C_{ini} + K_{a,f,oc} C_{ini}{}^{N_a} C_{coll} f_{oc} + K_{DOC} C_{ini} C_{DOC} \qquad [5.4]$$

where C_{tot} (t) is the leached concentration of pyrene as a function of time, $[C/C_{ini}]_{sim}$(t) is the simulated ratio between the leached dissolved concentration and the initial equilibrium concentration also as a function of time, C_{ini} is the initial dissolved concentration, $K_{a,f,oc}$ and N_a are the organic matter normalized Freundlich isotherm parameters, C_{coll} is the measured leached colloid concentration, f_{oc} is the fraction organic matter associated with the leached colloids, K_{DOC} is the distribution coefficient of pyrene and C_{DOC} is the measured leached amount of DOC.

(C/C_{ini}) was simulated on each soil using the fully dynamic two domain model used for the simulation of tracer transport and ionic strength in Paper II. C/C_{ini} was an estimate of the dissolved leaching relative to the initial dissolved concentration, if no mobile colloids or DOM were present and if no sorption or desorption to the stationary soil matrix took place. The organic matter normalized Freundlich parameters from the S*WDC* suspensions in 0.01 M $CaCl_2$ were used for the estimation of the colloid sorption parameters and a log(K_{DOC}) of 4.6 (Raber et al., 1998) for pyrene sorbed to DOC. For further descriptions of the experimental and modeling methods, please consult Appendix B.

5.3.1. CALIBRATION AGAINST LEACHING EXPERIMENTS

Figure 35 and Figure 36 show measured and simulated concentrations of pyrene in the effluent from the two soils and simulated concentrations using calibrated values of C_{ini}.

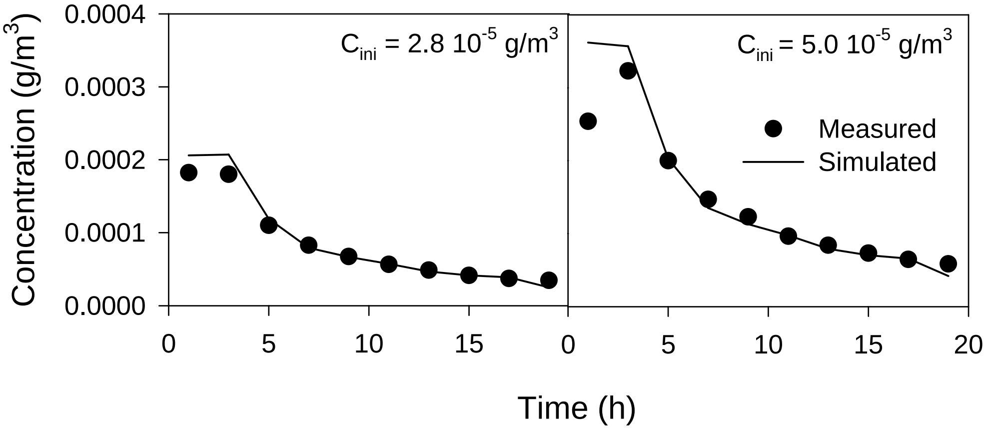

Figure 35: Measured and simulated leaching of pyrene from two replicate experiments on the *Manured soil*.

On the *Manured soil*, measured and simulated leaching concentrations were similar during the entire experimental period (Figure 35). On the *Depleted soil* the shape of the leaching curve was too flat (Figure 36). There was a poor agreement between the simulated and measured amount of pyrene in the initial peak. The exact reason for this cannot be deduced from the calculations, but may relate to the simplicity of the model. The characteristics of the organic matter associated with colloids actually mobilized may also vary from those of the S*WDC* colloids on the *Depleted soil.*

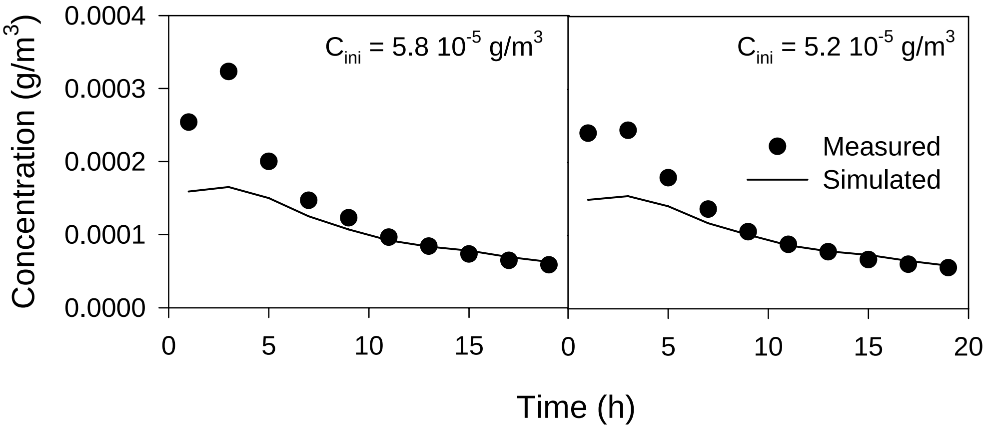

Figure 36: Measured and simulated leaching of pyrene from the *Depleted soil.*

5.3.2. DOM- AND COLLOID-FACILIATED TRANSPORT OF PYRENE

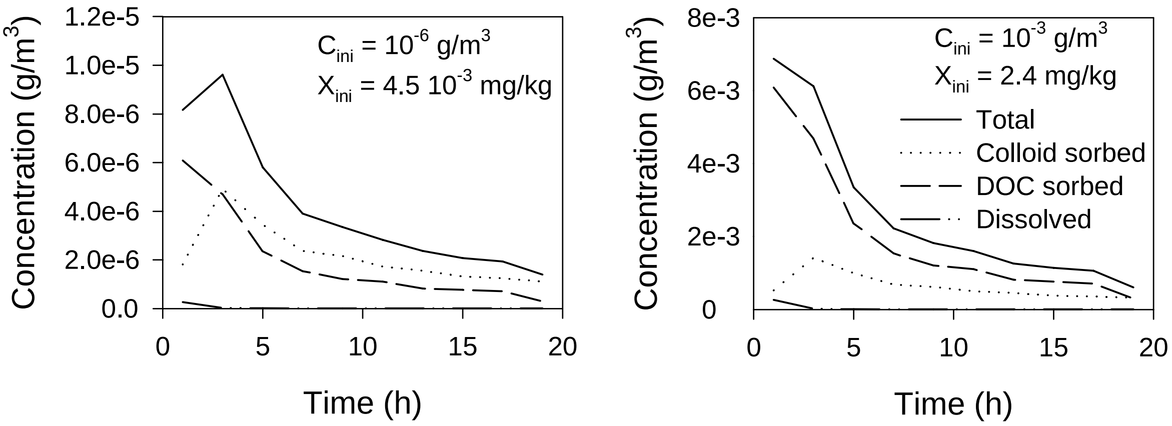

Figure 37: Simulated concentration of pyrene leached from *Manured soil* with low and high initial concentration of pyrene. “Total” denotes the simulated amount of pyrene, “colloid sorbed” the amount of pyrene transported by colloids, “DOC” the amount of pyrene transported by DOC and “dissolved” the leaching of dissolved pyrene.

The amount of dissolved pyrene was low on both soils (Figure 37 and Figure 38). When initial concentration of pyrene was low, two thirds of the leached pyrene was colloid-bound and with high initial concentration of pyrene, only one third was colloid-bound on the Manured soil (Figure 37). This difference was due to the non-linearity of the colloid sorption isotherm, since the amount of pyrene sorbed to DOM continues to increase with increasing dissolved concentration but the amount of colloid sorbed pyrene will be limited at higher concentrations due to the glassy SOM associated with the colloids. Approximately the same pattern was found in *Depleted soil* (Figure 38). However, at the same dissolved concentration leaching from the *Depleted soil* was lower than from the *Manured soil*, due to a lower amount of DOC, colloids and a lower f_{oc} of the colloids.

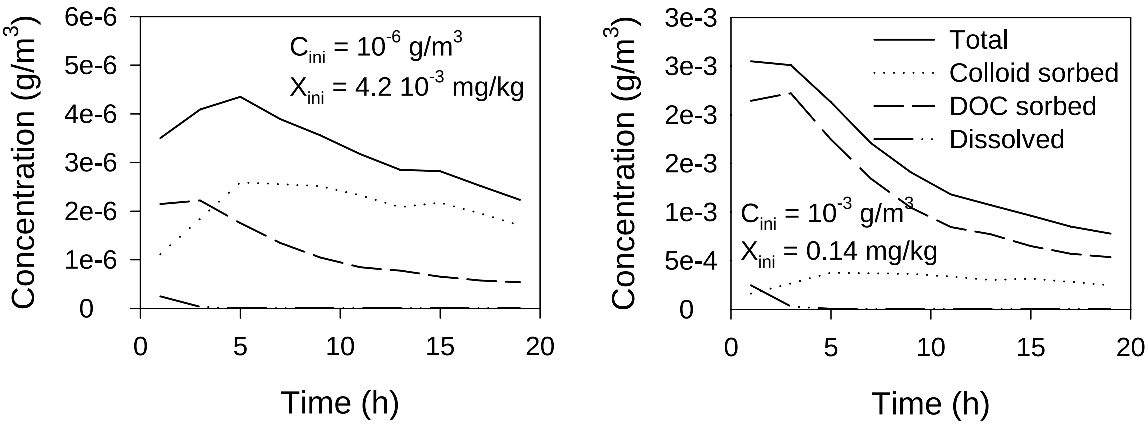

Figure 38: Simulated concentration of pyrene leached from the *Depleted soil*. "Total" denotes the simulated amount of pyrene, "colloid sorbed" the amount of pyrene transported by colloids, "DOC sorbed" the amount of pyrene transported by DOC and "dissolved" the leaching of dissolved pyrene.

5.3.3. SENSITIVITY TO THE RELEASE PROCESS OF THE COLLOIDS

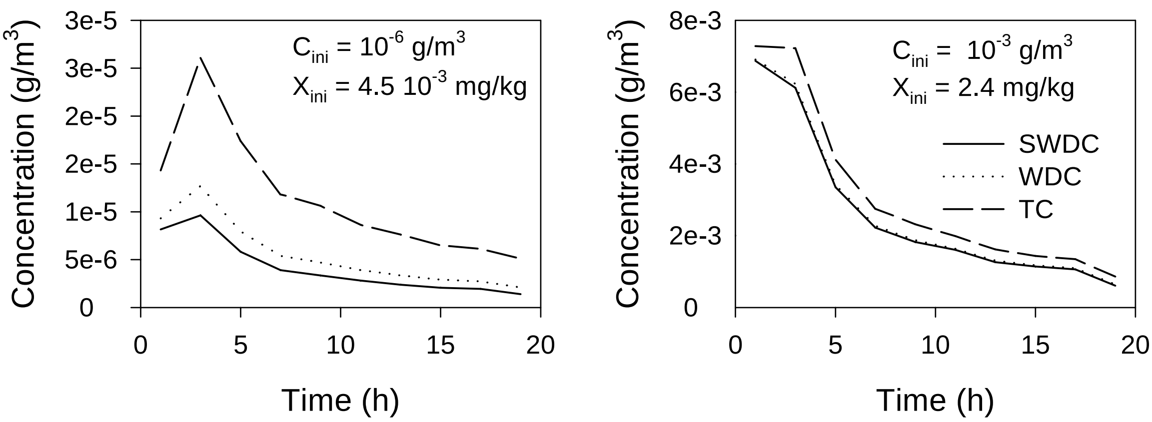

Figure 39: Sensitivity of the model towards the type of suspension used for the estimation of Freundlich parameters for colloids at high and low initial dissolved concentration of pyrene in the *Manured soil*.

If the estimation of the organic matter normalized Freundlich parameters for the colloids was conducted on the *WDC* isotherms instead of S*WDC* and the pyrene concentration was low, the simulated leaching was slightly higher on *Manured soil* (Figure 39). If the parameters based on the *TC* suspension were used, leaching was doubled with low pyrene concentration. With high concentration of pyrene the simulated leaching was more stabile to changes in the colloid parameters due to a relatively lower amount of colloid-sorbed pyrene. Using the *WDC* parameters on *Depleted soil* the simulated leaching was lower than S*WDC* and *TC* higher, but the differences were generally lower than for the *Manured soil* (Figure 40), due to the lower amount of colloids leached from the *Depleted soil*.

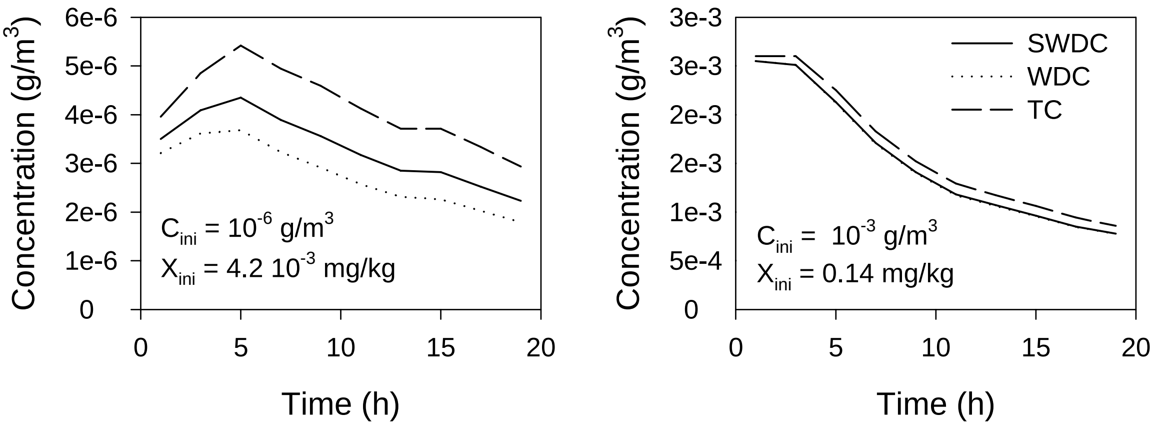

Figure 40: Sensitivity of the model towards the type of suspension used for the Freundlich parameter estimation at high and low initial dissolved concentration of pyrene in the *Depleted soil*.

5.3.4. SENSITIVITY TO SOLUTION CHEMISTRY

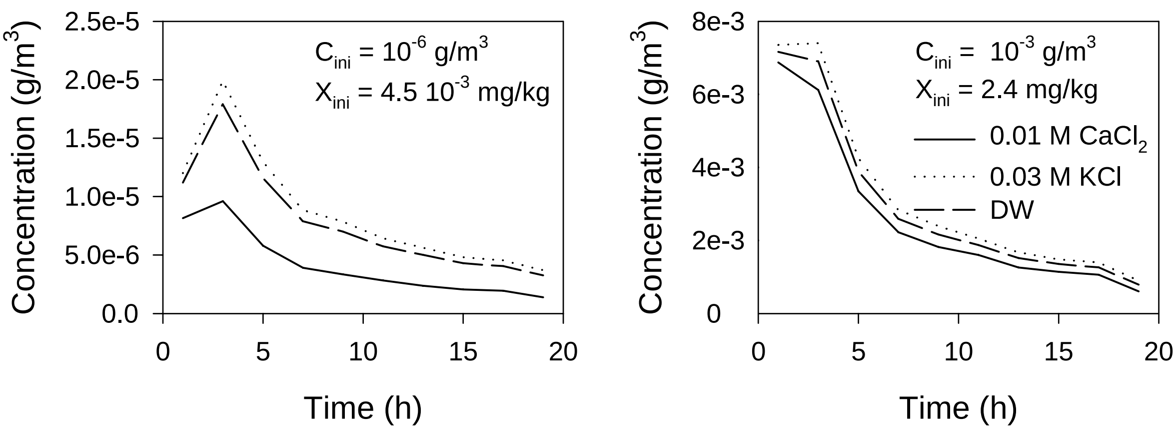

Figure 41: Sensitivity of the model to the solution chemistry in which the colloid Freundlich parameters are estimated at low and high initial dissolved concentration of pyrene in the *Manured soil*.

If the Freundlich parameters for the colloids were measured in 0.03 M KCl and DW instead of 0.01 M $CaCl_2$, the simulated leaching was increased on both *Manured* and *Depleted soil* (Figure 41 and Figure 42). However, the effect was higher with low concentration of pyrene due to the relatively higher amount of colloid-sorbed pyrene.

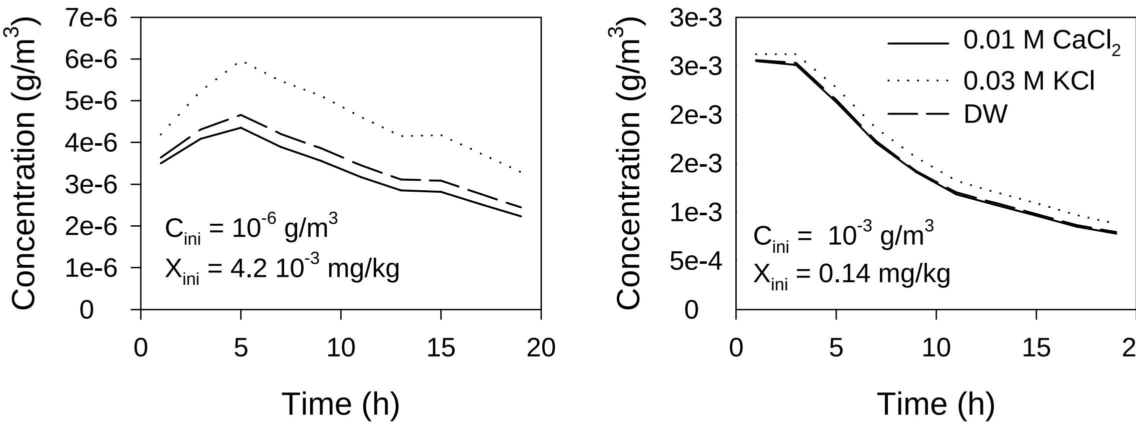

Figure 42: Sensitivity of the model to variable solution chemistry at low and high initial dissolved concentration of pyrene in the *Manured soil.*

5.4. CONCLUSIONS

The sorption of pyrene to colloids in suspension was affected by the process releasing the colloids from soil aggregates. The colloids released by both mechanical and chemical breakdown of aggregates had the highest sorption capacity and the highest degree of non-linearity of the isotherm.

The transport of pyrene was simulated well on the *Manured soil* but not on the *Depleted soil* when using a static leaching model and the estimated sorption parameters from spontaneously released colloids. The dominating transport processes shifted from colloid-facilitated to DOM-facilitated transport at increasing pyrene concentration due to the non-linear nature of the colloid isotherm and the linear nature of the DOM isotherm. Consequently, the sensitivity of the model to changes in the colloid sorption parameters was larger with low initial pyrene contamination compared with high.

If the hydrophobic sorption properties of the mobile colloids are to be measured for use in risc assessment models it is important that the sorption properties of the mobile colloids are not estimated on the basis of the clay fraction due to the higher sorption capacity and higher degree of non-linearity. The sorption properties of the mobile colloids should be measured in the solution relevant to the natural conditions since leaching is sensitive to the chemistry of the solution. It is important to include the non-linearity of the colloid isotherm in risk assessment models.

5.4.1. INDIGENOUS ORGANIC MATTER

The sorption of pyrene to colloids was depending on the amount of colloid-associated organic matter. The sorption relative to organic matter content was different for the colloids released spontaneously from aggregates of the two soils. The spontaneously released colloids of the *Depleted soil* had a lower K_{oc} and a lower degree of non-linearity.

The leaching of pyrene calculated with the static leaching model was higher from the *Manured soil* compared with the *Depleted soil* with the same dissolved pyrene concentration. This was due to a higher organic matter normalized sorption capacity of the colloids from the *Manured soil*, a higher amount of colloid-associated organic matter, and a higher release of colloids and DOM.

5.4.2. SOLUTION CHEMISTRY

Solution chemistry affected the sorption properties of the colloid suspension – the sorption capacity was higher with K^+ compared to Ca^{2+}. Higher ionic strength increased the effect of the Ca^{2+} and K^+.

The solution chemistry also affected the amount of pyrene leached, as calculated with a static leaching model. Leaching with deionized water and KCl was increased compared to with $CaCl_2$.

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6. CONCLUSIONS

The effect of indigenous organic matter and solution chemistry on the processes involved in colloid-facilitated transport of surface-applied chemicals from agricultural soils was investigated. The most important conclusions of this work were:

Release of colloids from aggregates in batch release experiments by mechanical/chemical disruption, mechanical and spontaneous release was increased by a higher organic matter content. This suggested that the structural stability controlled the release. The colloids released by spontaneous release had a higher amount of colloid-associated organic matter than did the colloids released by total mechanical and chemical disruption. Chemical/mechanical and mechanical dispersion affected the particle size distribution of colloids below 1 µm. With chemical/mechanical and mechanical dispersion fine colloid (< 0.3 µm) were released. No fine colloids were released during spontaneous release.

The leaching of colloids from aggregated unsaturated topsoil depended on the chemistry of the irrigation water. The ionic strength affected the leaching more than the valence of the ion. The organic matter content had a positive effect on the leaching of colloids from the soil. The amount of organic matter on the colloids (f_{oc}) was higher compared to the f_{oc} of the bulk soil on both soils, indicating preferential leaching of organic coated colloids. The steady-state flux of colloids out of the columns showed a positive correlation with irrigation intensity. This was due to a decreasing hydraulic boundary layer and a larger area of contact between the flowing water and the aggregate surface.

A model describing the leaching of colloids from an unsaturated aggregated soil system as a function of ionic strength was developed. The model could be calibrated to describe leaching experiments with three levels of ionic strength using a single parameter set on each soil. The simulations suggested that leaching in the initial stages were controlled by desorption of colloids from the air-water interface. Desorption from air-water interfaces was higher on Manured soil. High organic matter content increased the sorption capacity of the air-water interfaces and the concentration of colloids at the aggregate surface at high ionic strength. Key parameters for the leaching of colloids were the parameters accounting for the sorption to air-water interfaces and the diffusion of colloids from the aggregate surface to the mobile water.

Sorption of pyrene to colloids in suspension was affected by the release process of the colloids from soil aggregates and by the solution chemistry. Colloids released by chemical dispersion had higher sorption capacity and a higher degree of non-linearity than colloids released spontaneously from aggregates. Simulations of the leaching of pyrene from aggregated soil showed that the dominating process shifted from colloid-facilitated transport at low pyrene concentration to DOM-facilitated at high pyrene concentration. This was due to the non-linearity of the colloid sorption isotherm and the linear DOM sorption isotherm. It also showed that when determining the sorption properties of mobile colloids, care should be taken to find a colloid fraction representing the mobile fraction. If the clay fraction was used the sorption of pyrene was generally overestimated.

6.1. COLLOID FACILITATED TRANSPORT OF HYDROPHOBIC ORGANIC COMPOUNDS

6.1.1. EFFECT OF INDIGENOUS ORGANIC MATTER

Four different characteristics regarding the colloid-facilitated transport of hydrophobic organic compounds have been observed to be different for soils with different organic matter content.

- A higher organic matter content decreased the amount of colloids released by mechanical stress.
- A higher organic matter content increased the leaching of colloids due to infiltration of low ionic strength rain-water
- The amount of organic matter associated with colloids were higher if colloids were leached from a soil with a high organic matter content
- The organic matter normalized sorption coefficient (K_{oc}) of pyrene was higher when sorbing to colloids from a soil with high organic matter content

A higher organic matter content most likely increased the colloid-facilitated transport since: the amount of colloids leached by infiltration of low ionic strength water was higher, the amount of organic matter associated with the leached colloids was higher, and the leaching of dissolved organic matter was higher, and the organic matter normalized sorption capacity of the colloids released spontaneously was higher with higher organic matter content of the soil. Two important processes should however be considered: In naturally structured soils, the air-water interface may be smaller than it was in the columns packed with aggregates. This will lead to a much smaller difference in leaching from soils with different organic matter content, since much of the difference observed between leaching from the two soils was due to desorption from the air-water interface. Also, if a large portion of the mobile colloids are released by mechanical stress e.g. by raindrop impact or overland erosive flow, the effect of the organic matter on colloid leaching may be reduced. If colloids were exclusively released by mechanical impact, a higher organic matter content of the soil could reduce the leaching.

6.1.2. EFFECT OF SOLUTION CHEMISTRY

The solution chemistry is highly variable in soils over time, due to infiltration of low ionic strength water during rain-events. The following processes were found to rely on ionic strength:

- High ionic strength infiltrating water reduced the leaching of colloids
- The sorption of pyrene was only slightly influenced by the ionic strength

Low ionic strength may increase the colloid-facilitated transport of hydrophobic organic compounds mainly by a higher leaching of colloids and a slightly higher leaching of DOM. Low ionic strength is found in soils with a low amount of exchangeable cations, with heavy-rainfall, and with a large degree of preferential flow.

The population of cations in an agricultural soil is dominated by Ca^{2+} but fertilization may locally increase the amount of K^+ on the exchange complex and in the soil solution. The following processes were found to be influenced by the dominating cation in the system:

- Long-term leaching of colloids from columns packed with aggregates was slightly higher when irrigating with high concentration of K^+
- The sorption of pyrene to colloids was enhanced when K^+ was present in the soil solution

If an agricultural field has just been fertilized with K^+ the colloid-facilitated transport of hydrophobic organic compounds may be increased by a combination of a higher release of colloids from the soil, combined with a higher sorption of HOC to these colloids.

7. PERSPECTIVES AND FUTURE DIRECTIONS

This work has contributed to answer important questions regarding the colloid-facilitated transport in topsoil. But during the investigation many interesting new research topics and new questions have emerged.

It was observed that the release of fine colloids with no organic matter associated was related to the chemical and mechanical disruption of aggregates. This class of colloids was not found when colloids were released spontaneously. The reason for this is unknown, but it was hypothesized that the medium size colloids (0.3 – 1 μm) were really micro-aggregates held together by organic matter and that the micro-aggregates could be broken down by chemical and mechanical stress. The dynamics of the break-down of micro-aggregates in soils should be investigated further. This may have great practical importance in colloid characterization, since a colloid suspension is often pretreated by mechanical stress (shaking, end-over-end rotation, or sonication) prior to measurements.

The leaching experiments using columns packed with natural soil aggregates proved use-full for studying the processes of colloids leaching. The simple hydrology ensures that conclusions about the processes could be drawn from the experiments. This is not always the case with naturally structured soil samples. The different aspects of colloid diffusion in the stagnant water of the soil should be studied in saturated columns packed with aggregates of different sizes and with different flow velocities. The saturated flow will ensure that colloids are released exclusively from the aggregate surfaces.

The relative importance of the release of colloids from the soil surface (by rain-drop impact) and in the soil pores (by dispersion) has not been investigated. A more thorough investigation should determine the relative importance of rain-drop release and *in-situ* dispersion in natural soils.

The modeling work showed that the desorption of colloids from the air-water interface was probably an important release process, especially if the organic matter content of the soil was high and irrigation water had low ionic strength. A more thorough investigation of the importance of air-water interface sorption and desorption in naturally structured soil is essential for the further development of models of colloid leaching from natural topsoil.

The modeling work also showed that even with a relatively simple system the colloid leaching is highly complex and requires numerous parameters to be described correctly. The colloid leaching may be simulated in a mechanistic way for simple systems but not for prediction purposes in naturally structured soil. One way to avoid the very complex and parameter-demanding simulation in the topsoil will be to establish an empirical model taking into account: soil type, degree of preferential flow, ionic strength, water content, wetting history and rain intensity. The model should be calibrated against leaching from topsoil column experiments. The empirical model can then be used to estimate the net mobilization of colloids in the top-soil.